A. Ravve

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Third Edition

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Preface

This book, unlike the first and second editions, is primarily aimed to be a textbook for a graduate course in polymer chemistry and a reference book for practicing polymer chemists. The first and second editions, on the other hand, were aimed at both graduate and undergraduate students. Comments by some reviewers, that the first two editions are too detailed for use by the undergraduates, prompted the change.

The book describes organic and physical chemistry of polymers. This includes the physical properties of polymers, their syntheses, and subsequent use as plastics, elastomers, reagents, and functional materials. The syntheses are characterized according to the chemical mechanism of their reactions, their kinetics, and their scope and utility. Whenever possible, descriptions of industrial-scale preparations are included. Emphasis is placed on reaction parameters both in the preparation of the polymeric materials and in their utilization as reagents. Also, when possible, industrial or trade names of the polymeric materials are included to familiarize the students. This book also describes chemical modifications of polymers. A separate chapter is dedicated to utilization of polymers as reagents, supports for catalyst or for drug release, as electricity conductors, and in photonic materials.

Use of this book requires proficiency in organic and physical chemistries. While prior knowledge of polymer chemistry on the elementary level is not required, some exposure to the subject on the undergraduate level would probably be helpful. Each topic, however, is presented with the assumption that the reader has no prior knowledge of the subject.

This book consists of ten chapters. A separate chapter on physical properties and physical chemistry of polymers was added. In the previous editions, this subject was part of the introduction and handled on a limited scale. This book is aimed at graduate students, however, and a more rigorous treatment is required.

The kinetic treatment was expanded in the chapters that deal with polymer syntheses. In addition, discussions of the thermodynamics of these reactions were added to each of these chapters.

In the earlier two editions, a 5¼ in. diskette was included at the end of the books with some computer programs in Pascal. These programs were there to offer the students experience in calculating results from size exclusion chromatograph or to determine sequence distribution in polymers from NMR spectra, and some others. These programs have been omitted, however, because there are now considerably better programs, written by professional computer scientists, now commercially available.

This book, like the earlier editions, is dedicated to all the scientists whose names appear in the references.

Niles, IL, USA   A. Ravve

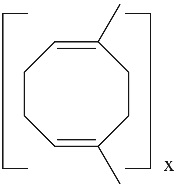
Contents

Chapter 1
Introduction and Nomenclature

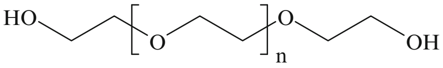
1.1 Brief Historical Introduction

The initial proof of the existence of very large organic molecules was supplied by Raoult [1] and van't Hoff [2], who carried out cryoscopic molecular weight determinations on rubber, starch, and cellulose nitrate. By the methods developed by Raoult and by van't Hoff and by the formulation of solution laws, molecular weights of 10,000–40,000 were demonstrated. Unfortunately, chemists of that day failed to appreciate this evidence and refused to accept it. The main reason for such a response was the inability to distinguish macromolecules from colloidal substances that could be obtained in low molecular weights. The opinion of the majority of that day was that "Raoul's solution does not apply to materials in colloidal state."

During the period 1890–1910, the idea of molecular complexes was generally accepted [3]. It was used to explain polymeric structures in terms of physical aggregates of small molecules. In fact, molecular association was considered polymerization. Thus rubber, for example, was assumed to be composed of short sequences of isoprene units, either as chains or as cyclic structures. The structure of isoprene itself was known, because it was isolated from natural rubber, in 1860. What added to the general confusion was the fact that no one was able to show the existence of end groups in the macromolecules studied. This enhanced the idea that rubber is a ring-like structure, a dimethyl cycloocatadiene. Large numbers of such rings were assumed to be held together by associations, giving rise to colloidal materials. This can be illustrated as follows:



Early synthetic polymeric products were usually discarded as being oils or tars ("gooks"), and considered as useless. To be fair to the chemists of that period, however, one should not forget that in spite of the general attitude of the time, the structures of some polymers, like polyethylene glycol ($n = 6$), for instance,



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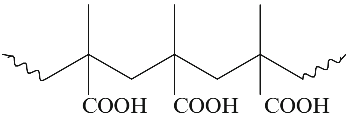
was correctly assigned in 1860, and the concept of extending the structure to very large molecular weights by continued condensation was understood [4–6].

At approximately the same time, poly(methacrylic acid), which we now know to be a linear molecule



was prepared in 1880 [7]. But, here too, a cyclic structure was assigned which was believed to be attached to other cyclic structures by "partial valences," thereby forming gels. What is more noteworthy is that Emil Fischer and his coworkers studied many natural polymers, such as rubber, starch, polypeptides, cellulose, and lignin. His work probably entitles him to be called the spiritual father of polymer chemistry. During that period, Willstätter worked on the synthesis of polysaccharides, and studied lignin and enzymes [8].

One should also acknowledge the fact that in spite of ignorance of structure, many inventors developed ways to convert cellulose into cellulose acetate and then to use the products to form fibers, films, and coatings. Cellulose was also converted to cellulose nitrate and was used to prepare explosives and other products. At the turn of the century, Baekeland formed a hard resin by condensing phenol with formaldehyde [9],

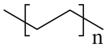
The evolvement of our present-day understanding of polymeric structures occurred in the early 1920s. Thus, Staudinger et al. firmly established the existence of macromolecules [10–15]. Others, by X-ray analyses and careful use of molecular weight determinations, confirmed his findings [16]. In 1929, a series of outstanding investigations were carried out by Carothers on other polymeric materials. This resulted in much of today's knowledge and understanding [17].

Now, we know that a typical molecule such as polyethylene can have a contour length of 25,000 Å, but a diameter of only 4.9 Å. Such a molecule can be compared in dimensions to a long, snarled clothesline, 75 ft long and 1 in. in diameter. Furthermore, work with naturally occurring macromolecules, such as nucleic acids, for instance, revealed even more startling dimensions. When molecules of virus dinucleic acids were tritium-labeled (whose nuclear emission is less than 1 μm) and then autoradiographs prepared, these showed molecules that were about 50 μm long [18]. Such length would signify a molecular weight of 100 million. Similar work carried out on dinucleic acids of bacteria revealed molecular weights of approximately 200 million.

The above figures are, of course, extremes in molecular dimensions. Typical synthetic polymers will range in molecular weights anywhere from ten to several hundred thousand, although synthetic polymers in molecular weight ranges of several million are well known and some are used commercially. Interestingly enough, many of these polymers are prepared through the use of organic reactions that have been known for a long time. Also, new reactions and catalysts are still being discovered and applied to polymer syntheses. It is probably safe to predict that this situation will undoubtedly continue into the distant future.

1.2 Definitions

The word polymer is commonly understood to mean a large molecule composed of repeating units, or mers (from the Greek word ***meros***—part), connected by covalent bonds. Such units may be connected in a variety of ways. The simplest is a linear polymer, or a polymer in which the units are connected to each other in a linear sequence, like beads on a string. Many examples of such linear polymers are possible, as, for instance, linear polyethylene:



repeat unit

The terminal units in such molecules must be different from the internal ones to satisfy valence requirements. Polyethylene, like all other polymers, can be written to show the number of repeat units, $-[-CH_2-CH_2-]_n-$, by using a number or a letter, like in this case n. It represents the ***average*** quantity of mers present in the polymer and is called ***the degree of polymerization*** or *DP*, or the average number of repeat units in the polymeric chain. Thus the average molecular weight of polystyrene with a DP of 100 is 104 × 100 or 10,400. (There are actually several ways of expressing the average molecular weights of polymers. This is discussed further in this chapter).

An alternative to a linear polymer is a branched one. The branches can be long or short. Low-density polyethylene, for instance, can have both short and long branches. Linear and branched molecules are shown in Fig. 1.1a, b. Branched polymers can also be star- or comb-shaped (Fig. 1.1c, d). In addition to the above, polymer molecules can also be double-stranded. Such polymers are called ladder polymers (Fig. 1.1e). It is also possible for polymers to have semi-ladder structures (Fig. 1.1f).

When branches of different polymers become interconnected, *network* structures form. Planar networks resemble the structure of graphite. Three-dimensional networks, or space networks, however, can be compared with diamonds. A network polymer is shown in Fig. 1.1g.

The term polymer canbe applied to molecules made up from either single repeating structural units, like in the above shown polyethylene, or from different ones. If there are two or more structural units then the term ***copolymer*** is used. An example would be a copolymer of ethyl methacrylate and styrene:

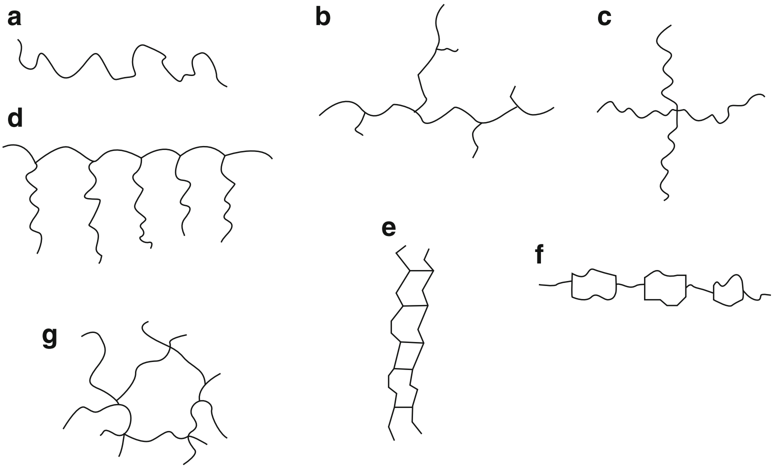
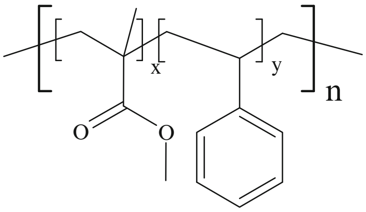


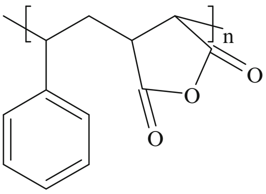
Fig. 1.1 Shapes of polymer molecules. (**a**) Linear polymer, (**b**) branched polymer, (**c**) star-shaped polymer, (**d**) comb shaped polymer, (**e**) ladder polymer, (**f**) semiladder polymer, and (**g**) network structure



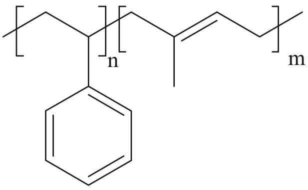
methyl methacrylate styrene
unit unit

A copolymer can also be linear or branched. Should there be regularity in the repetition of the structural units and should this repetition alternate, then the copolymer is called an ***alternating copolymer***. An absence of such regularity would make it a ***random copolymer***.

An example of an alternating copolymer can be a copolymer of styrene with maleic anhydride:

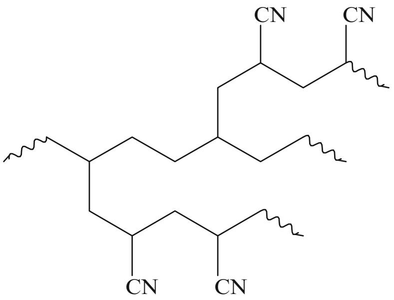


In addition to the random-sequence and an alternating one, sometimes called ordered-sequence, there are also ***block copolymers***. These are copolymers made up of blocks of individual polymers joined by covalent bonds. An example can be a block copolymer of styrene and isoprene:



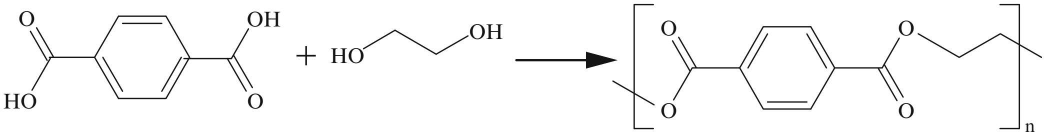
polystyrene block-polyisoprene block

Still another type of a copolymer is one that possesses backbones composed of one individual polymer and the branches from another one. It is called a ***graft copolymer,*** because many such materials were formed by grafting the branch polymers to the polymer backbone. This, however, is not always the case and many graft copolymers were formed by polymerizing the branch copolymer from a different polymer backbone. (The subject of block and graft copolymers is discussed in Chap. 9) A graft copolymer of polyacrylonitrile on polyethylene can serve as an example:

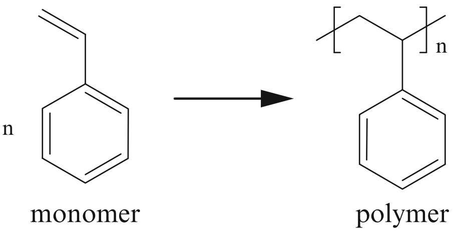


In both block and graft copolymers the length of the uninterrupted sequences may vary.

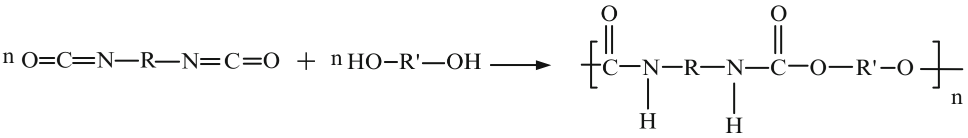
In 1929, Carothers [19] suggested a separation of all polymers into two classes, ***condensation*** and ***addition*** polymers. By condensation polymers he defined those polymers that lack certain atoms from the monomer units from which they were formed or to which they may be degraded by chemical means. An example would be a polyester:



He also defined addition polymers as polymers with identical structures of the repeat units to the monomers from which they are derived. According to the above definition, an example of an addition polymer can be polystyrene that is formed by addition of styrene monomers:



Note: The definition ignores loss of double bonds. The Carothers definition fails to describe all the polymers that can fit into the category of condensation polymers, yet form without an evolution of a byproduct. An example is polyurethane that can form from a reaction of a glycol with a diisocyanate:



$$n\,O{=}C{=}N{-}R{-}N{=}C{=}O \;+\; n\,HO{-}R'{-}OH \longrightarrow \left[\overset{O}{\overset{\|}{C}}{-}\underset{H}{\underset{|}{N}}{-}R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}O \right]_n$$

Flory proposed a superior definition [20]. It is based on the reaction mechanism involved in the formation of the two classes of polymers. Into the first category (it includes all the condensation polymers) falls the macromolecules that form through reactions that occur in ***discreet steps***. They are, therefore, called ***step-growth*** polymers. Such polymerizations require long periods of time for each macromolecule to form, usually measured in hours. Into the second category belong all polymers that form by ***chain propagating reactions***. They are, therefore, called ***chain-growth polymers***, as one might expect. Such reactions depend upon the presence of active centers on the ends of the growing chains. The chains grow by propagating these reactive sites through inclusion of monomers at such sites. These inclusions are very rapid and chain-growth can take place in a fraction of a second, as the chains successively add monomers.

The important features of step-growth polymerizations are:

1. The monomer is consumed early in the beginning of the reaction while the increase in molecular weight occurs only slowly.
2. The growth of polymeric chains takes place by reactions between monomers, oligomers, and polymers.

3. There is no termination step, and the end groups of the polymers are reactive throughout the process of polymerization.
4. The same reaction mechanism functions throughout the process of polymerization.

The important features of chain-growth polymerizations are:

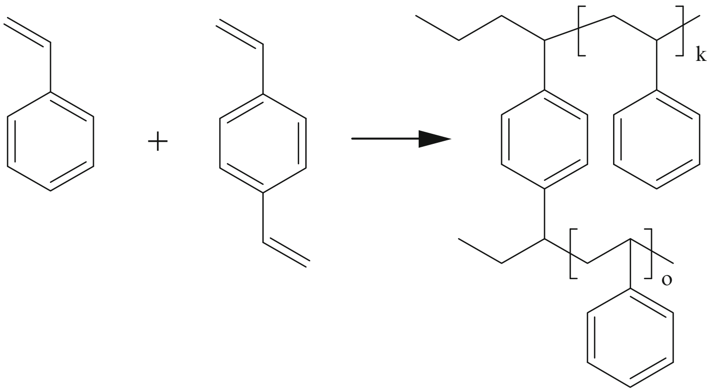
1. Chain-growth takes place by repeated additions of monomers to the growing chains at the reactive sites.
2. The monomer is consumed slowly and is present throughout the process of polymerization.
3. There are two distinct mechanisms during polymer formations. These are initiation and propagation.
4. In the majority of cases, there is also a termination step.

When the polymerization reaction takes place in three dimensions, after it has progressed to a certain point, gelation occurs. This well-defined change during polymerization is known as the *gel point*. At this point the reaction mixture changes from a viscous liquid to an elastic gel.

Before gelation, the polymer is soluble and fusible. After it, however, it is neither soluble nor fusible. This is a result of restraining effects of three-dimensional space networks. Another classification of polymers is also possible. It is based on whether the material can form crosslinked or gelled networks. The polymers that eventually reach gelation are called ***thermosetting***. Such polymers are also called ***crosslinkable*** polymers. Once past gelation, raising the temperature will no longer attain plasticity as the molecules can no longer move past each other. For the same reason they can no longer be dissolved in any solvent.

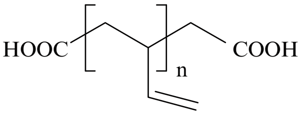
Polymers that never gel or become crosslinked are called ***thermoplastic***. Such polymers can always be reflowed upon application of heat. They can also be dissolved again in appropriate solvents.

The wiggly lines in the above illustration imply that the polymer extends further in their directions. The above illustration is one of a thermoset polymer that is formed by the step-growth mechanism. It is also possible to form crosslinked polymers by the chain-growth mechanism. This requires presence in the polymerization mixture of a comonomer that possesses multiple functionality. Copolymerization of styrene with a comonomer like divinyl benzene can serve as an example:



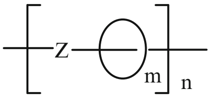
An ***oligomer*** is a very low molecular weight polymer. It consists of only a small number of mers. The definition of a ***telomer*** is that of a chain-growth polymer that is composed of molecules with end groups consisting of different species from the monomer units. Telomers can form by either free radical or by ionic chain-growth polymerization mechanism.

Telechelic polymers are macromolecules with reactive functional groups at the terminal ends of the chains. An example of telechelic polymer is polybutadiene with carboxylic acid end groups



Into a special category should be placed starburst ***dendrimer polymers***. These molecules are formed by growing them in three dimensions. These materials often possess radially symmetrical star-shaped structures with successive cascades of branched polymer structures. For additional discussions see Chap. 6.

Another group of polymers are the ***rotaxanes***. They too are discussed in Chap. 7. The materials consist of polymeric chains that are threaded through macrocycles:



Tables 1.1 and 1.2 illustrate some common chain-growth and step-growth polymers as well as monomers used in their preparations.

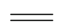
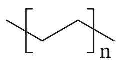
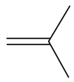
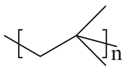
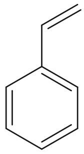
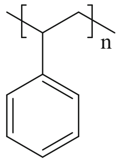
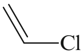
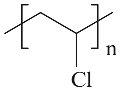
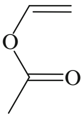
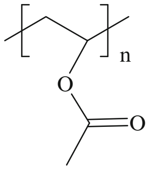
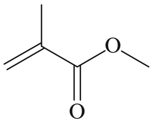
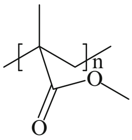
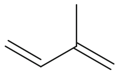
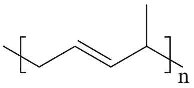
1.3 Nomenclature of Polymers

The names of many polymers are based on the monomers from which they were prepared. There is, however, frequent variation in the format. A nomenclature of polymers was recommended by IUPAC [21–23] and is used in some publications. Strict adherence to the recommendation, however, is mainly found in reference works. Also, problems are often encountered with complex polymeric structures that are crosslinked or have branches. In addition some polymers derive their names from trade names. For instance, a large family of polyamides is known as nylons. Also, when more than one functional group is present in the structure, the material may be called according to all functional groups in the structure. An example is a polyesteramide. A thermoset polymer prepared from two different materials may be called by both names. For instance, a condensation product of melamine and formaldehyde is called melamine–formaldehyde polymer.

1.3.1 Nomenclature of Chain-Growth Polymers

1. A polymer of unspecified chain length is named with a prefix *poly*. The prefix is then followed by the name of the monomer. Also, it is customary to use the common names of monomers and polymers. For instance, common names for phenylethene and polyphenylethene are styrene and polystyrene. This, however, is not an inflexible rule. When the monomer is named by a single word then the prefix poly is simply added like polyethylene for a polymer of ethylene or polystyrene for a polymer of styrene. If, however, the monomer is named by two words or is preceded by a number, like methyl methacrylate, parentheses are used. Examples are poly(methyl methacrylate) or poly(1-hexene).
2. End groups are usually not specified in high polymers. End groups, however, can be known parts of the structure. This can be the case with telomers. Here, the end groups are named as radicals,

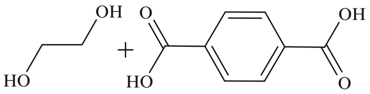
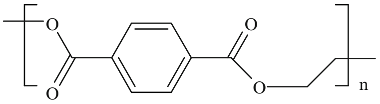
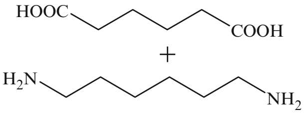
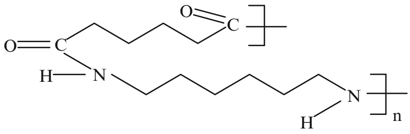
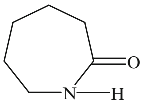
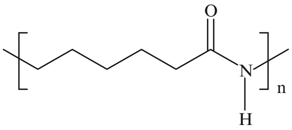
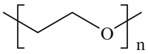
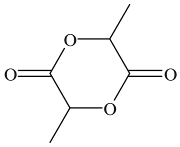
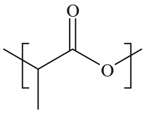
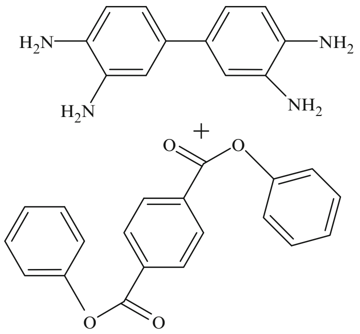
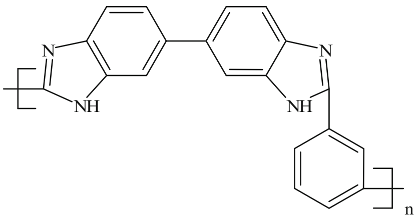
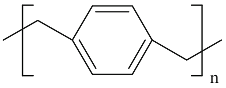
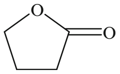
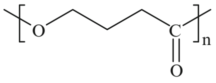
Table 1.1 Illustration of common chain-growth polymers

Name	Monomer	Polymer
Polyethylene		
Polyisobutylene		
Polystyrene		
Poly(vinyl chloride)		
Poly(vinyl acetate)		
Poly(methyl methacrylate)		
Polyisoprene		

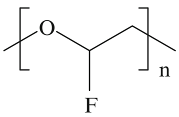
prefixed by Greek letters, **α** and **ω**. They appear before and after the name of the polymer. The structure of a telomer, like $Cl–(–CH_2–)_n–CCl_3$, is, therefore, called α-chloro-ω-trichloromethyl poly(methylene).

3. In naming the polymer the following steps are recommended by IUPAC: (1) identify the constitutional repeating unit, (2) orient the ***constitutional repeating unit***, and (3) name the constitutional repeating unit.
4. Random copolymers are designated by the prefix ***co***, as in poly(butadiene-*co* styrene) and poly (vinyl chloride-***co*** vinyl acetate). Alternating copolymers can be differentiated by substituting *alt* for *co*, as in poly(ethylene-*alt*-carbon monoxide).
5. The prefix *g* describes graft copolymers and the prefix *b* describes block copolymers. In this system of nomenclature, the first polymer segment corresponds to the homopolymer or copolymer that was formed during the first stage of the synthesis. Should this be a graft copolymer then this will represent the backbone polymer. For instance, if polystyrene is graft copolymerized with polyethylene, the product is called poly(ethylene-*g*-styrene). A more complex example can be poly(butadiene-*co*-styrene-*g*-acrylonitrile-*co*-vinylidine chloride). Similarly, examples of block copolymers would be poly(acrylonitrile-*b*-methyl methacrylate) or poly(methyl methacrylate-*b*-acrylonitrile).
6. Conventional prefixes indicating ***cis*** and ***trans*** isomers are placed in front of the polymer name. An example is *cis*-1,4-polybutadiene, or in *trans*-1,4-polyisoprene.

Table 1.2 Illustration of some step-growth polymers and monomers used in their preparation

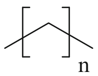
Poly(ethylene terephthalate)		
Poly(hexamethylene adipate); nylon 6,6		
Polycaprolactam; nylon 6		
Poly(ethylene oxide)		
Poly(lactic acid)		
Poly(benzimidazole)		
Poly(p-xylylene)		
Poly(butyrolactone)		

7. The nomenclature adopted by IUPAC rests upon selection of preferred *constitutional repeating* units [5] from which the polymer is a multiple. The unit is named wherever possible according to the definitive rules for nomenclature of organic chemistry [24]. For single-stranded polymers this unit is a bivalent group. An example is a polymer with oxy(1-fluoroethylene) constitutional repeat unit:

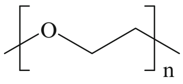


poly [oxy(1-fluoroethylene)]

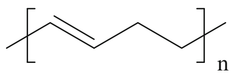
The following are examples of simple constitutional repeat units:



polymethylene

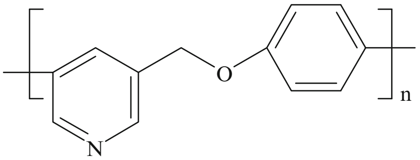


polyoxyethylene

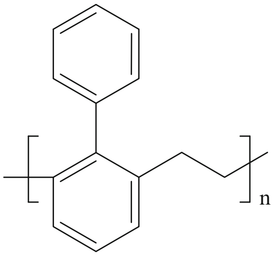


poly(1-butenylene)

8. Polymers with repeating units consisting of more than one simple bivalent radical should be named according to the order of seniority among the types of bivalent radicals: (a) heterocyclic rings, (b) chains containing hetero atoms, (c) carbocyclic rings, and (d) chains containing only carbons. This is illustrated below:

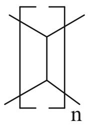


poly(3,5-pyridinediylmethyleneoxy -1,4-phenylene)

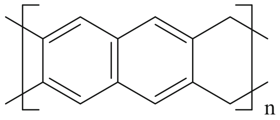


poly(2,6-biphenyleneethylene)

9. Double-stranded or "ladder" polymers that have tetravalent repeat units are named similarly to bivalent units. The relation of the four free valences is denoted by pairs of locants separated by a chain:

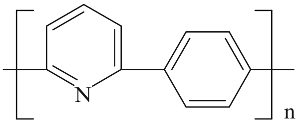


poly(1,2:1,2-ethane diylidene)



poly(2,3,6,7-naphthalenetetrayl-6,7-dimethylene)

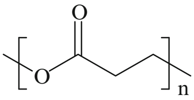
10. For polymers that contain heteroatoms or acyclic subunits containing heteroatoms there is a decreasing seniority in naming. It is in the following order, O, S, Se, Te, N, , Sb, Bi, Si, Ge, Sn, Pb, B. Similarly, for polymers containing ring structures, the seniority if for the heterocyclic ring to have greater seniority that heteroatoms or acyclic subunits. Similarly, heterocyclic subunits have greater seniority than do carbocyclic ring and they in turn have greater seniority than acyclic substructures. An example would be,



poly(2,4-pyridinediiyl-1,4-phenylene)

1.3.2 Nomenclature of Step-Growth Polymers

The nomenclature for step-growth polymers is more complicated due to the possibility of having many different repeat units. Usually, the polymers are referred to according to their functional units. A polyester from ethylene glycol and terephthalic acid is called poly(ethylene terephthalate). A product from ring opening polymerization, like, for instance, a polymer of caprolactam might be called polycaprolactam. Here, it is based on the source. The repeat unit is actually not a lactam but rather an open chain polyamide. Because it is derived from a lactam, it may still carry that name. In this particular instance, however, it is more common to call the polymer by its generic name, namely, nylon 6. The same would be true for a polymer from a lactone, like poly(β-propiolactone). The IUPAC name for this polymer, however, is:



poly[oxy(1-oxotrimethylene)]

The name is based on a presence of two subunits. Note that the carbonyl oxygen is called an *oxo* substituent. In addition, the presence of a 1-oxo substituent requires that parentheses enclose the subunit.

1.4 Steric Arrangement in Macromolecules

In linear polymers, due to the polymerization process, the pendant groups can be arranged into orderly configurations or they can lack such orderliness. Propylene, for instance, can be polymerized into two types of orderly steric arrangement. It can also be polymerized into one lacking steric order. The same can be true of other monosubstituted vinyl monomers. The steric arrangement in macromolecules is called ***tacticit***y. Polymers can be ***isotactic***, where all the chiral centers have the same configuration (see Fig. 1.2). By picturing the chain backbone as drawn in the plane of the paper and by picturing all the phenyl groups as oriented above the plane (Fig. 1.2a), isotactic polystyrene can then be visualized. The orderliness can also be of the type where every other chiral center has the same configuration. Such an arrangement is called ***syndiotactic*** (Fig. 1.2b). A lack of orderliness or randomness in the steric arrangement is called ***atactic*** or ***heterotactic***. Stereospecific polymers can also be prepared from 1,2 disubstitued olefins. These macromolecules can be distereoisomers, or ditactic polymers. To describe the arrangement of such polymers, a ***threo–erythro*** terminology is used. An erythrodiisotactic polymer is one possessing alternating substituents—(–CHR′CHR–)–*n*. If we draw the carbon chain backbone in the plane of the paper, then all the R groups would find themselves on one side of the chain and all the R′ groups on the other. They would, however, all be on the same side of the chain in a Fischer or in a Newman projection (Fig. 1.2c). A threo isomer or a threodiisotactic polymer is illustrated in Fig. 1.2d.

Polymerization of 1,4-disubstituted butadienes can lead to products that possess two asymmetric carbon atoms and one double bond in each repeat unit. Such ***tritactic*** polymers are named with prefixes of ***cis*** or ***trans*** together with ***erythro*** or ***threo*** (see Fig. 1.3).

In polymers with single carbon to carbon bonds, there is free rotation, provided that steric hindrance does not interfere. This allows the molecules to assume different spatial arrangements or ***conformations***. Most of the possible isomers, however, represent prohibitively high-energy states. The three lowest energy states that are most probable [8] are one *trans* and two gauche.

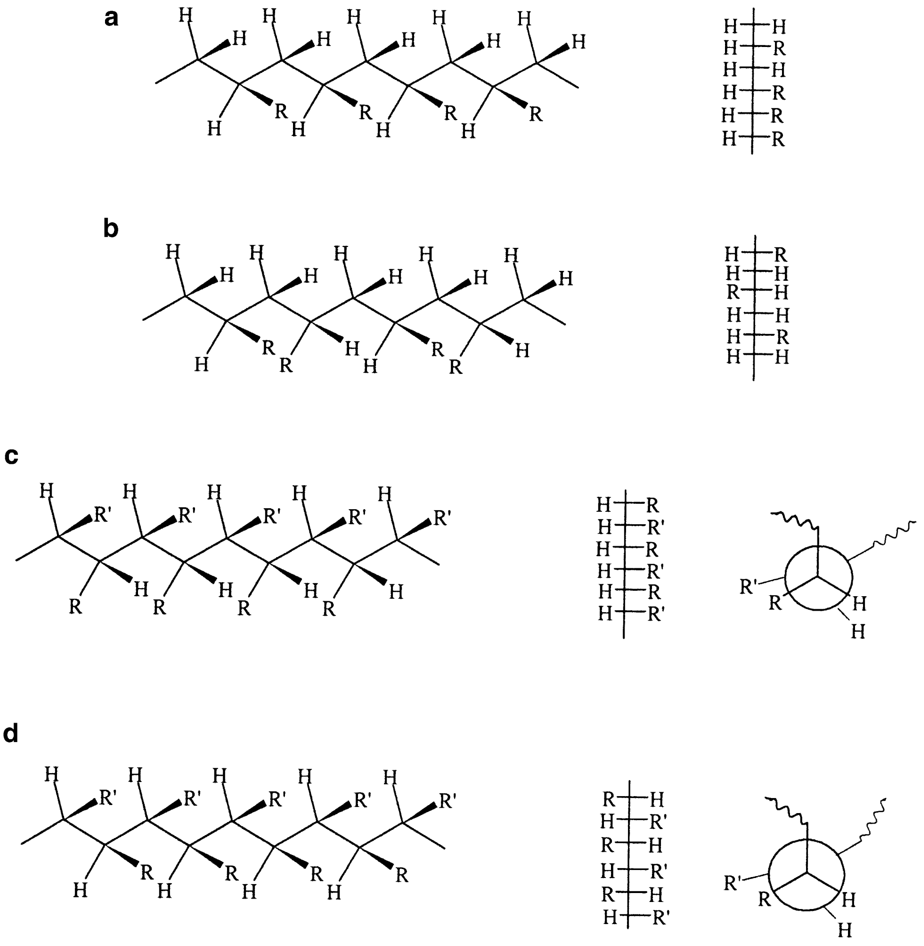


Fig. 1.2 Steric arrangement in macromolecules (R = phenyl). (**a**) Isotactic polymer, (**b**) syndiotactic polymer (**c**) erythrodiisotactic polymer, and (**d**) threodiisotactic polymer

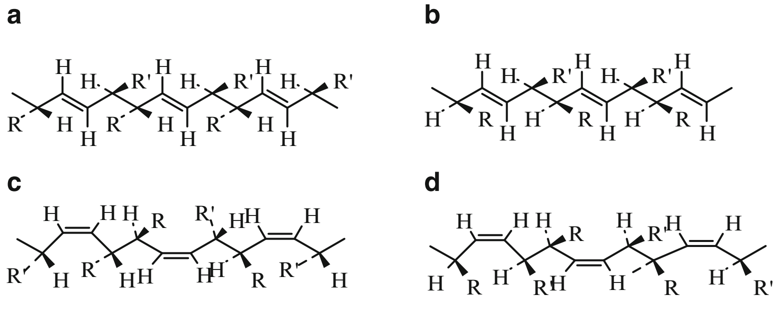


Fig. 1.3 Tritactic polymers. (**a**) *Trans-erythro* tritactic polymer, (**b**) *trans-threo* tritactic polymer, (**c**) *cis-erythro* tritactic polymer, and (**d**) *cis-threo* tritactic polymer

Several rules that govern the configuration of repeat units along the polymeric chains were elucidated by Natta and Carradini [24]. A basic assumption is used to predict the lowest energy conformation. This assumption is known as the ***equivalence postulate***. It says that all the structural units along the chain are geometrically equivalent with regard to the axis of the chain. All stereoregular polymers appear to meet this condition, with a few exceptions [25].

It should be possible to calculate (in principle) the lowest internal conformational energy of a given polymer molecule. To do that it is necessary to know: (1) the energy vs. the bond rotation curve that relates the interactions within the structural units; and (2) the interaction energy vs. the distance curve for the neighboring pendant groups of the adjacent structural units. It should be noted that the neighboring units approach each other close enough for substantial interaction. As a result, the interaction energies between the groups may distort the basic energy–rotation curves. The core electron repulsion between the units contributes most significantly to the deviations from the simple *trans* or gauche conformation. The specific chain conformation, therefore, is very dependent upon the exact nature of the repulsive potential. A contour plot, which represents the internal energy per mole of the polymer, can be prepared. The variables in such a plot are the relative bond rotations of the successive bonds.

Appendix

Additional Definitions:

Term	Definition
Tensile strength	Ability to resist stretching
Flexural strength	Resistance to breaking or snapping
Tensile stress (σ)	σ = force/cross-section area $\sigma = F/A$
Tensile strain (ε)	Change in sample length (when stretched) divided by the original length $\varepsilon = \Delta l/l$
Tensile modulus (E)	Ratio of stress to strain $E = \sigma/\varepsilon$

Recommended Reading

R.B. Seymour, *History of Polymer Science and Technology*, Dekker, New York, 1982
H. Morawetz, *The Origin and Growth of a Science*, Wiley-Interscience, New York, 1982
M.P. Stevens, *Polymer Chemistry*, 3rd Ed., Oxford University Press, 1998, (Chapter 1)
G. Odian, *Principles of Polymerization*, 3rd Ed. Wiley, New York, 1991, (Introduction)

Review Questions

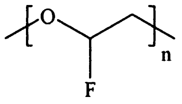
Section 1.2

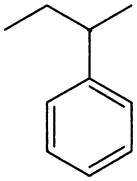
1. Define the degree of polymerization.
2. Polystyrene has a DP of 300. What is the molecular weight of the polymer?
3. What is a linear, a branched, a star-shaped, a comb-shaped, and a ladder polymer? Explain.
4. What is a network structure?
5. How can a network structure be formed by step-growth polymerization and also by chain-growth polymerization?
6. What is the difference between random and alternating copolymers?
7. What is meant by graft and block copolymers? Illustrate such copolymers of styrene and methyl methacrylate?

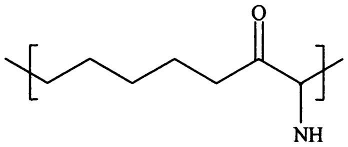
8. What are the important features of chain-growth and step-growth polymerizations. Explain the difference between the two? Can you suggest an analytical procedure to determine by what mechanism a particular polymerization reaction takes place?
9. What is the DP of polystyrene with molecular weight of 104,000 and poly(vinyl chloride) with molecular weight of 63,000?
10. Explain the differences between thermosetting and thermoplastic polymers and define gel point. How would you determine the gel point of a thermoset polymer?
11. Give the definitions of oligomer, telomer, and telechelic polymers.
12. What is a dendrimer polymer and what is a rotaxane polymer?
13. Illustrate three chain-growth polymers and three step-growth polymers.

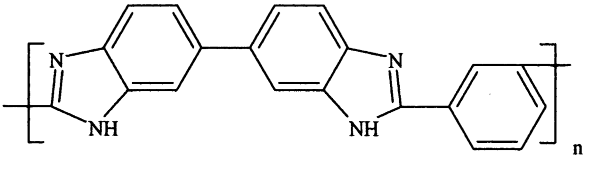
Section 1.3

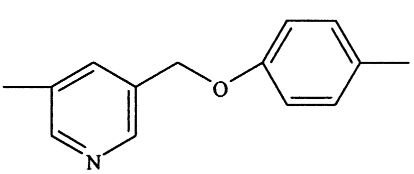
1. Name the following chain-growth polymers by the IUPAC system and by giving them trivial names:

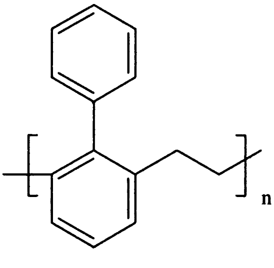












Section 1.4

1. What is meant by tacticity?
2. Give a definition of and illustrate by examples on polystyrene, isotactic, syndiotactic, and atactic arrangement of the macromolecules. This should include Fischer and Newman projections.
3. Explain what is meant by erythrodiisotactic, threodiisotaactic polymers. Illustrate. Do the same for erythrodisyndiotactic and threodisyndiotactic.
4. What are tritactic polymers? Draw *cis* and *trans* tritactic polymers.

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Chapter 2
Physical Properties and Physical Chemistry of Polymers

2.1 Structure and Property Relationship in Organic Polymers

For a very large proportion of polymeric materials in commercial use, mechanical properties are of paramount importance, because they are used as structural materials, fibers, or coatings and these properties determine their usefulness. Properties that also determine their utilization are compressive, tensile, and flexural strength, and impact resistance. Hardness, tear, and abrasion resistance are also of concern. In addition, polymers may be shaped by extrusion in molten state into molds or by deposition from solutions on various surfaces. This makes the flow behaviors in the molten state or in solution, the melting temperatures, the amount of crystallization, as well as solubility parameters important.

The physical properties of polymer molecules are influenced not only by their composition, but also by their size and by the nature of their primary and secondary bond forces. They are also affected by the amount of symmetry, by the uniformity in their molecular structures, and by the arrangements of the macromolecules into amorphous or crystalline domains. This, in turn affects melting or softening temperatures, solubilities, melt and solution viscosities, and other physical properties [1].

Due to the large sizes of polymeric molecules, the secondary bond forces assume much greater roles in influencing physical properties than they do in small organic molecules. These secondary bond forces are van der Waal forces and hydrogen bonding. The van der Waal forces can be subdivided into three types: dipole–dipole interactions, induced dipoles, and time varying dipoles.

2.1.1 Effects of Dipole Interactions

Dipole interactions result from molecules carrying equal and opposite electrical charges. The amounts of these interactions depend upon the abilities of the dipoles to align with one another. Molecular orientations are subject to thermal agitation that tends to interfere with electrical fields. As a result, dipole forces are strongly temperature dependent. An example of dipole interaction is an illustration of two segments of the molecular chains of a linear polyester. Each carbonyl group in the ester linkages sets up a weak field through polarization. The field, though weak, interacts with another field of the same type on another chain. This results in the formation of forces of cohesion. Because polymeric molecules are large, there are many such fields in polyesters. While each field is weak, the net effect is strong cohesion between chains. The interactions are illustrated in Fig. 2.1.

A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_2,

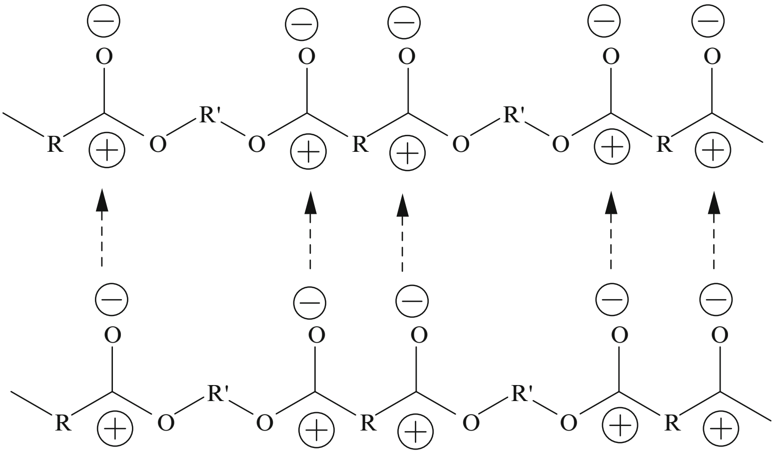


Fig. 2.1 Intramolecular forces

2.1.2 Induction Forces in Polymers

Electrostatic forces also result from slight displacement of electrons and nuclei in covalent molecules from proximity to electrostatic fields associated with the dipoles from other molecules. These are ***induced dipoles***. The displacements cause interactions between the ***induced dipoles*** and the ***permanent dipoles*** creating forces of attraction. The energy of the induction forces, however, is small and not temperature-dependent.

There are additional attraction forces that result from different instantaneous configurations of the electrons and nuclei about the bonds of the polymeric chains. These are time varying dipoles that average out to zero. They are polarizations arising from molecular motions. The total bond energy of all the secondary bond forces combined, including hydrogen bonding, ranges between 2 and 10 kcal/mole. Of these, however, hydrogen bonding takes up the greatest share of the bond strength. In Table 2.1 are listed the intramolecular forces of some linear polymers [2, 3].

As can be seen in Table 2.1., polyethylene possesses much less cohesive energy than does a polyamide. This difference is primarily due to hydrogen bonding. A good illustration is a comparison of molecules of a polyamide, like nylon 11, with linear polyethylene. Both have similar chemical structures, but the difference is that nylon 11 has in its structure periodic amide linkages after every tenth carbon, while such linkages are absent in polyethylene. The amide linkages participate in hydrogen bonding with neighboring chains. This is illustrated in Fig. 2.2.

Due to this hydrogen bonding, nylon 11 melts at 184–187°C and is soluble only in very strong solvents. Linear polyethylene, on the other hand, melts at 130–134°C and is soluble in hot aromatic solvents.

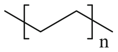
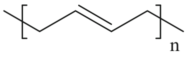
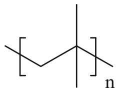
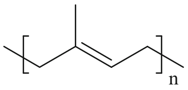
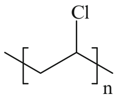
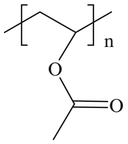
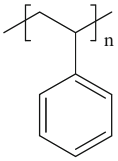
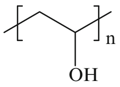
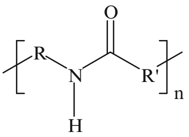
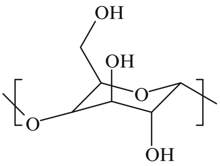
The energy of dipole interactions, (ϵ_k) can be calculated from the equation [1]:

$$\epsilon_k = -(2\mu^4/3RT)r^{-6}$$

where, μ represents the dipole moment of the polarized section of the molecule, r is the distance between the dipoles, T is the temperature in Kelvin, and R is the ideal gas constant.

Intermolecular forces affect the rigidity of all polymers. Should these forces be weak, because the cohesive energy is low (1–2 kcal/mole), the polymeric chains tend to be flexible. Such chains respond readily to applied stresses and can exhibit typical properties of elastomers. High cohesive energy, on the other hand, (5 kcal/mole or higher) causes the materials to be strong and tough. These polymers exhibit resistance to applied stresses and usually possess good mechanical properties. The temperatures and the flexibility of polymeric molecules govern both the sizes of molecular segments,

Table 2.1 Molecular cohesion of some linear polymers[a]

Polymer	Cohesion/5 Å chain length	Polymer structure
Polyethylene	1.0	
Polybutadiene	1.1	
Polyisobutylene	1.2	
Polyisoprene (*cis*)	1.3	
Poly(vinyl chloride)	2.6	
Poly(vinyl acetate)	3.2	
Polystyrene	4.0	
Poly(vinyl alcohol)	4.2	
Polyamides	5.8	
Cellulose	6.2	

[a] From refs [2, 3], and other literature sources

the motion, and the frequency at which that occurs. This in turn determines the rate at which the polymer molecules respond to molecular stresses. In flexible polymers, if the thermal energy is sufficiently high, large segments can disengage and slip past each other quite readily in response to applied stress. All elastomers possess such properties. Properties of polymers depend also upon ***morphology*** or upon the arrangement of their polymeric chains. This arrangement can be amorphous or crystalline. The term ***amorphous*** designates a lack of orderly arrangement. Crystalline

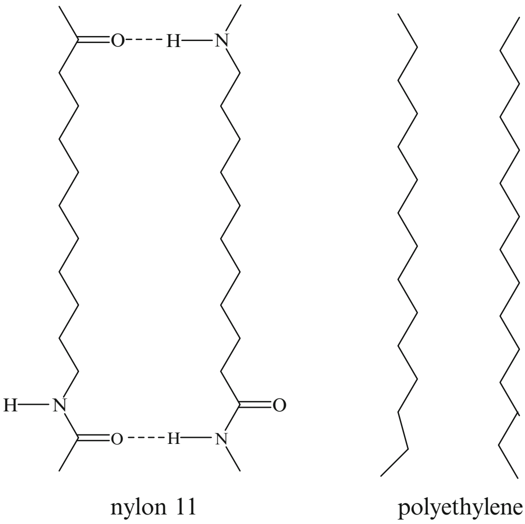
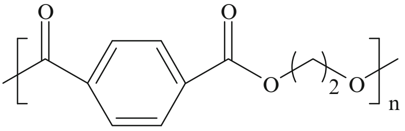
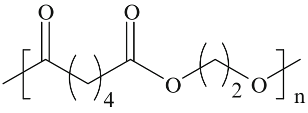


Fig. 2.2 Hydrogen bonding in (**a**) nylon 11, and absent in (**b**) polyethylene

morphology, on the other hand, means that the chains are aligned in some orderly fashion. Generally, the freedom of molecular motion along the backbones of polymeric chains contributes to lowering the melting temperature. Substituents that interfere with this motion tend to raise the melting point. For instance, isotactic polypropylene melts at a higher temperature than does linear polyethylene. If the substituent is bulky or rigid it raises the melting point because it interferes with molecular motion. Dipole interactions, as discussed above, have a similar effect [4]. A good illustration is a comparison of poly(ethylene terephthalate) that melts at 265°C with poly(ethylene adipate) that melts at only 50°C. In the first polyester, there is a rigid benzene ring between the ester groups while in the second one there is only a flexible chain of four carbons.



poly(ethylene terephthalate)

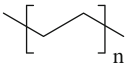


poly(ethylene adipate)

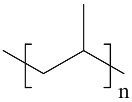
This flexibility of the four carbon segment in poly(ethylene adipate) contributes significantly to the lowering of the melting point.

Linear polymers that possess only single bonds between atoms in their backbones, C–C, or C–O, or C–N, can undergo rapid conformational changes [5]. Also ether, imine, or *cis*-double bonds reduce energy barriers and, as a result, “soften” the chains, causing the polymer to become more rubbery and more soluble in various solvents.

The opposite is true of cyclic structures in the backbones, as was shown in poly(ethylene terephthalate). Actually, cyclic structures not only inhibit conformational changes but can also make crystallization more difficult. Among the polymers of α-olefins the structures of the pendant groups can influence the melting point [6]. All linear polyethylene melts between 132 and 136°C [7]. Isotactic polypropylene, on the other hand melts at 168°C [8].



m.p. = 132-136 °C



m.p. = 168 °C

As the length of the side chain increase, however, melting points decrease and are accompanied by increases in flexibility [7] until the length of the side chains reached six carbons. At that point, the minimum takes an upturn and there is an increase in the melting points and decrease in flexibility. This phenomenon is believed to be due to crystallization of the side-chains [9].

Alkyl substituents on the polymers of α-olefins that are on the α-carbon yield polymers with the highest melting points. Isomers substituted on the β-carbon, however, if symmetrical, yield polymers with lower melting points. Unsymmetrical substitutions on the β-carbon, on the other hand, tend to lower the melting points further. Additional drop in the melting points result from substitutions on the γ-carbon or further out on the side-chains. Terminal branching yields rubbery polymers [10].

Copolymers melt at lower temperatures than do homopolymers of the individual monomers. By increasing the amount of a comonomer the melting point decreases down to a minimum (this could perhaps be compared to a eutectic) and then rises again.

The tightest internal arrangement of macromolecules is achieved by crystallinity. As a result, the density of a polymer is directly proportional to the degree of crystallinity, which leads to high tensile strength, and to stiff and hard materials that are poorly soluble in common solvents [11]. The solubility of any polymer, however, is not a function of crystallinity alone, but also of the internal structure and of the molecular weight. The solubility generally decreases with increases in the molecular weight. The fact that crystalline polymers are less soluble than amorphous ones can be attributed to the binding forces of the crystals. These binding forces must be overcome to achieve dissolution. Once in solution, however, crystalline polymers do not exhibit different properties from the amorphous ones. One should also keep in mind the fact that crosslinked polymers will not melt and will not dissolve in any solvent. This is due to the fact that the crosslinks prevent the chains from separating and slipping past each other.

2.2 The Amorphous State

A number of macromolecules show little tendency to crystallize or align the chains in some form of an order and remain disordered in solid form. This, of course, is also the condition of all molten polymers. Some of them, however, due to structural arrangement, remain completely amorphous upon cooling. The crystalline polymers, which crystallized from the melt, on the other hand, while containing areas of crystallinity, also contain some amorphous material. All crystalline polymers are also amorphous above their melting temperature. When sufficiently cooled, amorphous polymers can resemble glass. Above this glassy state, long-range segmented motions are possible and the molecular chains are free to move past each other. On the other hand, in the rigid, glass like state, only short-range vibrational and rotational motions of the segments are possible. At temperatures above the glassy state, amorphous polymers resemble rubbers, if crosslinked. If not crosslinked, amorphous polymers resemble very viscous liquids in their properties and there is molecular disorder. Tobolsky suggested [12] that polymer molecules in an amorphous state might be compared to a bowl of very long strands of cooked spaghetti. When molten, such molecules are in a state of wriggling motion, though the amplitude and speed depend very much on the temperature [13]. The important thing is to know that the chains possess random conformations. These conformations were characterized with the aid of statistical analysis [14].

2.2.1 The Glass Transition and the Glassy State

When the polymer cools and the temperature lowers, the mobility in the amorphous regions of the polymer decreases. The lower the temperature, the stiffer the polymer becomes until a point of transition is reached. This transition is called ***glass transition*** or ***second-order transition*** [15]. The temperature at that transition is called the ***glass transition temperature***, designated by T_g. Beyond stiffness, a change is manifested in specific volume, heat content, thermal conductivity, refractive index, and dielectric loss.

Bueche illustrated glass transition as follows [16]. In measuring the force necessary to force a needle into a polymer, like polystyrene, at various temperatures, there is a relationship between the force required to insert the needle and the temperature [16]. As the temperature is being lowered, maximum resistance to penetration is reached at T_g.

As stated, above T_g chains undergo cooperative localized motion. It is actually estimated that above T_g segmental motion of anywhere between 20 and 50 chain atoms is possible. Below the second-order transition temperature, however, there is insufficient energy available to enable whole segments of the polymeric chains to move. The structure is now stiff and brittle and resists deformation. When, however, sufficient amount of heat energy enters the material again and the temperature rises above T_g larger molecule motion involving coordinated movement returns. This requires more space, so the specific volume also increases and the polymer is in a rubbery or a plastic state. Above T_g, because large elastic deformations are possible, the polymer is actually both tougher and more pliable. Chemical structures of the polymers are the most important factors that affect the glass transition temperatures. Molecular weights also influence T_g, as it increases with the molecular weight. In addition, T_g also varies with the rate of cooling. Table 2.2. shows the structures of and lists relative T_g values of some common polymers.

One way to obtain T_g is by studying thermal expansion of polymers. It is generally observed that the thermal coefficient of expansion is greater above the glass transition temperature than below it, though the magnitude of the change differs from one polymer to another. By plotting volume vs. temperature for a polymer, one can obtain T_g as shown in Fig. 2.3, which illustrates obtaining T_g from specific volume-cooling temperature curves [17].

Polymers with bulky, tightly held side groups or stiff bulky components in the backbone have high T_g values. This is due to the fact that such side groups or bulky components interfere with segmental motion. Such polymers require higher temperatures to acquire sufficient free volume for segmental motion. This can be observed in Table 2.2. which shows that the glass temperature of polystyrene with stiff benzene ring side groups is much higher than that of polyethylene.

Also polymers with high attractive forces between chains will require more heat energy to go from a glassy to a rubbery or a plastic state. On the other hand, polymeric chains with loose hanging side chains that tend to loosen the polymer structure and increase the free volume for segmental movement will have lower T_g. For instance, the glass transition temperature of poly(methyl methacrylate) is higher than that of poly(*n*-butyl methacrylate) as can be seen from Table 2.2.

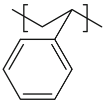
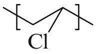
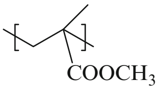
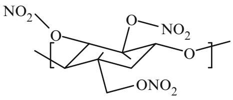
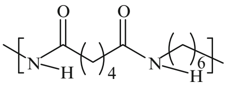
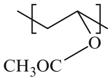
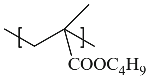
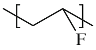
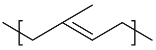
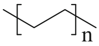
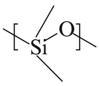
The transition to the glassy state from an equilibrium liquid results in changes in enthalpy, H, and volume, V. The specific heat is related to the enthalpy by definition:

$$C_p = (\partial H/\partial T)_p$$

The glassy state is nonequilibrium in nature and exhibits a tendency to undergo structural relaxation toward equilibrium. This tendency of the glassy state to relax structurally toward equilibrium is often referred to as ***structural recovery***. It was observed, however, that the progress towards structural recovery with time varies significantly between a down-quench and an up-quench. This is referred to as **asymmetry of structural recovery**. The nonlinearity of the process is described by the following equation [16]:

$$d(\upsilon - \upsilon_0)/dt = -(\upsilon - \upsilon_0)/\tau$$

Table 2.2 Glass transition temperatures, T_g, of some common polymers[a]

Repeat unit	Polymer	T_g (°C)
	Polystyrene	81; 90
	Poly(vinyl chloride)	75
	Poly(methyl methacrylate)	57–68
	Cellulose nitrate	53
	Nylon 6,6	47
	Poly(vinyl acetate)	30
	Poly(butyl methacrylate)	22
	Poly(ethyl acrylate)	−22
	Poly(vinyl fluoride)	−39
	Poly(butyl acrylate)	−56
	Polyisoprene	−70
	Polyethylene	−80; −90
	Silicone rubber	−123

[a] From ref [15] and other sources in the literature

where, τ is the relaxation time and υ is the specific volume. The value of T_g is also affected by other parameters, such as molecular weight, diluent concentration, tacticity, external pressure, crosslinking, chain stiffness, and mechanical deformation. For linear polymer, the ***Fox–Flory equation*** [18] described the relationship between T_g and the molecular weight:

$$T_g(M) = T_g(\infty) - K/\overline{M}$$

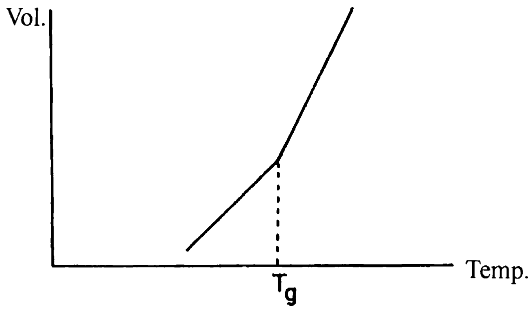


Fig. 2.3 The relationship of the specific volume of a polymer to the temperature

This equation, however, is limited in scope. It is actually neither valid for very high molecular weight polymers nor is it applicable to low molecular weight polymers.

The transition in a polymer from a molten state to a glassy one actually occurs over a temperature range. This range also includes T_g. At the glass transition temperature, however, the change in viscosity is rapid, from very viscous to a glassy one. Polymeric materials that undergo rearrangements in response to outside stimulus, like light, are becoming increasingly important in various industrial application (see Chap. 10). Urban and coworkers [19] studied stimuli-responsive (T_{SR}) transitions and correlated them to the glass transition temperatures (T_g). Based on their empirical data obtained from a copolymer, they concluded that the relationship between T_g and T_{SR} is

$$\log(V_1/V_2) = (P_1(T_{SR} - T_g))/(P_2(T_{SR} - T_g))$$

where the V_1 and V_2 are the copolymer's total volumes below and above the T_{SR}, respectively, T_g is the glass transition temperature of the copolymer, and P_1 and P_2 are the fraction of the free volume (f_{free}) at T_g (P_1) and $(T_{g,\text{ midpoint}} - T_{SR})_{50/50}$ for each random copolymer (P_2), respectively. They feel that this relationship can be utilized to predict the total volume changes as a function of $T_{SR} - T_g$ for different copolymer compositions.

2.2.2 *Elasticity*

The phenomenon of elasticity of rubber and other elastomers is a result of a tendency of large and very flexible amorphous polymeric chains to form random, thermodynamically favorable, conformations [18]. If a certain amount of crosslinking is also present, then these random conformations occur between the crosslinks. In a vulcanized (crosslinked) rubber elastomer, the crosslinks may occur at every five hundred to a thousand carbon atoms. The distance between the ends in such polymers is much shorter than when these elastomers are fully stretched. Deformation or stretching of rubber straightens out the various conformations in the molecules. They tend to return to the original state, however, when the forces of deformation are removed. So each segment behaves in a manner that resembles a spring. Some elastomeric materials are capable of high elongation and yet still capable of returning to the original conformation. Some soft rubbers, for instance, can be extended as high as 800% and even higher with full recovery. There is a preference for *trans* conformation, a planar zigzag at high extension. Rigidity of the chains, however, or crystallinity would hinder extension and, particularly, the recovery. High viscosity and a glassy state would do the same.

The high degree of elasticity of rubbers is due in part to the effects of thermal motions upon the long polymeric chains. These motions tend to restrict vibrational and rotational motions about the single bonds in the main chain. Such restrictive forces in the lateral direction, however, are much weaker than are the primary valence forces in the longitudinal direction. Greater amplitudes of motion also take place perpendicular to the chains rather than in the direction of the chains. These increased motions in the perpendicular direction result in repulsive forces between extended or parallel chains. Such forces cause them to draw together after stretching. So, the stretched rubber molecules retract due to longitudinal tension until the irregular arrangement of molecules is achieved again. This more random conformation is actually a higher entropy state.

When unstretched rubber is heated it increases in dimension with an increase in the temperature, as one might expect. At higher temperatures, however, rubbers, upon elongation, have a higher tendency to contract. This can be written as follows:

$$\text{retractive force, } f = -T(\partial \mathrm{S}/\partial L)_{\mathrm{Tv}}$$

$$(\partial f/\partial T)_{\mathrm{adiabatic}} = -(\partial L/\partial T)T/C_{\mathrm{p}}$$

In summary, polymeric materials exhibit rubber elasticity if they satisfy three requirements: (a) the polymer must be composed of long-chain molecules, (b) the secondary bond forces between molecules must be weak, and (c) there must be some occasional interlocking of the molecules along the chain lengths to form three-dimensional networks. Should the interlocking arrangements be absent, then elastomers lack memory, or have a fading memory and are not capable of completely reversible elastic deformations.

2.2.2.1 Thermodynamics of Elasticity

Stretching an elastomer reduces its entropy and changes its free energy. The retractive force in an elastomer is primarily the result of its tendency to increase the entropy towards the maximum value it had in the original deformed state Current explanations of rubber-like elasticity are based on several assumption [20]. The first one is that rubber-like elasticity is entirely intramolecular in origin. The second one is that the free energy of the network is separable into two parts, an elastic one and a liquid one. The liquid one is presumably not dependent on deformation. When an elastomer is stretched, the free energy is changed, because it is subjected to work. If we consider the stretching in one direction only, the work done W_{el} is equal to $f\partial l$, where f is the retractive force and ∂l is the change in length. The retractive force is then [19–21].

$$f = (\partial F/\partial L)_{\mathrm{T,p}} = (\partial H/\partial L)_{\mathrm{T,p}} - T(\partial S/\partial L)_{\mathrm{T,p}}$$

where F is the free energy, H is the enthalpy, and S is the entropy of the system. An ideal elastomer can be defined as one where $(\partial H/\partial L)_{\mathrm{T,p}} = 0$ and $f = -T(\partial S/\partial L)_{\mathrm{T,p}}$. The negative sign is due to the fact that work has to be done to stretch and increase the length of the elastomer. This description of an ideal elastomer is based, therefore, on the understanding that its retractive force is due to a decrease in entropy upon extension. In other words, the ***entropy of elasticity*** is the distortion of the polymer chains from their most probable random conformations in the unstretched condition. The probability that one chain end in a unit volume of space coordinates, x, y, z is at a distance r from the other end is [21, 22]:

$$W(x,y,z) = (b/\pi^{0.5})^3 e^{-b^2r^2}$$

where $b^2 = 3/2xL^2$. The number of links is x and the length is L. The entropy of the system is proportional to the logarithm of the number of configurations. Billmeyer expresses it as follows [7]:

$$S = (\text{constant}) - kb^2r^2$$

where k is the Boltzmann's constant. The retractive force for a single polymer chain, f' stretched to a length dr at a temperature T is, therefore,

$$f' = -T(\mathrm{d}S/\mathrm{d}r) = 2kTb^2r$$

It is generally assumed that the total retractive force of a given sample of an elastomer is the sum of all the f' forces for all the polymeric chains that it consists of. This is claimed to be justified in most cases, though inaccurate in detail [22].

Tobolsky wrote the equation for the entropy change of an unstretched to a stretched elastomer as depending upon the number of configurations in the two states [12]:

$$S - S_\mathrm{u} = k \ln \Omega/\Omega_\mathrm{u}$$

where Ω and Ω_u represent the number of configurations. The evaluation of these configurations by numerous methods allows one to write the equations for the change in entropy as:

$$S - S_\mathrm{u} = -\frac{1}{2}N_0k\left[(L/L_\mathrm{u})^2 + 2L/L_\mathrm{u} - 3\right]$$

where N_0 and L and L_u are the relative lengths of the unstretched and stretched elastomer. Tobolsky derived the tensile strength as being [12]:

$$X = (N_0kT/L_\mathrm{u})\left[(L/L_\mathrm{u}) - (L/L_\mathrm{u})^2\right]$$

By dividing both sides of the equation by the cross-sectional area of the sample, one can obtain the stress–strain curve for an ideal rubber.

The retractive force of an elastomer, as explained above, increases with the temperature. In other words, the temperature of elastomers increases with adiabatic stretching [21, 22]. The equation for the relationship was written by Kelvin back in 1857 [22]:

$$(\partial f/\partial T)_{\mathrm{p,l}} = (C_\mathrm{p}/T)(\partial T/\partial L)_{\mathrm{p,adiabatic}}$$

where C_p is specific heat and ∂l again is the change in length of the elastomer. Experimental evidence supports this, as the temperature of elastomers, like rubber, rises upon stretching. This equation can also be written in another form:

$$(\partial T/\partial f')_{\mathrm{p,adiabatic}} = T/C_\mathrm{p}(\partial l/\partial T)_{\mathrm{p},f'}$$

In actual dealing with polymers, stretching rubber and other elastomers requires overcoming the energy barriers of the polymeric chains with the internal energy of the material depending slightly on elongation, because

$$(\partial H/\partial L)_{\mathrm{T,p}} = (\partial E/\partial l)_{\mathrm{T,p}} + p(\partial V/\partial L)_{\mathrm{T,p}}$$

∂V is the change in volume. At normal pressures the second term on the right becomes negligible. It represents deviation from ideality. The contribution of the internal energy E to the force of retraction is

$$f = (\partial E/\partial L)_{\mathrm{T,p}} - T(\partial S/\partial L)_\mathrm{T}$$

Bueche [16] expressed differently the work done on stretching an elastic polymeric body. It describes deforming an elastomer of x length, stretched to an increase in length α in a polymeric chain composed of N freely oriented segments. The other dimensions of this polymeric chain are y and z. These are coordinates that become reduced as a result of stretching to $1/(\alpha)^{0.5}$.

$$\text{Work done per chain} = (3kT/2N\alpha^2)[(\alpha^2 - \alpha^{-1})x_0{}^2 + (\alpha^{-1} - 1)r_0{}^2]$$

where the chain ends are initially r_0 distance apart [16],

$$r_0{}^2 = x^2 + y^2 + z^2$$

Bueche [16] also described the average energy per chain as

$$\text{Ave. energy/chain} = (3kT/2)(1/3)[(\alpha^2 - \alpha^{-1}) + (\alpha^{-1} - 1)]$$

The modulus of elasticity, G, was shown to be related to strain in elongation of polymeric elastomers. For up to 300% elongation, or more, the following relationship [22] applies:

$$G = 2mkTb^2(1 + 2/\gamma^3)$$

Where k is Boltzmann's constant, m represents the number of polymeric chains in the sample, and γ is the strain. The relationship of stress to strain is:

$$\text{Stress} = 2mkTb^2(\gamma + 2/\gamma^3)$$

There are several molecular theories of rubber-like elasticity The simplest one is based on a Gaussian distribution function for the end to end separation of the network chains: [23] (the dimensions of the free chains as unperturbed by excluded volume effect are represented by $(r^2)_0$)

$$\omega(r) = (3/2\pi(r^2)_0)^{3/2} \exp(3r^2/2(r^2)_0)$$

Within this Gaussian distribution function $(r^2)_0$ applies to the network chains both in the unstretched and stretched state. The free energy of such a chain is described by a Boltzmann relationship [23]:

$$F(T) = -KT \ln \omega(r) = C(T) + (3kT/2(r^2)_0)r^2$$

$C(T)$ is a constant at a specified absolute temperature T. The change in free energy for a stretched elastomer can be expressed as follows:

$$\Delta F = [3kT/2(r^2)_0][(\alpha_x^2 x^2 + \alpha_y^2 y^2 + \alpha_z^2 z^2) - (x^2 + y^2 + z^2)]$$

where α is the molecular deformation ratio of r components in x,y,z directions from the unstretched or elastomer to one that was stretched and deformed. Additional discussions of this theory and other theories of elasticity are not presented here because thorough discussions of this subject belong to books dedicated to physical properties of polymers.

2.2.3 *Rheology and Viscoelasticity of Polymeric Materials*

When an amorphous polymer possesses a certain amount of rotational freedom, it can be deformed by application of force. Application of force will cause the polymer to flow and the molecules will move past each other. The science of deformation and flow is called ***rheology***. In the event that the force is applied quickly, and then withdrawn rapidly, the polymer molecules will tend to revert back to their previous undisturbed configuration. This is called ***relaxation***. Thus, the amorphous polymers exhibit some ***elastic*** behavior due to disruption of thermodynamically favorable arrangements. If, however, the force is applied gradually and consistently, the molecules will flow irreversibly. Due to chain entanglement that increases with molecular weight and due to frictional effects, the viscosity of the flowing liquid will be high. Thus, molecular weight control is very important in polymer processing. In a way this is a paradoxical situation. Higher molecular weights usually yield better mechanical properties. On the other hand, higher molecular weight materials are harder to process. The molecular weight control, therefore, is quite critical. The combination of properties of polymeric liquids, elasticity, and viscous flow is referred to as ***viscoelasticity***. It means reversible uncoiling of the polymeric chains. By the same terminology, ***viscous flow*** means irreversible slipping of the chains past each other. Thus, viscoelastic materials exhibit simultaneously a combination of elastic and viscous behavior. This type of behavior is particularly prominent in polymeric materials. The flow behavior of polymeric liquids is also influenced by the molecular weight distribution.

At proper temperatures the mechanical properties of many amorphous polymers may approach the physical properties of three idealized materials individually. These are [20, 22, 24]:

1. *A **Hookian or an ideal elastic solid***, whose small reversible deformations are directly proportional to the applied force.
2. *A **Newtonian liquid*** that flows with a viscosity independent of the rate of shear.
3. *An **ideal elastomer*** that is capable of reversible extension of several hundred percent, with a much smaller stiffness than that of a Hookian solid.

In the elastic response for a Hookian liquid the stress–strain relationship is: $\sigma(t) = G\gamma(t)$. For the Newtonian liquid it is $\sigma(t) = \eta\gamma'(t)$. In these equations, $\gamma(t)$ and $\gamma'(t)$ represent shear strain and shear rate at time t, while $\sigma(t)$ is the shear stress.

Many forces can be applied to polymer deformation. The force that rheologists are particularly concerned with is ***tangential stress*** or ***shear***. This is due to the fact that many polymers are extruded and forced to flow into dies for shaping and commercial use. If a shearing force f is applied to a cube of molten polymer per unit area it causes the top layer of the liquid to move a distance x from a fixed point at the bottom of the material with a velocity v. Shear causes the molecules to move past each other. This is illustrated in Fig. 2.4.

The above assumes that the viscosity of the material is sufficiently small so that the cube is not very distorted during the process. The viscosity of the material, η is defined as the ratio between the applied force and the velocity gradient, $\partial v/\partial x$ or as the rate of shear γ, where

$$\text{free energy, } F = \eta(v/x)$$

The above equation can be rearranged into another form,

$$\eta = Fv/v^2$$

Fv is the energy used up per second on the cube.

The ***shear stress***, $\boldsymbol{\tau}$ is defined as

$$\tau = \eta\partial v/\partial x = \eta\gamma$$

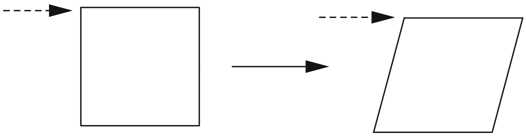


Fig. 2.4 Illustration of the movement of the upper layer due to applied force

where γ is the ***shear rate***. In this instance it should be equal to v. If the viscosity η is independent of the shear rate, the liquid exhibits ideal flow and is a ***Newtonian*** liquid. Tobolsky commented [12] that probably all Newtonian liquids, even those like water and benzene, that are very fluid, possess some elastic as well as viscous behavior. However, flow of most polymer liquids deviates strongly from an ideal behavior and either the viscosity decreases with the rate of shear, or no flow occurs until a certain minimum force is applied. The decrease of viscosity with the rate or shear is called ***shear thinning***. It is believed to be a result from the tendency of the applied forces to disturb the long chains from their favored equilibrium conformations. In this case, the polymer is at an ***yield point*** or at an ***yield value***. A liquid with an yield point is called a ***Bingham Newtonian fluid***, provided that it exhibits Newtonian behavior once it starts flowing. It is defined by

$$\tau = \tau_c + \eta\gamma$$

where τ_c is the critical shear stress, or threshold stress that is needed to initiate the flow. The Bingham fluid behavior might be attributed to structural arrangements of the molecules that give rise to conformational and secondary bonding forces. The **non-Newtonian** behavior occurs when shear stress does not increase in proportion to shear rate. In addition, there are ***thixotropic*** liquids that exhibit high viscosity or even resemble gelation at low shear rate but flow readily and exhibit low viscosity upon application of high shear. High shear rates can cause chain rupture and result in loss of molecular weight. In some cases, the shear rate may increase due to increase in molecular entanglement. In the case of flexible chain polymers, there is a critical molecular weight at which chain entanglement may show an increase. For most common polymers this may be in the molecular weight range of 4,000–15,000. Flow is also influenced by chain branching. The higher the degree of branching in a polymer, the lower will be the degree of entanglement at a given molecular weight. In general, the viscosity is higher with linear polymers than with branched ones at a given shear rate and molecular weight. Flow behavior is also influenced by molecular weight distribution (see Sect. 2.7.1). Usually, the broader the molecular weight distribution in polymers the lower is the shear rate that is needed to cause ***shear thinning***. On the other hand, for polymers with narrow molecular weight distribution, shear thinning, once it starts, is more pronounced. This is due to absence of chain entanglement of the higher molecular weight polymeric chains.

The viscosity of low molecular weight polymers is related to their temperature by an Arrhenius-type relationship [19, 22, 25]:

$$M_\eta = Ae^{-E/RT}$$

where E is the ***activation energy for viscous flow***, and A is a constant related to molecular motion, and M_η is the viscosity average molecular weight. For branched polymers, the larger or bulkier the side chains the greater is the activation energy, E. The same is true of polymers with large pendant groups. The activation energy of flow, E does not increase proportionately to the heat of vaporization for polymers but rather levels off to a value that is independent of molecular weight. This implies that for long chains the unit of flow is much smaller than the whole molecule. Instead, segments of the molecules, no larger than 50 carbon atoms move by successive jumps.

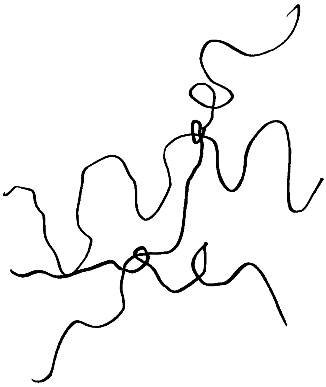


Fig. 2.5 Illustration of a physical crosslink in molten polymers

This is accomplished with some degree of coordination, but results in the whole chain shifting. Based on experimental evidence, the viscosity can be defined as,

$$\ln \eta = 3.4 \ln M_\mathrm{w} + C + E/RT$$

where C is a constant. M_w is weight average molecular weight (see Sect. 2.7) Chain length, Z, or the molecular weight of polymers is an important variable that influences flow properties of polymers. The relationship of a Newtonian viscosity of an amorphous polymer to the chain length when shear stress is low can be expressed as [19, 22, 25],

$$\log \eta = 3.4 \log Z_\mathrm{w} + k$$

where the constant k is temperature-dependent. By the same token, based on experimental evidence, the relationship of viscosity to temperature and to chain length at low shear rates, for many polymers can be expressed as follows:

$$\log \eta = 3.4 \log Z_\mathrm{w} - 17.44(T - T_\mathrm{g})/(51.6 + T - T_\mathrm{g}) + k'$$

where constant k' is specific for each polymer and T_g is the glass transition temperature (T_g is discussed in Sect. 2.2.3). Although linear molten polymers exhibit well-defined viscosities, they also exhibit elastic effects. These effects are present even in the absence of any crosslinks or a rubber network. It is referred to as ***creep***. This creep is attributed to entanglement of polymeric chain to form temporary physical crosslinks: This is illustrated in Fig. 2.5.

Deviations from Newtonian flow can occur when shear stress does not increase in direct proportion to shear rate. Such deviation may be in the direction of thickening (called **dilatent flow**) and in the direction of thinning (called **pseudo plastic**). Related to non-Newtonian flow is the behavior of thixotropic liquids when subjected to shear, as explained above. Flow behavior can be represented by the following equation:

$$\tau = A\gamma^B$$

where A is a constant and B is the index of flow. For Newtonian liquids $A = \eta$ and $B = 1$. All polymers tend to exhibit shear thinning at high shear rates. This is commonly explained by molecular entanglement, as mentioned above. Certainly, in the amorphous state there is considerable entanglement of the polymeric chains. Low shear rates may disrupt this to a certain degree, but the chains will still remain entangled. As the shear rates increases, disruption can occur at a faster rate than the chain

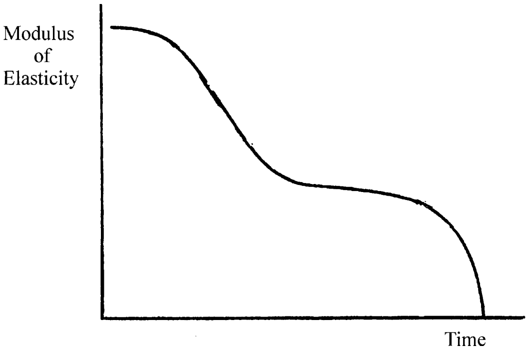


Fig. 2.6 Illustration of a plot of modulus of elasticity against time

can reentangle. The decreased amount of entanglement results in lower viscosity of the liquid, allowing the molecules to flow with less resistance. Actually, two factors can contribute to chain entanglement. These are high length of the chains for very large molecules and/or bulky substituents. Stress applied to a Newtonian liquid, outside of an initial spike, is zero. Stress, however applied to a viscoelastic fluid starts at some initial value. This value decreases with time until it reaches an equilibrium value due to the viscoelastic property of the material. Figure 2.6 illustrates what a plot of the modulus of elasticity $G(t)$, which depends on the temperature, when plotted against time, looks like:

The equation for ***shear–stress relaxation modulus*** that varies with temperature can be written as follows:

$$G(t) = \sigma(t)/\gamma_0$$

With constant stress, $\sigma(t) = G\gamma_0$, where creep strain $\gamma(t)$ is constant $[\gamma(t) = \sigma_0/G]$ for a Hookean solid. It would be directly proportional to time for a Newtonian liquid $[(\gamma(t) = \sigma_0/\eta)t]$. Here t is the initial time at which recovery of the viscoelastic material begins. For a viscoelastic fluid, when stress is applied, there is a period of creep that is followed by a period of recovery. For such liquids, strains return back toward zero and finally reach an equilibrium at some smaller total strain. For the viscoelastic liquid in the creep phase, the strain starts at some small value, but builds up rapidly at a decreasing rate until a steady state is reached. After that the strain simply increases linearly with time. During this linear range, the ratio of shear strain to shear stress is a function of time alone. This is ***shear creep compliance***, $J(t)$ The equation of shear creep compliance can be written as follows:

$$J(t) = \gamma(t)/\sigma_0$$

The stress relaxation modulus and the creep compliance are both manifestations of the same dynamic process at the molecular level and are closely related. This relationship, however, is not a simple reciprocal relations that would be expressed as $G(t) = 1/J(t)$, but rather in an integral equation that is derived from the Boltzman superposition principle. It relates recoverable compliance, J_s^0 to η_0, zero shear viscosity [22].

$$J_s^0 = \frac{1}{\eta_0^2}\int_0^{\infty} tG(t)\mathrm{d}t$$

$$\eta_0 = \int_0^{\infty} G(t)\mathrm{d}t$$

In relaxation back to equilibrium, the polymer assumes a new conformation. At first, the response is glassy. The modulus for such an organic glass is large, $G_g \sim 10^9$ Pa. This modulus decreases with

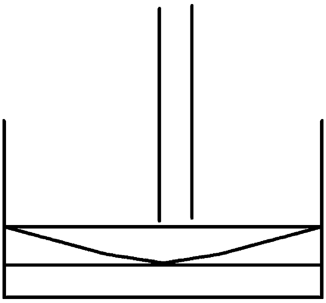


Fig. 2.7 Illustration of a cone and plate rheometer

time as the polymer begins to relax and continues along the whole length of the chain. For short chains this relaxation to zero takes place at a fairly constant rate. For very long chains, however, the relaxation rate tends to be in three stages. It starts at a certain rate at stage one, but after a while, noticeably slow down at some point, and at stage two the modulus remains relatively constant over some period of time. After that, at stage three, the relaxation is resumed again at a rapid rate until full equilibrium is reached. At stage two there is a period of relatively constant modulus that is not affected by the chain architecture and the material resembles a rubber network. The length of the third stage, however, is profoundly affected by the molecular weight, by the molecular weight distribution and by long-chain branching of the polymer.

Koga and Tanaka [23] studied the behavior of normal stresses in associated networks composed of telechelic polymers under steady shear flow. They showed numerically that the first and second normal stress coefficients reveal thickening as a function of shear rate and that the sign of the second normal stress coefficient changes depending on the nonlinearity in the chain tension, the dissociation rate of the associative groups from junctions and the shear rate by analytic calculation they showed that in the limit of small shear-rate, the sign inversion occurs by the competition between the nonlinear stretching and dissociation of associative groups. Thus, the molecular mechanism of the sign inversion is shown to be similar to that of thickening of the shear viscosity.

In the behavior of polymeric liquids two quantities are important. These are steady-state recoverable shear compliance, J_s^0 (as shown above) and steady-state viscosity at zero shear rate, η_0. These quantities are related:

$$\text{recoverable shear compliance } J_s^0 = \gamma_r/\sigma_0$$

$$\text{zero shear viscosity } \eta_0 = \sigma_0/\gamma'_{ss}$$

where γ'_{ss} is the shear rate and γ_r is the total recoil strain. Both shear compliance and shear viscosity can be obtained from creep studies. The product of the two, zero shear compliance and zero shear viscosity is the characteristic relaxation time of the polymer:

$$\tau_0 = J_s^0\eta_0$$

There are various techniques for determining the viscosity of molten polymers. One commonly used piece of equipment is a cone and plate rotational viscometer. The equipment is illustrated in Fig. 2.7:

The molten polymer is placed between the bottom plate and the cone, and the cone is rotated at constant speed. Shear stress is obtained from the following relationship:

$$\tau = 3M/2\pi R$$

where M is the torque in dynes per centimeter, and R is the cone radius in centimeters (or meters). The shear rate can be obtained from the following equation

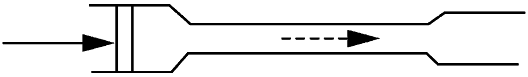


Fig. 2.8 Illustration of a capillary viscometer

$$\gamma' = \Omega/\alpha$$

where α is the cone angle in radians or in degrees, and Ω is the angular velocity in radians per second or in degrees per second. The viscosity is obtained from the following relationship [15, 16]:

$$\eta = \tau/\gamma' = 3\alpha M/2\pi R^3\Omega = kM/\Omega$$

k is a constant, specific for the viscometer used. It can be obtained from the relationship [7]:

$$k = 3\alpha/2\pi R^3$$

The cone and plate rheometers are useful at relatively low shear rates. For higher shear rates capillary rheometers are employed. They are usually constructed from metals. The molten polymer is forced through the capillary at a constant displacement rate. Also, they may be constructed to suit various specific shear stresses encountered in commercial operation. Their big disadvantage is that shear stress in the capillary tubes varies from maximum at the walls to zero at the center. On the other hand, stable operation at much higher shear rates is possible. Determination, however, of η_0 is usually not possible due to limitations of the instruments. At low shear rates. one can determine the steady-state viscosity from measurements of the volumetric flow rates, Q and the pressure drop:

$$\Delta P = P - P_0$$

where, P_0 is the ambient pressure. A capillary viscometer is illustrated in Fig. 2.8, where the diameter of the capillary can be designated as D. For Newtonian liquids the viscosity can be determined from the following equation:

$$\eta = \pi D^4 \Delta P/128LQ$$

where L represents the length of the capillary. The shear stress at the capillary wall can be calculated from the pressure drop:

$$\sigma_{\text{wall}} = D\Delta P/4L$$

Also, the shear rate at the walls of the capillary can be calculated from the flow rate [22]:

$$\gamma'_{\text{wall}} = 8Q\left(3 + \frac{\mathrm{d}\log Q}{\mathrm{d}\log \Delta P}\right)/\pi D^3$$

Wang et al. studied the homogeneous shear, wall slip, and shear banding of entangled polymeric liquids in simple-shear rheometry, such as in capillary viscometry, shown above [20]. They observed that recent particle-tracking velocimetric observations revealed that well-entangled polymer solutions and melts tend to either exhibit wall slip or assume an inhomogeneous state of deformation and flow during nonlinear rheological measurements in simple-shear rheometric setups.

It is important to control the viscoelastic properties of confined polymers for many applications. These applications are in both, microelectronics and in optics. The rheological properties of such films, however, are hard to measure. Recently, Chan et al. [27] reported that the viscoelasticity can be measured through thermal wrinkling. Thermally induced instability develops when polymer films are compressed between rigid, stiffer layers. This is due to differences in coefficients of thermal expansion between the polymer and the inorganic layers. A net compressive stress develops at the polymer–substrate interface when the composite layers are heated to temperatures that promote mobility of the polymer layer. Such wrinkling substrate surface is characterized by an isotropic morphology that can be approximated as a sinusoidal profile. Chan et al. utilized the thermal wrinkling to measure the rubbery modulus and shear viscosity of polystyrene thin films as a function of temperature. They used surface laser-light scattering to characterize the wrinkled surface in real-time in order to monitor the changes in morphology as a function of annealing time at fixed annealing temperatures. The results were compared with a theoretical model, from which the viscoelastic properties of the PS thin film are extracted.

2.3 The Crystalline State

Mendelkern [5] pointed out that essentially all properties of polymers are controlled by the molecular morphology. In contrast to the amorphous or liquid state, the crystalline state is relatively inelastic and rigid. In the crystalline state, the bonds adopt a set of successive preferred orientations, while in the liquid state the bond orientation is such that the chains adopt statistical conformations. In the crystalline state the properties of the polymers differ considerably. If a polymer molecule is coiled randomly, then it cannot fit readily into a geometrically arranged, regular crystalline lattice. So the molecules must change into a uniform shape to fit into a crystal pattern. In many cases they assume either a helix or a zigzag conformation. Such arrangements are more regular than in a random coil [29–40]. This can even be detected by spectral and thermodynamic studies. During crystallization, polymers with bulky substituents that are spaced close to each other on the polymeric chains tend to form helical conformations that remain in the crystalline phase. The arrangement allows close packing of the substituents without much distortion of the chain bonds. That is particularly true of many isotactic polymers that crystallize in helical conformations, taking on ***gauche*** and ***trans*** positions. For the *gauche* position steric hindrance always forces the rotation to be such as to place the substituents into a juxtaposition generating either a right-hand or a left-had helix. The helical conformations of isotactic vinyl polymers were illustrated by Gaylord and Mark [41] as shown in Fig. 2.9:

When macromolecules possess a certain amount of symmetry, then there is a strong accompanying tendency to form ordered domains, or crystalline regions. ***Crystallinity***, however, in polymers differs in nature from that of small molecules. When the small molecules crystallize, each crystal that forms is made up of molecules that totally participate in its makeup. But, when polymers crystallize from a melt, which means that certain elements of the polymeric system or segments of the polymeric chains have attained a form of a three-dimensional order. Complete crystallization, from the melt, however, is seldom if ever achieved The ordered conformations may be fully extended or may be in one of the helical forms as shown above. This resembles orderly arrangement of small molecules in crystals. The crystalline domains, however, are much smaller than the crystals of small molecules and possess many more imperfections.

2.3.1 *Crystallization from the Melt*

Certain basic information was established about the ***crystallization from the melt*** [5]: The process is a first-order phase transition and follows the general mathematical formulation for the kinetics of a

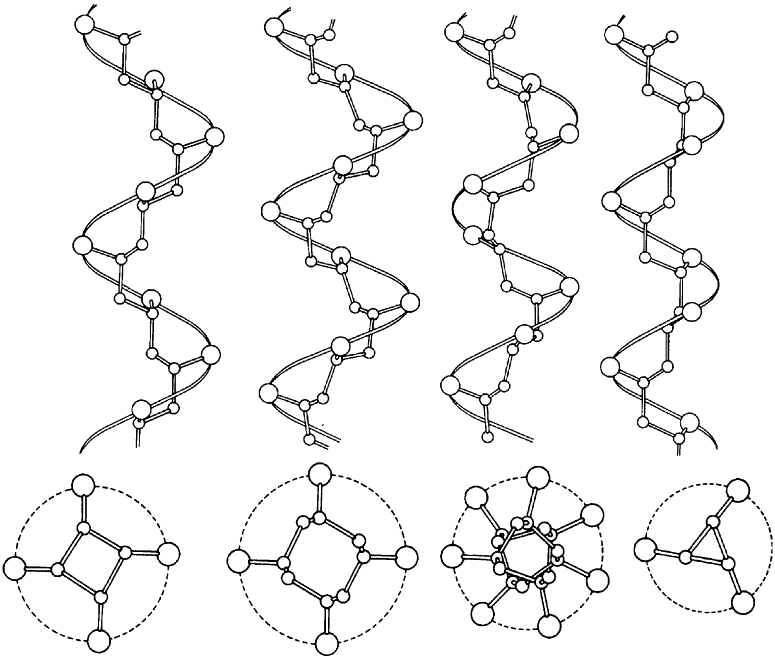


Fig. 2.9 Illustration of the helical conformation of isotactic vinyl polymers

phase change. Equilibrium conditions, however, are seldom if ever attained and as a result complete crystallinity, as stated above, is not reached. The tendency to crystallize depends upon the following:

1. Structural regularity of the chains that leads to establishment of identity periods.
2. Free rotational and vibrational motions in the chains that allow different conformations to be assumed.
3. Presence of structural groups that are capable of producing lateral intermolecular bonds (van der Wall forces) and regular, periodic arrangement of such bonds.
4. Absence of bulky substituents or space irregularity, which would prevent segments of the chains from fitting into crystal lattices or prevent laterally bonding groups from approaching each other close enough for best interaction.

Natta and Carradini [30] postulated three principles for determining the crystal structures of polymers These are:

1. It is possible to assume that all mer units in a crystal occupy geometrically equivalent positions with respect to the chain axis. This is known as the ***Equivalence Postulate***.
2. The conformation of the chain in a crystal is assumed to approach the conformation of minimum potential energy for an isolated chain oriented along an axis. This is the ***Minimum Energy Postulate***.
3. As many elements of symmetry of isolated chain as possible are maintained in the lattice, so equivalent atoms of different mer units along an axis tend to assume equivalent positions with respect to atoms of neighboring chains. This is the ***Packing Postulate***.

X-ray diffraction studies of polymers crystallized from the melt show recognizable features in some of them. The Bragg reflections, however, appear more broad and diffuse than those obtained from well-developed single crystals. Such broadening could be the result of the crystals being small. It could also be the result lattice defects. Because diffraction patterns are too weak, it is impossible to reach a conclusion. The majority opinion, however, leans toward the small crystal size as being the

Fig. 2.10 Illustration of a fringed micelle

cause of the broadening [5]. The crystals from the melt are approximately 100 × 200 × 200 Å in size. Rough estimates from these diffraction studies indicate that the size of crystals, or crystallites, rarely exceeds a few hundred angstroms. The fact that there is a substantial background of diffuse scattering suggests that considerable amorphous areas are also present. Because the chains are very long, it has often been suggested that individual chains contribute to several different crystalline and amorphous domains. This resulted in a proposal of a composite single-phase structure [5], a ***fringed micelle*** or a ***fringed crystallite*** model. This is illustrated in Fig. 2.10. The fringes are transition phases between the crystalline and the amorphous regions. Some analytical studies, however, failed to support this concept.

The proportion of crystalline matter in a polymer is defined as the ***degree of crystallinity***. It can be expressed in volume or in mass. By expressing it in volume, it would be:

$$\text{degree of crystallinity}\, X_{\mathrm{v}} = V_{\mathrm{c}}/(V_{\mathrm{c}} + V_{\mathrm{a}}) = V_{\mathrm{c}}/V$$

where, V_{c}, V_{a}, and V represent the respective volumes of the crystalline and amorphous regions and the total volume.

When expressed in terms of mass, the equation would be:

$$X_{\mathrm{m}} = m_{\mathrm{c}}/(m_{\mathrm{c}} = m_{\mathrm{a}}) = m_{\mathrm{c}}/m$$

where, m_{c}, m_{a}, and m are the masses of crystalline, amorphous phases, and the total mass.

2.3.2 Crystallization from Solution

For many polymers, crystal growth can also take place from dilute solutions and from such solutions they yield **single crystals**. Crystal formations in polymers were studied intensively almost from the time of recognition of their existence in macromolecules. **Single crystals** of organic polymers were recognized as early as 1927 [26]. It became the subject of intensive investigations after observations that linear polyethylene can crystallize into single crystals. The observations made on polyethylene were followed by observations that it is possible to also grow single crystals of other polymers. Some of them are polyoxymethylene [30], polyamides [31], polypropylene [32], polyoxyethylene [33],

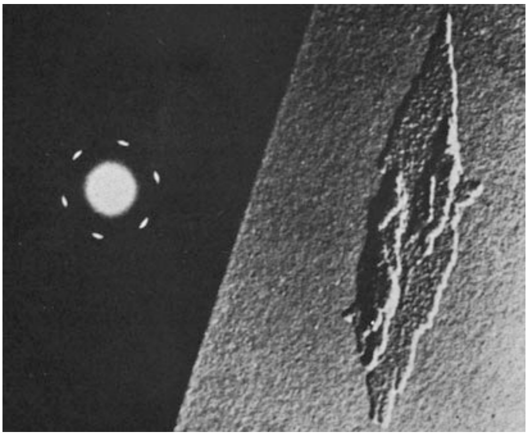


Fig. 2.11 Electron diffraction pattern and single crystal of polyacrylonitrile (from ref [50])

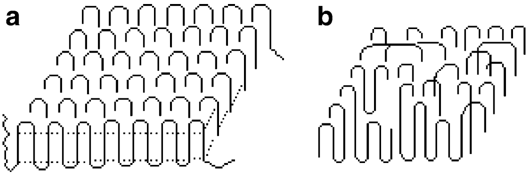


Fig. 2.12 Models of chain folding. (**a**) adjacent reentry model, and (**b**) nonadjacent reentry model

cellulose [34], and others [35]. The electron diffraction pattern and a single crystal of polyacrylonitrile are shown in Fig. 2.11.

There is good correlation between the structural regularity of a specific polymer and the appearance of its single crystals. Relatively larger single crystals with smooth, sharp edges, and little random growth are formed only from polymers that are known to have high regularity in their structures.

To explain the arrangement of the chains in the single crystals a theory of ***folded chain lamella*** was proposed in 1947 [36]. It states that the basic units in single crystals are ***lamellae*** about 100 Å thick. The evidence for the existence of lamellae-like crystallites comes from microscopic observations. Direct microscopic observations, however, do not yield information about chain structure on the molecular level. The thickness of the lamellae relative to the chain length led some to postulate that the molecules are arranged perpendicular or nearly so to the layers. Also that sharp, folded configurations form with the fold length corresponding to the layer thickness. In this view, one polymer molecule is essentially constrained to one lamellae and the interface is smooth and regularly structured with the chain folding back and forth on itself like an accordion during crystallization. Two models of chain folding are visualized. In one model, the chain folding is regular and sharp with a uniform fold period. This is called the ***adjacent-reentry model***. In the other one, the molecules wander through the irregular surface of a lamella before reentering it or a neighboring lamella. This mode is called ***switchboard*** or ***nonadjacent-reentry model***. The two are illustrated in Fig. 2.12. Some early experimental evidence failed to support the lamellae concept [37]. Since, much evidence was presented to support it, today it is accepted as an established fact [5]. Recently, Hosoda and coworkers [37] reported studies of the morphology of specially synthesized polyethylene with *n*-butyl branches precisely spaced on every 39th carbon. This was compared with a commercial ethylene/1-hexene copolymer possessing the same branching probability. The goal of their work was to elucidate the effect of the intramolecular sequence length heterogeneity on the lamella crystal thickness and its distribution. The commercial copolymer was found to have an orthorhombic crystalline polymorphism, which is normal for such polyethylenes and different from that of the specially synthesized material. The synthesized one exhibits a narrow lamella thickness distribution with the average thickness corresponding exactly to the space length between two consecutive branches. This suggests to them. complete exclusion of *n*-butyl branches from the crystal stem. On the other hand, the 1-hexene copolymer forms much thicker lamellae and a broader thickness distribution than the synthesized polyethylene with butyl branches. Here, the average thickness is 1.5 times larger than that calculated from the most probable ethylene sequence length obtained from NMR, or for a theoretical ethylene sequence Length distribution, indicating that the lamellae are composed predominantly of the sparsely branched longer ethylene sequences.

Linear polyethylene single crystals often exhibit secondary structural features that include corrugations and pleats. It was suggested that the crystals actually grow in form of pyramids, but that these pyramidal structures collapse when the solvent is removed during preparation for microscopy [42]. Various investigators described other complex structures besides pyramidal. Typical among these descriptions are sheaf-like arrays that would correspond to nuclei. Also there were observations of dendridic growths, of clusters of hollow pyramids, of spiral growths, of epitaxial growths, of moiré patterns, etc. [42, 43].

2.3.3 Spherulitic Growth

For polymers that **crystallize from the melt**, an important parameter in the characterization of the two-phase systems, is the weight fraction of the crystalline regions. The degree of crystallinity that can be reached is dependent on the temperature at which crystallization takes place. At low temperatures one attains a much lower degree of crystallization than at higher temperatures. This implies that crystallization remains incomplete for kinetic reasons [7].

Normal conditions of cooling of the molten polymer establish the crystalline texture of the polymer and usually result in formation of very tiny crystals. These crystals are part of a closely spaced cluster called ***spherulite***. The formation of a single nucleus in a polymer cooled below its melting point favors the formation of another nucleus in its vicinity due to creation of local stresses.

Microscopic examinations with polarized light of many polymeric materials that crystallized from the melt show the specimen packed with spherulites. Often these appear to be symmetrical structures with black crosses in the center [38]. It is believed [39] that these spherulites grow from individual nuclei. Ribbons of crystallites grow from one spherulitic center and fan out in all directions. Initially they are spherical but because of mutual interference irregular shapes develop. The diameters of spherulites range from 0.005 to 0.100 mm. This means that a spherulite consists of many crystalline and noncrystalline regions. The black crosses seen in the spherulites are explained [39] by assuming that the crystallites are arranged so that the chains are preferentially normal to the radii of the spherulites. Spherulitic morphology is not the universal mode of polymer crystallization. Spherulitic morphology occurs usually when nucleation is started in a molten polymer or in a concentrated solution of a polymer. Spherulitic growth is illustrated in Fig. 2.13.

The size and number of spherulites in the polymer tends to affects the physical properties. Thus, the impact strength of polymer films or their flex life usually increases as the spherulite size decreases. On the other hand, there does not appear to be any correlation between the yield stress and ultimate elongation and the size of the spherulites.

Rhythmic crystal growth is generally encountered in thin films of semicrystalline polymers. This is believed to be due to formation of ring-banded spherulites and attributed to the periodical lamellae twisting along the radial growth direction of the spherulites [42]. Recently, Gu and coworkers [43] reported that by using mild methylamine vapor etching method, the periodical cooperative twisting of lamellar crystals in ring-banded spherulites was clearly observed.

When the melt or the solutions are stirred ***epitaxial*** crystallinity is usually observed. One crystalline growth occurs right on top of another. This arrangement is often called **shish-kebab**

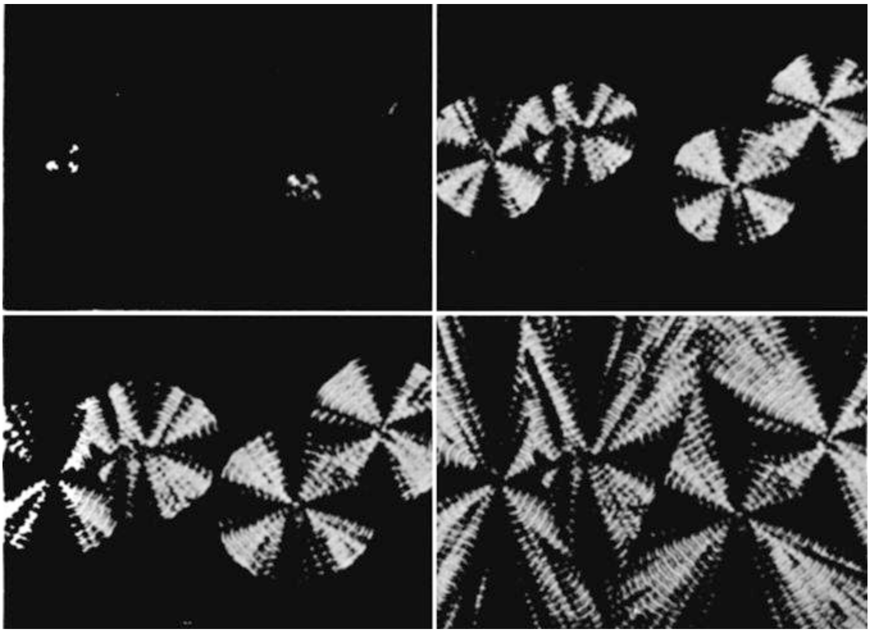


Fig. 2.13 Spherulitic growth (from ref [50])

morphology. It contains lamella growth on long fibrils. Drawing of a crystalline polymer forces the spherulites to rearrange into parallel arrangements known as ***drawn fibrilar morphology***.

In order for the ordered phase to crystallize from an amorphous melt a nucleation barrier must be overcome. This barrier is a result of interfacial energy between the ordered phase and the melt that causes super cooling. Sirota [44] suggested that in order for the nucleation barrier of the stable phase to be sufficiently high to form out of the melt, another phase with a lower nucleation barrier and a free energy intermediate between that of the stable phase and the melt must form. This, he points out, is implied by Oswald's rule [45] and evidence presented by Keller [35] that crystallization in semicrystalline polymer systems is mediated by a transient metastable phase [47, 48].

Stroble and coworkers demonstrated that lamellar thickness is determined by a transition between the metastable phase and the stable crystal phase [46–49]. In addition, by relating the crystallization temperature, melting temperature, and crystalline lamellar thickness, he suggested that lamellar growth fronts are thin layers of a mesomorphic phases. He feels that these phases thicken until such thickness is reached that stable crystal phases are favored. The conversion occurs in a block wise fashion but results in granular structures that were observed in many polymers [46–49]. This conversion is a stabilization process that lowers the free energy of the newly formed crystallites and prevents them from returning to the mesomorphic phase upon subsequent elevation of the temperature [46–49]. Such a concept of crystallization, however, is not universally accepted. Sirota [49], pointed out, however, that this picture and the thermodynamic framework are generally correct in many cases.

Sirota [49] believes that the origin of granular structures, mentioned above, can be understood in the following way. The initial nucleation and growth take place by stem addition. into mesophases. Lamellae thickness occurs while the chains are in the more mobile mesophase. When the thicknesses grow large enough to allow conversion from mesophases to crystals, the average densities in the lamellae have been set and the crystals break up into blocks. The transitions from mesophases to crystals also involves increases in lateral packing densities. In semicrystalline polymers, the entanglements in the amorphous regions, as well as the folding of the chains and the lamellar spanning the chains, will also have an effect. These effects limit the allowable lateral displacements of the crystalline stems during the rapid solid-state transformation from the mesophases to the crystal forms. As a result, over long distances, on molecular scale, and short times, the stems are kinetically constrained to be close to the lateral position that is maintained as they grew in the mesophase. At the same time, the local packing now favors the more stable crystal phase with a higher lateral density. The constraints on the chain ends favoring the lateral density of the mesophases, and forces competition with the density of the thermodynamically favored crystal structures. This causes the crystal to break up into domains. Sirota then suggests that the granular structures observed in many polymer crystals are fingerprints of the transitions from the transient intermediates from which the crystals have formed [49].

It was reported recently, that polymeric can also form quasicrystals. Hayashida et al. [50] demonstrated that certain blends of polyisoprene, polystyrene, and poly(2-vinylpyridine) form star-shaped copolymers that assemble into ***quasicrystals***. By probing the samples with transmission electron microscopy and X-ray diffraction methods, they conclude that the films are composed of periodic patterns of triangles and squares that exhibit 12-fold symmetry. These are signs of quasi-crystalline ordering. Such ordering differ from conventional crystals lack of periodic structures yet are well-ordered, as indicated by the sharp diffraction patterns they generate. Quasi-crystals also differ from ordinary crystals in another fundamental way. They exhibit rotational symmetries (often five or tenfold). There are still some basic questions about their structure.

2.3.3.1 Thermodynamics of Crystallization

The free energy change of a polymer from liquid to crystal is

$$\Delta F = \Delta H - T\Delta S$$

At the melting point T_{m} the crystals and the liquid polymer are at equilibrium. The change in free energy, therefore, $\Delta F = 0$. That means that at the melting point:

$$T_{\mathrm{m}} = \Delta H / \Delta S$$

If the heat of fusion is large, then the melting temperature of the polymer crystals will be high (due to high intermolecular attraction) or if the entropy of fusion is small.

Mendelkern [42] noted that there are three different interfacial free energies that are characteristic of crystallites. One, σ_{e}, is for the equilibrium extended chain crystallite, a second one σ_{ec} represents the mature, but non-equilibrium crystallite, and the third one is σ_{en} is the interfacial free energy involved in forming a nucleus. These quantities cannot be identified with one another. Because only portions of the polymeric chains participate in the formations of crystallites, the section or sections of the chains of x length that participate in crystallite formation can be designated as $\zeta_{\mathrm{e}'}$ and the sections of the chains that remain in disorder and amorphous, as $x - \zeta_{\mathrm{e}'}$.

The dependence of the melting temperature of such a system upon chain length is [42]:

$$1/T_{\mathrm{m}} - 1/T_{\mathrm{m}}^{0} = (R/\Delta H_{\mathrm{u}})\{[(1/x) + (1/x - \zeta_{\mathrm{e}'} + 1)]\}$$

where, ΔH_{u} is the enthalpy of fusion per repeat unit and ζ_{e} is the equilibrium crystalline length. The effective interfacial free energy associated with the basal plane of an equilibrium crystalline length $\zeta_{\mathrm{e}''}$ designated as σ_{e} is [42]:

$$2\sigma_{\mathrm{e}} = RT_{\mathrm{me}}\{[\zeta_{\mathrm{e}}/(x - \zeta_{\mathrm{e}} + 1)] + \ln[(x - \zeta_{\mathrm{e}} + 1)x]\}$$

where T_m^0 is the equilibrium melting temperature for an infinite molecular weight chain and T_{me} is the corresponding melting temperature for a fraction that contains x repeat units. From the stand point of thermodynamics, T_{me} is a ***first-order transition temperature*** [15]. The melting points, when measured very carefully, can in many cases be sharp. On the other hand, melting points of ordinary crystals may melt over a range (Table 2.3). Table 1.2 shows some first-order transition temperatures, commonly designated as T_m.

For systems that are polydisperse, with a most probable chain-length distribution, the melting temperature molecular weight relation is expressed as [42]:

$$1/T_m^* - 1/T_m^0 = (R/\Delta H_u)(2/\overline{X}_n)$$

where $\overline{X}_n$ is the number average degree of polymerization. In this equation, the quantity $2/\overline{X}_n$ represents the mole fraction of non-crystallizing units. This equation is based on the stipulation for conditions for phase equilibrium. It is specific to and valid only for polymers that have a most probable molecular weight distribution. This relationship for the melting temperature of each polydisperse system has to be treated individually [42]. By applying the Clapeyron equation and from measurements of applied hydrostatic pressure the value of ΔH_u can be determined.

This equation, $T_m = \Delta H_m/\Delta S_m$ applies to very high molecular weight polymers. For polymers that are medium or low in molecular weight, the degree of polymerization (X) has to be included:

$$T_m = (\Delta H_0 + X\Delta H_1)/(\Delta S_0 + X\Delta S_1)$$

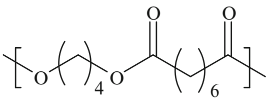
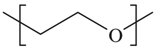
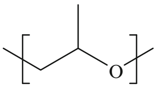
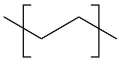
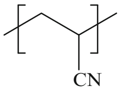
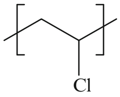
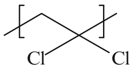
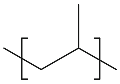
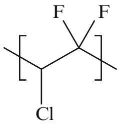
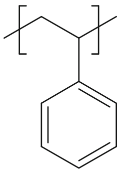
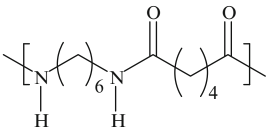
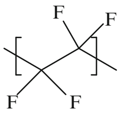
Mandelkern points out [38] that the experimental data shows that there is no correlation between the melting temperature of a polymeric crystal and the enthalpy of fusion, as is found in many small molecules. The ΔH values of polymers generally fall into two classes. They are ether within a few thousand calories per more or about 10,000 cal/mole. Polymers that fall into the category of elastomers have low melting temperatures and high entropies of fusion. This reflects the compacted highly flexible nature of the chains. At the other extreme are the rigid engineering plastics. These materials possess high melting points and correspondingly lower entropies of fusion [42].

2.3.3.2 Kinetics of Crystallization

The rate of crystallization in polymeric materials is of paramount importance. For some polymers, like atactic polystyrene or some rubbers, rapid cooling can lead to the glassy state without any formation of crystallites. The amount of crystallinity actually depends very much upon the thermal history of the material. The amount of crystallinity, in turn, influences the mechanical properties of the material. Microscopic observation of the growth of the spherulites as a function of time will yield information of the crystallization rate. The rate is a function of the temperature. As the temperature is lowered, the rate increases. This growth is usually observed as being linear with time. Presence of impurities will slow down the growth rate. When the growth rate is plotted against crystallization temperature, a maximum is observed. This is due to the fact that as the temperature is lowered the mobilities of the molecules decrease and the process eventually becomes diffusion-controlled. According to the Avrami equation, the fraction that crystallizes during the time t, and defined as $1 - \lambda(t)$, can be written as [42]:

$$1 - \lambda(t) = 1 - \exp\left(-\frac{\rho_c}{\rho_l}\int_0^t V(t,\tau)N(\tau)\mathrm{d}\tau\right)$$

Table 2.3 Melting points, T_m of some crystalline polymers[a]

Repeat unit	Polymer	Melting point (°C)
	Poly(tetramethylene suberate)	45
	Poly(ethylene oxide)	66
	Poly(propylene oxide)	70
	High-density polyethylene	132–138
	Polyacrylonitrile	317
	Poly(vinyl chloride)	212
	Poly(vinylidene chloride)	210
	Polypropylene	168
	Polychlorotrifluoroethylene	210
	Polystyrene	230–248
	Poly(hexamethylene adipamide)	250
	Polytetrafluoroethylene	327

[a] From ref [15] and other sources in the literature

where, $N(\tau)$ is the nucleation frequency per untransformed volume, $V(t,\tau)$ is the corresponding volume of the growing center, and ρ_c and ρ_l represent the densities of crystalline and liquid phases. Based on that, the rate constant for crystallization kinetics can be described [42]:

$$\ln[(V_\infty - V_t)/(V_\infty - V_0)] = -(1/w_c)kt^n$$

where, V_∞, V_t, and V_0 are specific volumes at the times shown by the subscripts, and w_c is the weight fraction of the polymer crystallized. k is the rate constant for crystallization It was found, however, that crystallization continues in polymeric materials for much longer periods of time than the Avrami equation predicts.

For all homopolymers the rate of crystal growth increases linearly with time, or $G = \mathrm{d}r/\mathrm{d}t$. Mandelkern defines the steady-state nucleation rate, N as follows [42]:

$$N = N_0 \exp(-E_D T/RT - \Delta G^*/RT)$$

where E_D is the energy of activation for transporting the chain segments across the crystal–liquid interface.

If the crystallization takes place over an extended temperature range, most if not all homopolymers display a maxima in rates of spherulitic growth and in the overall crystallization. The equation for spherulitic growth is written as follows [42]:

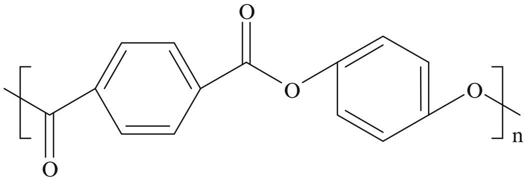
$$G = G^0 \exp(-U^*/(T - T_\infty)) \exp(KT_m^0/T_c \Delta G_u T)$$

where T_∞ is the temperature at which all molecular and segmental motion stops.

2.4 The Mesomorphic State, Liquid Crystal Polymers

The state of mesomorphism is a spontaneously ordered liquid–fluid crystalline state. Liquid crystals were discovered as early as 1888. They are materials that exhibit order in one or two dimensions but not in all three. By comparison, the amorphous materials lack any order, while the crystalline ones exhibit order in three dimensions. All liquid crystalline polymers exhibit some degree of fluidity. They were investigated extensively in the 1900s and became commercially important in 1960s.

These are macromolecules that can align into crystalline arrays while they are in solution (***lyotropic***) or while in a molten state (***thermotropic***). Such liquids exhibit ***anisotropic*** behavior [51, 52]. The regions of orderliness in such liquids are called ***mesophases***. Molecular rigidity found in rigid rod-shaped polymers, for instance, is the chief cause of their liquid crystalline behavior. It excludes more than one molecule occupying a specific volume and it is not a result of intermolecular attractive forces. Some aromatic polyesters or polyamides are good examples, like polyphenylene terephthalate:



Because the molecules posses anisotropy, they are aligned while still in a fluid form. This differs from ordinary liquids, that are **isotropic**, where the molecules lack any kind of arrangement.

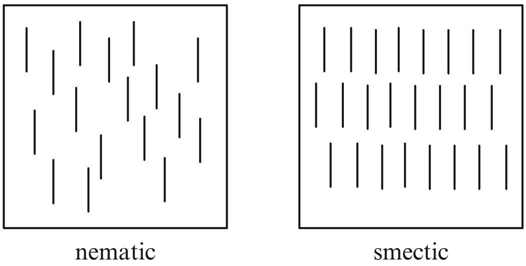


Fig. 2.14 Illustration of the arrangement of liquid crystal into nematic and smectic orders

Anisotropy is not affected by conformational changes. Generally, molecules that are rigid rod like and elongated or disc like in shape are the type that can form liquid crystal arrangements. Some biological polymers exhibit liquid crystalline behavior due to their rigid helical conformations. Among synthetic polymers, on the other hand, rigid rod structures, mentioned above are the ones that exhibit most of the liquid crystalline behavior. Polymers that form liquid crystals may exhibit multiple mesophases at different temperatures. Based on the arrangement of the liquid crystals in the mesophases, they are further classified as ***nematic, smectic,*** and ***cholesteric*** [51, 52].

Both, smectic and nematic are parallel arrangements along molecular axes. The smectic liquid crystals are more ordered, however, than the nematic ones. This is a result of differences in the orientations of the chain ends. In smectic liquid crystals the chain ends are lined up next to each other. In nematic ones, however, they lack any particular orientation. Also the smectic liquid crystals are layered while the nematic ones are not. Microscopic observations [51] can help distinguish between the two forms.

Smectic elastomers, due to their layered structure, exhibit distinct anisotropic mechanical properties and mechanical deformation processes that are parallel or perpendicular to the normal orientation of the smectic layer. Such elastomers are important due to their optical and ferroelectric properties. Networks with a macroscopic uniformly ordered direction and a conical distribution of the smectic layer normal with respect to the normal smetic direction are mechanically deformed by uniaxial and shear deformations. Under uniaxial deformations two processes were observed [53]: parallel to the direction of the mechanical field directly couples to the smectic tilt angle and perpendicular to the director while a reorientation process takes place. This process is reversible for shear deformation perpendicular and irreversible by applying the shear force parallel to the smetic direction. This is illustrated in Fig. 2.14.

If the mesogens are chiral, a twisted nematic, suprarmolecular, ***cholesteric*** (twisted) phase can form [51, 52]. The achiral nonlinear mesogens can also form chiral supramolecular arrangements in tilted smectic phases.

Recently, Tokita and coworkers [54] reported a direct transition from isotropic to smectic arrangement in a liquid crystalline polymer and determined experimentally the existence of metastable nematic orientational ordering that preceded the formation of translational smectic ordering. A polymeric material was used that exhibits very slow liquid crystalline transition dynamics [55]. This enabled use of conventional methods to study the transitions, such as of polarized light scattering and synchrotron wide-angle X-ray diffraction analyses. It was observed that at high quench rates or super cooling, metastable nematic (orientational) ordering occurs preceding full smectic (orientational and translational) order. Also, the occurrence of nematic preordering (high super cooling) resulted in morphological changes of growing liquid crystalline domains compared to solely smectic growth. Specifically, samples cooled at rates high enough to exhibit nematic preordering formed well-oriented or "neat" tactoidal smectic domains. Samples cooled at lower rates, where only smectic ordering was observed, formed radially oriented or textured spherulitic domains [55]. In commenting on this observation, Abukhdeir and Rey [56] point out that through a simulation model the isotropic to smectic liquid crystalline transition experimental observations of preordering of smectic liquid crystalline transitions can be studied. Phase transition kinetics results presented by them show that nematic preordering results from both thermodynamic potential and dynamic differences in phase-ordering time scales.

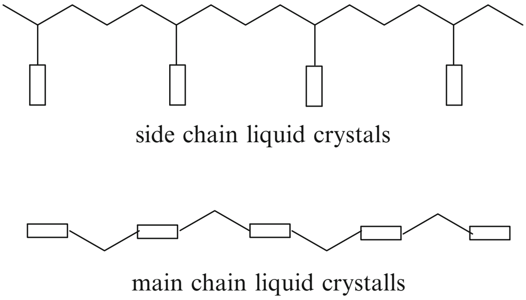


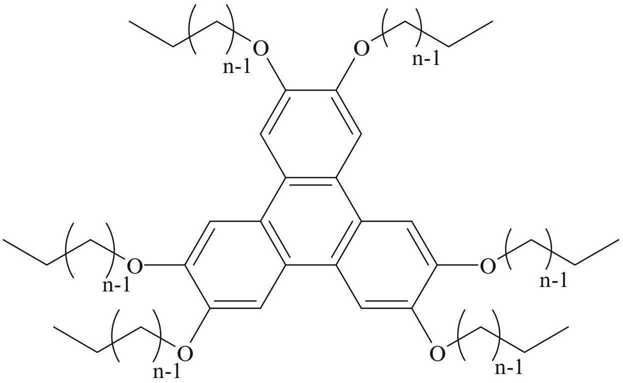
Fig. 2.15 Illustration of arrangements of liquid crystal structure

The chemical structure of the polymers determines whether the molecules can form rigid rods. If the backbone of the polymer is composed of rigid structures then it tends to form ***main chain*** liquid crystals. If, however, the side chains are rigid, then the polymer will tend to form ***side chain*** liquid crystals. From practical considerations, these two properties are of prime interest. The structures are illustrated in Fig. 2.15.

Liquid crystalline behavior affects the melt viscosity of the polymer and the ability of the polymer to retain the ordered arrangement in the solid state. Thus, liquid crystalline behavior during the melt results in lower viscosity because the rigid polymeric mesophases align themselves in the direction of the flow. As a result, the polymer is easier to process. Also, retention of the arrangement upon cooling yields a material with greatly improved mechanical properties. Several thermotropic liquid crystalline copolyesters and polyamides are available commercially.

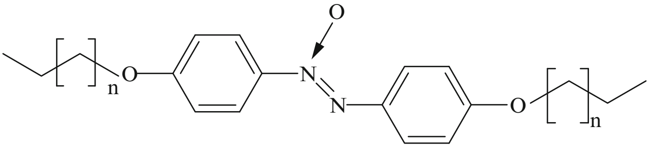
Samulski [57] gives examples of molecules that can typically form liquid crystals These are

1. A discotic liquid crystal



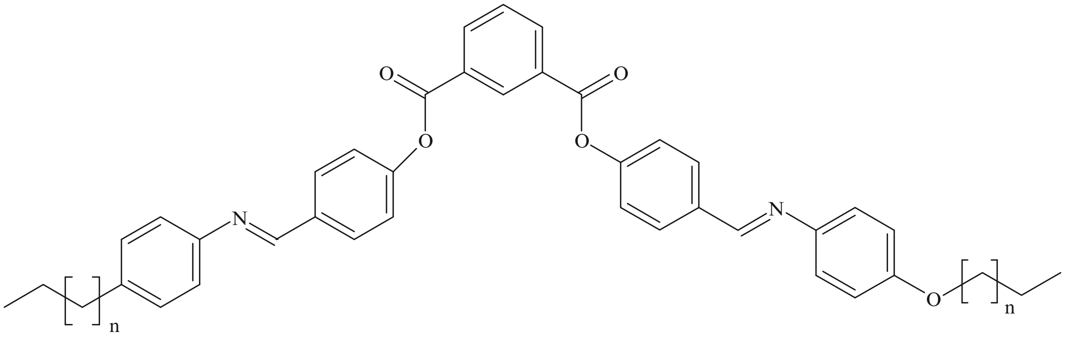
The above shown structure has a ***mesogenic core***, (hard central segment) correlated with dynamic packing of anisometric shapes. The flexible tales, often hydrocarbon chains, extend from the mesogenic core and facilitate the transformation from the solid state to the liquid crystalline phase.

2. A calamitic liquid crystal



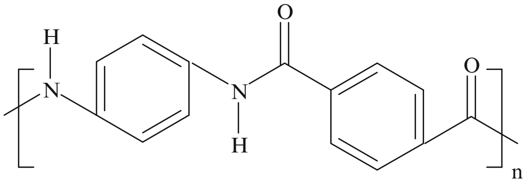
In this case there is a prolate mesogen axis and flexible hydrocarbon chains that extend from it.

3. A nonlinear liquid crystal



Many liquid crystal polymers tend to exhibit multiple mesophases at different pressures and temperatures [57]. When heated, these polymers will go through multiple first-order transitions. Such transitions are from more ordered to less ordered arrangements. This is referred to as the **clearing temperature** with the last one resulting in isotropic melts.

A lyotropic liquid crystalline aromatic polyamide, sold under the trade name of Kevlar, is an example of such a polymer that is available commercially:

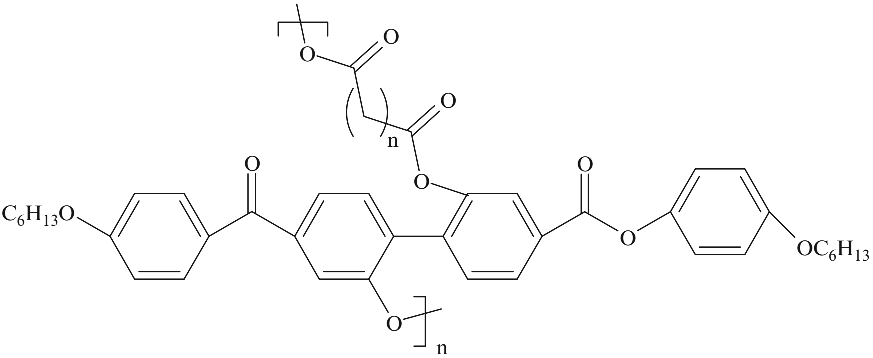


Kevlar

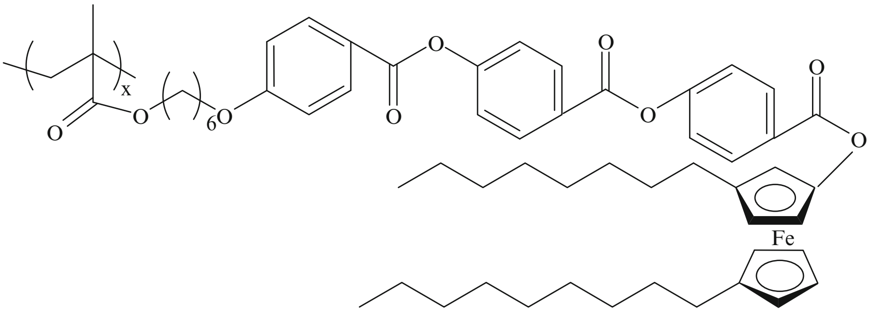
The polyamide forms liquid crystals in sulfuric acid solution from which it is extruded as a fiber. After the solvent is removed, the remaining fiber possesses greater uniform alignment than would be obtained by mere drawing. This results in superior mechanical properties.

There are polymers, however, that exhibit liquid crystalline behavior, but are very high melting and insoluble in most common organic solvents. This is a drawback, because such materials are hard to process.

A preparation of new liquid crystal polymers with bilaterally linked mesogens in main-chain was reported [57]. Such materials exhibit biaxial fluctuation in the nematic phase. This is interesting because most commonly encountered polymeric liquid crystals have mesogens linked at their ends to the polymer backbone by flexible spacers. On the other hand, liquid crystal polymers with mesogens linked bilaterally by flexible spacers are not common and only a few examples were reported [58]. One such material can be illustrated as follows:



It was also shown that it is possible to synthesize polymethacrylate liquid crystal polymers with mesomorphic properties that contain ferrocenes with two flexible chains at the 1,1′-positions [59]. Based on dilatometric measurements, a head-to-tail molecular arrangement of the monomeric units occurs within the smectic A phase. Because of special electrochemical properties of ferrocene, these materials are of interest for developing electroactive mesomorphic polymers. The structure of the polymer can be shown as follows [59]:



Finkelmann reported synthesis of a novel cross-linked smectic-C main-chain liquid-crystalline elastomer that was formed by polycondensation of vinyloxy-terminated mesogens, tetramethyldisiloxane, and pentamethyl-pentaoxapentasilicane. The introduction of the functional vinyloxy group allows the synthesis of well-defined networks with good mechanical properties due to elimination of side reactions as in the case of vinyl groups [60].

Large amplitude oscillatory shear is frequently capable of generating macroscopic alignment from an initially random orientation distribution in ordered polymer fluids. Berghardt and coworkers [61] reported that by combined rheological and in situ synchrotron X-ray scattering to investigate of such induced alignment in smectic side-groups *pf* liquid crystalline polymers. In all cases, they found that shear promotes anisotropic orientation states in which the lamellar normal tends to align along the vorticity direction of the shear flow (“perpendicular” alignment). Rheological measurements of the dynamic moduli by them revealed that large amplitude shearing in the smectic phase causes a notable decrease in the modulus. They also observed that increasing strain promotes higher degrees of orientation, while increasing molecular weight impedes development of smectic alignment.

Ahn et al. reported [62] preparation of a smetic liquid crystalline elastomer with shape memory properties. Shape memory polymeric materials can recover their equilibrium, permanent shapes from nonequilibrium, temporary shapes as a result of external stimuli, like heat or light. Such materials have application in medical practice. Main-chain polynorbornenes were linked with three different side-chains, cholesterol, poly(ethylene glycol), and butylacrylate.

2.5 Orientation of Polymers

There is no preferred direction or arrangement in the manner in which the macromolecules align themselves in a polymeric mass during crystallization. If, however, after crystallization an external stress is applied, the crystalline material undergoes a rearrangement. From the X-ray diffraction patter it is surmised that the chains realign themselves in the direction of the applied stress. Polymeric films and fibers usually show considerable increase in strength in the direction of that stress. Oriented fibers are considerably stronger along their length then perpendicularly to them. Generally, if the degree of crystallinity in crystalline polymers is well developed prior to the drawing, the process does not change the amount of crystallinity appreciably.

The orientation in the direction of applied stress occurs also in amorphous materials. The amorphous polymers, like the crystalline ones, also exhibit increased strength in the direction of orientation. If there is a small amount of crystallinity in polymers, the crystallinity often increases as a result of cold drawing.

Orientation of fibers and films is generally carried out above the glass transition temperature. At the same time, there usually is a desired limit on T_m. Thus it is preferred that the crystalline melting temperature does not exceed 300°C.

2.6 Solutions of Polymers

Polymers usually dissolve in two stages. First the materials tend to swell and form gels. The gels then tend to disintegrate into true solutions. Agitation only speeds up the process in the second stage. Chains held together by crosslinks will only swell. Crystallinity or strong hydrogen bonding might also keep some polymeric materials from dissolution and the materials only swell.

Some general rules about polymer solubility are:

(a) Solubility is favored by chemical and structural similarity between the solvent and the polymer.
(b) Solubility of the polymer tends to decrease with an increase in molecular weight.

When a polymer dissolves, the free energy of solution, ΔF is negative, while the entropy change, ΔS is positive, because of increased conformational mobility of the polymer. The magnitude of the enthalpy of solution determines whether ΔF is positive or negative. The heat of mixing, ΔH_{mix} for binary systems was suggested to be related to the concentration and energy parameters by the expression [7]:

$$\Delta H_{\text{mix}} = V_{\text{mix}}[(\Delta E_1/V_1)^{0.5} - (\Delta E_2/V_2)^{0.5}]^2 \Phi_1 \Phi_2$$

where V_{mix} is the total volume of the mixture, the molar volumes of the two components are, V_1 and V_2, respectively, and Φ_1 and Φ_2 are their volume fractions. The energies of vaporization are ΔE_1 and ΔE_2, while the ***cohesive densities*** (energy required to remove a molecule from its nearest neighbor) are $\Delta E_1/V_1$ and $\Delta E_2/V_2$.

2.6.1 Radius of Gyration

In solution, polymeric chains can form different conformations, depending upon the solvent. When the solvent is such that the chains are fully solvated, they are relatively extended and the molecules are randomly coiled. The polymer–solvent interaction forces determine the amount of space that the molecular coil of the polymer occupies in solution. While quite extended in a good solvent, if the solvent is a "poor" one, the chains are curled up. A measure of the size of the polymer molecule in solution, or the amount of space that a polymer molecule occupies in solution is determined as ***radius of gyration.***, or ***root mean square radius of gyration***, S. Qualitatively, it is the average distance of the mass of the molecule from the center of its mass (from its center of gravity). The following equation

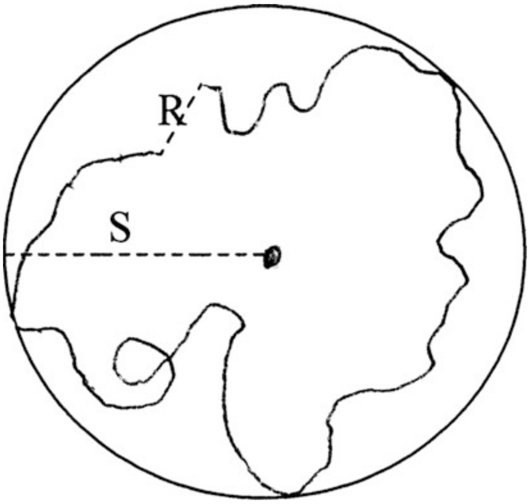


Fig. 2.16 Illustration of a molecular coil

defines this relationship [7]. To put it in other words, it is the square of the distances between various masses and the center of the mass:

$$S^2 = \sum_i m_i s_i^2 \bigg/ \sum_i m_i$$

$$S^2 = \left\{\sum ms^2\right\}_{\text{av.}} (1/Nm)$$

where m is the mass associated with each of the N chain bonds, and S is the vector distance from the center of the mass to the terminal chain bond. The size of randomly coiled polymer molecules is commonly designated by the root-mean square distance between the ends, R^2. A molecular coil is illustrated in Fig. 2.16.

The distance between the chain ends is often expressed in terms of ***unperturbed dimensions*** (S_0 or R_0) and an ***expansion factor*** (α) that is the result of interaction between the solvent and the polymer

$$S^2 = S_0{}^2\alpha^2 \quad \text{and} \quad R^2 = R_0{}^2\alpha^2$$

The unperturbed dimensions refers to molecular size exclusive of solvent effects. It arises from intramolecular polar and steric interactions and free rotation. The expansion factor is the result of solvent and polymer molecule interaction. For linear polymers, the square of the radius of gyration is related to the mean-square end-to-end distance by the following relationship:

$$\overline{S}^2 = \overline{R}^2/6$$

This follows from the expansion factor, α is greater than unity in a good solvent where the actual "perturbed dimensions" exceed the unperturbed ones. The greater the value of the unperturbed dimensions the better is the solvent. The above relationship is an average derived at experimentally from numerous computations. Because branched chains have multiple ends it is simpler to describe them in terms of the radius of gyration. The volume that a branched polymer molecule occupies in solution is smaller than a linear one, which equals it in molecular weight and in number of segments.

The volume that these molecules occupy in solution is important in determinations of molecular weights It is referred to as the ***hydrodynamic volume***. This volume depends upon a variety of factors.

These are interactions between the polymer molecule and the solvent, chain branching, conformational factors arising from polarity, restricted rotation due to resonance, and the bulk of substituents. The above, of course, assumes that the polymer molecules are fully separated from each other.

2.6.2 The Thermodynamics of Polymer Solutions

Solutions of polymers deviate to a great extent from Raoult's law, except at extreme dilution. In extremely dilute solutions the ideal behavior is approached as an asymptotic limit. These deviations arise largely from small entropies of mixing. That is mostly due to the large difference in size between the solute and the solvent. The change in the ***entropy of mixing***, according to ***Flory–Huggins theory*** of polymer solutions [63] is:

$$\Delta S = -k(N_1 \ln v_1 + N_2 \ln v_2)$$

where subscript 1 denotes the solvent and subscript 2 the solute. v_1 and v_2 are ***volume fractions***. They are defined as follows

$$v_1 = N_1/(N_1 + xN_2)$$

$$v_2 = xN_2/(N_1 + xN_2)$$

where x is the heat of mixing. The change in the heat content of mixing of polymer solutions is similar to that of other solutions

$$\Delta H = x_1 kTN_1 v_2$$

where x_1 characterizes the internal energy per solvent molecule. The change in free energy of mixing, according to Flory–Huggins [63], is

$$\Delta F = kT(N_1 \ln v_1 + N_2 \ln v_2 + x_1 N_1 v_2)$$

The Flory–Huggins treatment overlooks the fact that dilute solutions of polymers consist of domains or clusters of polymeric chains that are separated by regions of pure solvent that is free from the solute. **Flory–Krigbaum** treatment assumes a model of dilute polymeric solutions where the polymeric clusters are approximately spherical and their density reaches a maximum at their centers and decreases in an approximately Gaussian function away from the center. The volume that is occupied by the segments of each molecule excludes the volumes of all other molecules. Long range intramolecular interactions take place within such excluded volumes. The thermodynamic functions of such interactions can be derived, such as the free energy change, the enthalpy change, and the entropy change:

$$\Delta F_1 = kT(k_1 - \Psi_1){v_2}^2$$

$$\Delta \overline{H}_1 = kTk_1{v_2}^2$$

$$\Delta S_1 = k\Psi_1{v_2}^2$$

where Ψ is an entropy parameter and can be expressed as,

$$k_1 - \Psi_1 = x_1 - 0.5$$

In addition, ***Flory temperature***, Θ is treated as a parameter, $\Theta = k_1T/\Psi_1$ At Θ temperature the partial molar free energy due to the solute–solvent interaction is assumed to be zero and deviations from ideality (ideal solution) become zero. What this means is that as the temperature of the solution of a polymer approaches Θ, the solvent becomes increasingly poorer and the excluded volume effect becomes smaller and approaches zero with the molecules interpenetrating one another with zero net interaction. The solvent is referred to as a Θ, solvent. Below Θ temperature the polymer molecules attract each other, the excluded volume is negative, and the polymer precipitates. This can be expressed as [63]:

$$\Psi_1 - k_1 = \Psi_1(1 - \Theta/T) = 0.5 - x_1$$

When the chains are extended, their conformations may be considered as being determined by equilibrium between the forces of expansion due to excluded volume and the forces of contraction due to chain segments expanding into less probable conformations. Based on random flight statistics, the chains are extended linearly by a factor α over their dimensions. The actual root-mean-square end-to-end distance is equal to $\alpha(R_0{}^2)^{0.5}$. The change in the elastic part of free energy is

$$\Delta F_{\mathrm{el}} = kT[1.5(\alpha^2 - 1) - \ln \alpha^2]$$

where the parameter α can be expressed in terms of thermodynamic quantities:

$$\alpha^5 - \alpha^3 = 2C_{\mathrm{m}}\Psi_1(1 - \Theta/T)M^{0.5}$$

In the above equation, C_{m} represents a combination of molecular and numerical constants. Based on the above equation, at Θ temperature $\alpha = 1$. It has been stated that the Flory–Krigbaum treatment must be treated with some reservations, because it predicts that α increases without limit with increasing molecular weight [63].

2.7 Molecular Weights and Molecular Weight Determinations

The physical properties of polymers are also related to their molecular weights. Melt viscosity, hot strength, solvent resistance, and overall toughness increase with molecular size. Table 2.4 illustrates the effect of molecular weights (size) upon physical properties of polyethylene [64].

2.7.1 Molecular Weight Averages

Random events govern the process of synthetic polymer formation, whether it is by a chain propagating process or by a step-growth reaction. The result is that the chains vary in lengths. (There are special methods available, however, in chain-growth polymerizations that lead to formation of polymer molecules that are almost equal in length. This is discussed in subsequent chapters) As a result, most polymeric materials cannot be characterized by a single molecular weight, but instead must be represented by statistical averages [64]. These averages can be expressed in several ways. One way is to present an average as a ***number average*** molecular weight. It is the sum of all the molecular weights of the individual molecules present divided by their total number. Each molecule contributes equally to the average and can be obtained by averaging the measurements of all the colligative properties. If the total number of moles is N_i, the sum of these molecules present can be expressed as, ΣN_i. The total weight ω of a sample is similarly the sum of the weights of all the molecular species present

Table 2.4 Properties of low density polyethylene [48, 49]

DP	Molecular weight	Softening temperature (°C)	Physical state 25°C
1	28	−169 (mp)	Gas
6	170	−12 (mp)	Liquid
35	1,000	37	Grease
140	4,000	93	Wax
250	7,000	98	Hard wax
430	12,000	104	Plastic
750	21,000	110	Plastic
1,350	38,000	112	Plastic

$$\omega = \sum \omega_i = \sum M_i N_i$$

By dividing the total weight of the molecules by their total number we have the ***number average*** molecular weight,

$$\overline{M_n} = \omega \Big/ \sum N_i = \sum M_i N_i \Big/ \sum N_i$$

Another way to express a molecular weight average is as a ***weight average***. Each molecule in such an average contributes according to the ratio of its particular weight to that of the total,

$$\overline{M_w} = \sum M_i^2 N_i \Big/ \sum N_i$$

The above can be illustrated quite readily by imagining that a sample of a polymer consists of five molecules of molecular weights of 2,4,6,8, and 10, respectively. To calculate the number average molecular weight all the weights of the individual molecules are added. The sum is then divided by the total number of molecules in the sample (in this case 5):

$$\overline{M_n} = 2/5 + 4/5 + 6/5 + 8/5 + 10/5 = 6$$

To calculate the weight average molecular weight of the above sample, the squares of each individual weight are divided by the total sum of their molecular weights, in this case it is 30:

$$\overline{M_w} = 2^2/30 + 4^2/30 + 6^2/30 + 8^2/30 + 10^2/30 = 7.33$$

$\overline{M_w}$ is more sensitive to the higher molecular weight species, while $\overline{M_n}$ is sensitive to the lower ones. This can be seen by imagining that equal weights of two different sizes of molecules are combined, $M_1 = 10{,}000$ and $M_2 = 100{,}000$. The combination would consist of ten molecules of M_1 and one molecule of M_2. The weight average molecular weight of this mixture is $(10^8/2 \times 10^5 + 10^{10}/2 \times 10^5) = 55{,}000$ while the number average molecular weight is only 18,182. If, however, the mixture consists of an equal number of these molecules, then the weight average molecular weight is 92,000 and the number average molecular weight is 55,000.

The ratio of the weight average molecular weight to the number average molecular weight is important because it affects the properties of polymers. This ratio is called the ***molecular weight distribution***:

$$\text{Molecular weight distribution} = \overline{M_w}/\overline{M_n}$$

When all macromolecular species are of the same size, the number average molecular weight is equal to the weight average molecular weight. On the other hand, the greater the distribution of molecular sizes, the greater is the disparity between averages. The ratio of this disparity, M_w/M_n is a measure of ***polymeric dispersity***. A ***monodisperse*** polymer has a ratio of:

$$M_w/M_n = 1$$

In all synthetic polymers and in many naturally occurring ones the weight average molecular weight is greater than the number average molecular weight. Such polymers are ***polydisperse***.

Two samples of the same polymer equal in weight average molecular weight may exhibit different physical properties, if they differ in the molecular weight distributions. Molecular weight distribution can affect elongation, relaxation modulus, tensile strength, and tenacity of the materials [65]. An additional average molecular weight that is obtained with the aid of ultracentrifugation is referred to as sedimentation average molecular weight, or Z-average molecular weight, M_z This was more often used in the past, particularly with naturally occurring polymeric materials. It is not used, however, as much today.

$$\overline{M_z} = \sum M_i{}^3 N_i \Big/ \sum M_i{}^2 N_i$$

In solutions of polymers the viscosities are more affected by the long chains than by the short ones. A correlation of the viscosity of the solution to the size of the chains or to molecular weight of the solute, allows an expression of a ***viscosity average*** molecular weight:

$$\overline{M_\eta} = \left(\sum M_i{}^{\beta+1} N_i \Big/ \sum M_i N_i\right)^{1/\beta}$$

where, β is a constant., usually less than unity. When $\beta = 1$, then M_η becomes equal to M_w. Actually, though, the values of M_η are usually within 20% of the weight average molecular weights. For polydisperse polymers M_w is larger than M_η and M_η in turn is larger than M_n.

Most of the methods for determining the molecular weights and sizes of polymers (with the exception of small-angle neutron scattering) require dissolving the polymers in proper solvents first. The measurements are then carried out on dilute solutions.

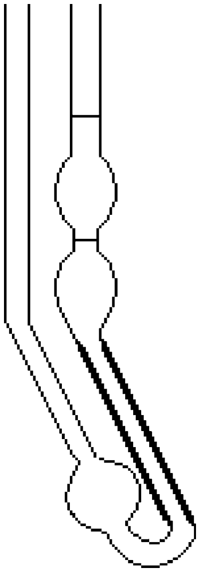
Solution viscosities of linear polymers relate empirically to their molecular weights. This is used in various ways in industry to designate the size of polymers. The values are obtained by measuring the efflux time t of a polymer solution through a capillary. It is then related to the efflux time t_o of pure solvent. Typical viscometers, like those designed by Ubbelohde, Cannon–Fenske, (shown in Fig. 1.3), and other similar ones are utilized and measurements are carried out in constant temperature baths. The viscosity is expressed in following ways:

Common name	Symbol	Definitions
1. Relative viscosity	η_{rel}	$\eta/\eta_o = t/t_o$
2. Specific viscosity	η_{sp}	$(\eta - \eta_o)/\eta_o = \eta_{rel} - 1 \propto (t - t_o)/t_o$
3. Reduced viscosity	η_{red}	$\eta_{sp}/C = \eta_{rel^{-1}}/CZ$
4. Inherent viscosity	η_i	$\ln \eta_{rel}/C$
5. Intrinsic viscosity	$[\eta]_{c\rightarrow 0}$	$(\eta_{sp}/C)_{c=0} = (\eta_i)_{c=0}$

2.7.2 Methods for Measuring Molecular Weights of Polymers

To determine the intrinsic viscosity, both inherent and reduced viscosities are plotted against concentration (C) on the same graph paper and extrapolated to zero. If the intercepts coincide then this is taken

Fig. 2.17 Cannon–Fenske capillary viscometer



as the intrinsic viscosity. If they do not, then the two intercepts are averaged. The relationship of intrinsic viscosity to molecular weight is expressed by the Mark–Houwink–Sakurada equation [66]:

$$[\eta]_{c=0} = K\overline{M}_{\eta}^{\alpha}$$

where K and a are constants. Various capillary viscometers are available commercially. Figure 2.17 illustrates a typical capillary viscometer.

The logarithms of intrinsic viscosities of fractionated samples are plotted against log M_w or log M_n. The constants a and K of the Mark–Houwink–Sakurada equation are the intercept and the slope, respectively, of that plot. Except for the lower molecular weight samples, the plots are linear for linear polymers. Many values of K and a for different linear polymers can be found in the literature [66].

Actually, the Mark–Houwink–Sakurada equation applies only to narrow molecular weight distribution polymers. For low molecular weight polydisperse polymers this equation is useful, because the deviations due to chain entanglement are still negligible. On the other hand, chain entanglement in high molecular weight polydisperse polymers affects viscosity and this equation does not really apply.

The determinations of molecular weights of polymers rely, in most cases, upon physical methods. In some special ones, however, when the molecular weights are fairly low, chemical techniques can be used. Such determinations are limited to only those macromolecules that possess only one functional group that is located at the end of the chain ends. In place of the functional group, there may be a heteroatom. In that case, an elemental analysis might be sufficient to determine the molecular weight. If there is a functional group, however, a reaction of that group allows calculating the molecular weight. Molecular weights above 25,000 make chemical approaches impractical. In chemical determination each molecule contributes equally to the total. This determination, therefore, yields a number average molecular weight. With the development of gel permeation chromatography (discussed below), this method is hardly ever used today.

There are various physical methods available. The more prominent ones are ebullioscopy, cryoscopy, osmotic pressure measurements, light scattering, ultracentrifugation, and gel permeation chromatography (also called size exclusion chromatography). All these determinations are carried out on solutions of the polymers. Also, all, except gel permeation chromatography, require that the results

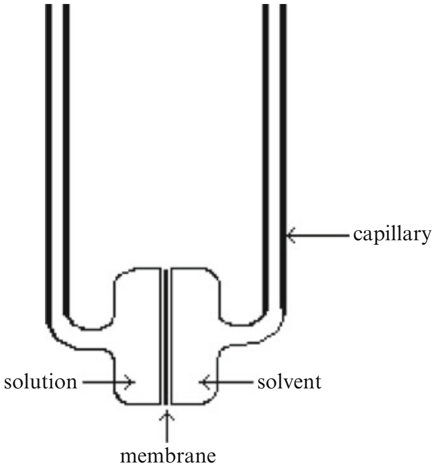


Fig. 2.18 Membrane osmometer

of the measurements be extrapolated to zero concentrations to fulfill the requirements of theory. The laws that govern the various relationships in these determinations apply only to ideal solutions. Only when there is a complete absence of chain entanglement and no interaction between solute and solvent is the ideality of such solutions approached. A brief discussion of some techniques used for molecular weight determination follows

Ebullioscopy, or boiling point elevation, as well as ***cryoscopy***, or freezing point depression, are well-known methods of organic chemistry They are the same as those used in determining molecular weights of small molecules. The limitation to using both of these methods to determine the molecular weight of macromolecules is that ΔT_b and ΔT_f become increasingly smaller as the molecular sizes increase. The methods are limited, therefore, to the capabilities of the temperature sensing devices to detect very small differences in temperature. This places the upper limits for such determinations to somewhere between 40,000 and 50,000. The thermodynamic relationships for these determinations are:

$$[\Delta T_{b/c}]_{c\to 0} = RT^2/\rho\Delta H_b M \qquad [\Delta T_{f/c}]_{c\to 0} = RT^2/\rho\Delta H_f M$$

boiling point rise elevation freezing point depression

The above two determinations, because each molecule contributes equally to the properties of the solutions, yield number average molecular weights. How much this technique is used today is hard to tell.

A method that can be used for higher molecular weight polymers is based on ***osmotic pressure measurements***. It can be applied to polymers that range in molecular weights from 20,000 to 500,000 (some claim 1,000,000 and higher). The method is based on van't Hoff's law. When a pure solvent is placed on one side of a semi-permeable membrane and a solution on the other, pressure develops from the pure solvent side. This pressure is due to a tendency by the liquids to equilibrate the concentrations. It is inversely proportional to the size of the solute molecules. The relationship is as follow:

$$\overline{M}_n = RT/(\pi/C)_{C=0} + A_2 C$$

where π is the osmotic pressure, C is the concentration, T is temperature, and R is the gas constant, A_2 is a measure of interaction between the solvent and the polymer (second viral coefficient).

A *static* capillary osmometer is illustrated in Fig. 2.18. Rather than rely on the liquid to rise in the capillary on the side of the solution in response to osmotic pressure, as is done in the static method, a ***dynamic equilibrium*** method can be used. Here a counter pressure is applied to maintain equal levels of the liquid in both capillaries and prevents flow of the solvent. Different types of dynamic membrane osmometers are available commercially. The principle is illustrated in Fig. 2.19.

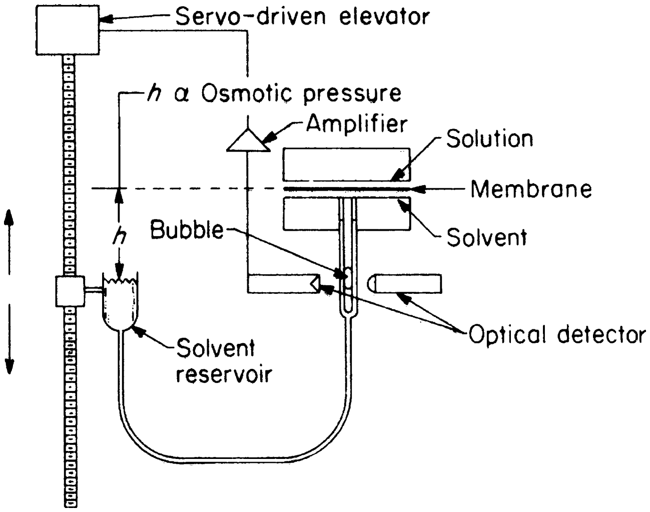


Fig. 2.19 Schematic of a high speed osmometer (from ref [68])

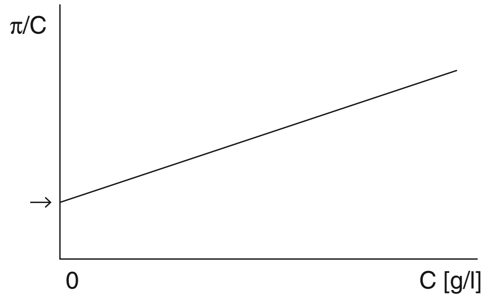


Fig. 2.20 Extrapolation to zero concentration

The results obtained from either method must still be extrapolated to zero concentration for van't Hoff's law to apply. Such extrapolation is illustrated in Fig. 2.20. Because all molecules contribute equally to the total pressure, osmotic pressure measurements yield a number average molecular weight.

Light scattering measurement is a technique for determining the weight average molecular weight. When light passes through a solvent, a part of the energy of that light is lost due to absorption, conversion to heat, and scattering. The scattering in pure liquids is attributable to differences in densities that result from finite nonhomogenuities in the distribution of molecules within adjacent areas. Additional scattering results from a presence of a solute in the liquid. The intensity or amplitude of that additional scattering depends upon concentration, the size, and the polarizability of the solute plus some other factors. The refractive index of pure solvent and a solution is also dependent upon the amplitude of vibration. The turbidity that arises from scattering is related to concentration:

$$\text{turbidity}\,\tau = \sum \tau_1 - H \sum C_i M_i = H_c \overline{M_w}$$

$$H = 32\pi^3 {n_o}^2 (\mathrm{d}n/\mathrm{d}c)^2 / 3\lambda^4 N_o$$

where n_o is the refractive index of the solvent, n is the refractive index of the solution, λ is the wavelength of the incident light, N_o is Avogadro's number, and c is the concentration. The dn/dc relationship is obtained by measuring the slope of the refractive index as a function of concentration. It is constant for a given polymer, solvent, and temperature and is called the ***specific refractive increment***.

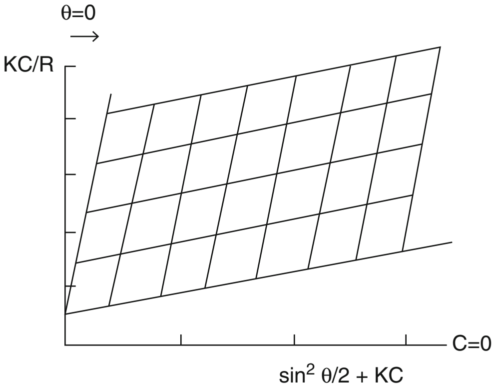


Fig. 2.21 A typical Zimm plot

Because scattering varies with different angles from the main beam of light, the results must be extrapolated to zero concentration and zero angle of scattering. This is done simultaneously by a method developed by Zimm. A typical Zimm plot is illustrated in Fig. 2.21.

A very popular technique for determining molecular weights and molecular weight distributions is ***gel permeation chromatography***. It is also called size exclusion chromatography [69, 70]. The procedure allows one to determine M_w and M_n, and the molecular weight distribution in one operation. The procedure resembles HPLC. It separates molecules according to their hydrodynamic volumes or their effective sizes in solutions. The separation takes place on one or more columns packed with small porous particles. As the solution travels down the columns, there is retention of the polymer molecules by the pores of the packing. It was postulated in the past that the separation that takes place by molecular sizes is due to smaller molecules diffusing into all the pores while the larger ones only into some of the pores. The largest molecules were thought to diffuse into none of the pores and pass only through the interstitial volumes. As a result, polymer molecules of different sizes travel different distances down the column. This means that the molecules of the largest size (highest molecular weight) are eluted first because they fit into the least number of pores. The smallest molecules, on the other hand, are eluted last because they enter the greatest number of pores and travel the longest path. The rest fall in between. The process, however, is more complex than the above postulated picture. It has not yet been fully explained. It was found, for instance, that different gels display an almost identical course in the relation of dependence of V_R (retention volume) to the molecular weight. Yet study of the pores of different gels show varying cumulative distributions of the inner volumes. This means that there is no simple function correlating the volume and/or the size of the separated molecules with the size and distribution of the pores [69]. Also, the shape of the pores that can be inferred from the ratio of the area and volume of the inner pores is very important [70]. Different models were proposed to explain the separation phenomenon. These were reviewed thoroughly in the literature. They are beyond the scope of this book.

As indicated above, the volume of the liquid that corresponds to a solute eluting from the columns is called the retention volume or elution volume (V_R). It is related to the physical parameters of the column as follows:

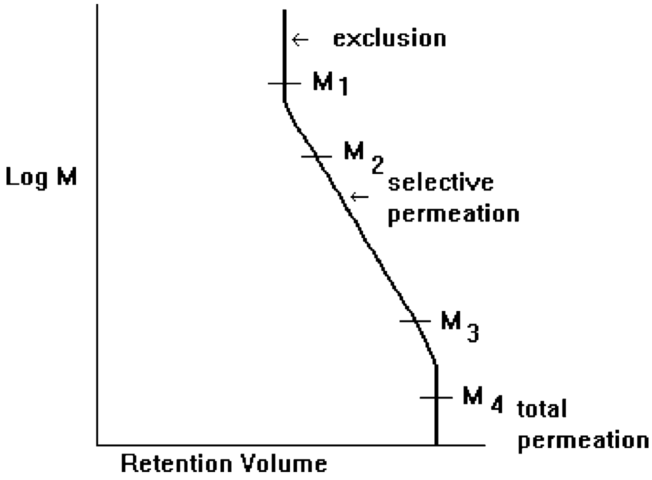
$$V_R = V_o + KV_1$$

where, V_o = the interstitial volume of the column(s)
K = the distribution coefficient
V_1 = the internal solvent volume inside the pores

The total volume of the columns is V_T that is equal to the sum of V_O and V_1. The retention volume can then be expressed as follows:

$$V_R = V_O(1 + K) + KV_T$$

Fig. 2.22 Molecular weight calibration curve for gel permeation chromatography



From the earlier statement it should be clear that polymer fractionation by gel permeation chromatography depends upon the spaces the polymer molecules occupy in solution. By measuring, experimentally, the molecular weights of polymer molecules as they are being eluted one obtains the molecular weight distribution. To accomplish this, however, one must have a chromatograph equipped with dual detectors. One must detect the presence of polymer molecules in the effluent. The other one must measure their molecular weights. Such detectors might be, for instance, a refractive index monitor and a low angle laser light scattering photogoniometer to find the absolute value of M.

Many molecular weight measurements, however, are done on chromatographs equipped with only one detector that monitors the presence of the solute in the effluent. The equipment must, therefore, be calibrated prior to use. The relationship of the ordinate of the chromatogram, commonly represented by $F(V)$, must be related to the molecular weight. This relationship varies with the polymer type and structure. There are three methods for calibrating the chromatograph. The first, and most popular one, makes use of narrow molecular weight distribution reference standards. The second one is based upon a polydisperse reference material. The third one assumes that the separation is determined by molecular size. All three methods require that an experimentally established calibration curve of the relationship between the molecular size of the polymer in solution and the molecular weight be developed. A chromatogram is obtained first from every standard sample. A plot is then prepared from the logarithms of the average weights against the peak retention volumes (V_R). The values of V_R are measured from the points of injection to the appearances of the maximum values of the chromatograms. Above M_1 and below M_4 there is no effective fractionation because of total exclusion in the first place and total permeation in the second case. These are the limits of separation by the packing material.

To date the standard samples of narrow molecular weight distribution polymers that are available commercially are mainly polystyrenes. These samples have polydispersity indexes that are close to unity and are available over a wide range of molecular weights. For determining molecular weights of polymers other than polystyrene, however, the molecular weights obtained from these samples would be only approximations. Sometimes they could be in error. To overcome this difficulty a ***universal calibration method*** is used. The basis for universal calibration is the observation [51] that the multiplication products of intrinsic viscosities and molecular weights are independent of the polymer types. Thus, $[\eta]M$ is the ***universal calibration parameter***. As a result, a plot of log $([\eta]M)$ vs. elution volume yields a curve that is applicable for many polymers. The log $([\eta]M)$ *for* ***a given column (or columns), temperature, and elution volume*** is assumed to be a constant for all polymers. This is illustrated in Fig. 2.22.

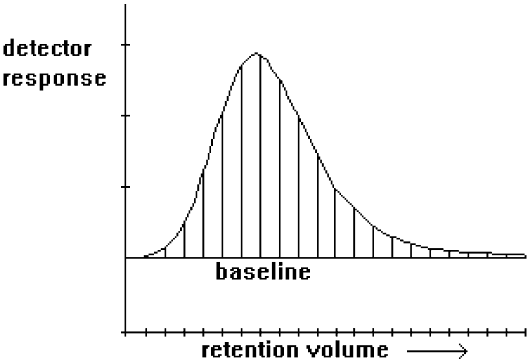


Fig. 2.23 A typical digitized gel permeation chromatogram

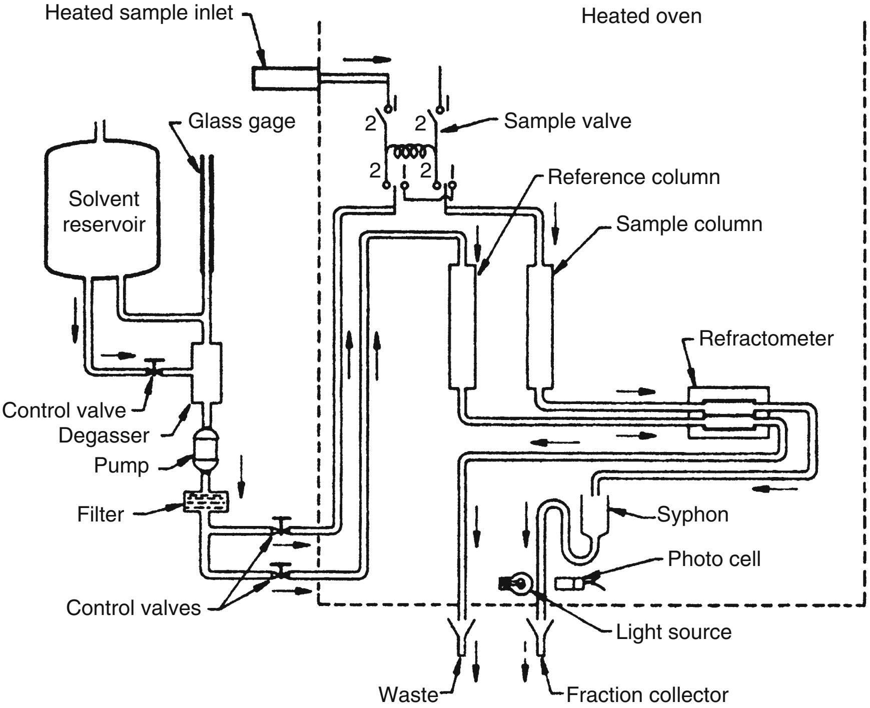


Fig. 2.24 Schematic illustration of gel permeation equipment (the illustration only shows one sample column. Several sample columns are often used) (from ref [68])

Numerous materials have been used for packing the columns. Semi rigid crosslinked polystyrene beads are available commercially. They are used quite frequently. Porous beads of glass or silica are also available. In addition, commercial gel permeation equipment is usually provided with automatic sample injection and fraction collection features. The favorite detectors are refractive index and ultraviolet light spectroscopic detectors. Some infrared spectroscopic detectors are also in use. Commercially available instruments also contain pumps for high-pressure rapid flow and are usually equipped with a microcomputer to assist in data treatment. Also, they come with a plotter in the equipment to plot the detector response as the samples are eluted through the column or columns. A typical chromatogram is illustrated in Fig. 2.23 and a schematic for the basic equipment is shown in Fig. 2.24. When polydisperse samples are analyzed, quantitative procedures consist of digitized chromatograms with indication of equally spaced retention volumes. These can be every 2.5 or 5.0 mL of volumes. The resultant artificial fractions are characterized by their heights h_i, their solute concentrations C_i, and by the area they occupy within the curve A_i. The cumulative polymer weight values is calculated according to:

$$I(V) = 1\Big/A_\mathrm{T}\sum A_i$$

After conversion of the retention volumes V_i into molecular weights (using the calibration curve), the molecular weights, M_w, M_n, and M_z can be calculated:

$$M_\mathrm{n} = \sum h_I\Big/\left(\sum h_I/M_i\right);\quad M_\mathrm{w} = \sum h_iM_I\Big/\sum h_i;\quad M_\mathrm{z} = \sum h_iM_i{}^2\Big/\sum h_iM_I$$

If the chromatogram is not equipped with a microcomputer for data treatment, one can easily determine results on any available PC. Programs for data treatment have been written in various computer languages. They are available from many sources.

Recently, there were several reports in the literature on combining size exclusion with high pressure liquid chromatography for more comprehensive characterization of polymers. Thus, Gray et al. reported that a combination of high pressure liquid chromatography with size exclusion chromatography allows comprehensive structural characterization of macromolecules [71].

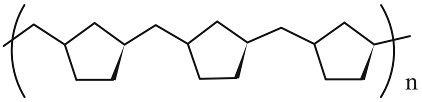
On the other hand, Chang et al. reported on using a modified form of high pressure liquid chromatography analysis, referred to as **interaction chromatography** for polymer characterization. The process utilizes enthalpic interaction of polymeric solutes with the stationary phase. Such interaction depends on both, the chemical composition and on molecular weight. It is claimed to be less sensitive to chain architecture and to offer superior resolution to SEC. The typical HPLC instrument is modified to precisely control the temperature of the column. The temperature of the column and the mobile phase is controlled by circulating a fluid through the column jacket from a programmable bath/circulator. The mobile and stationary phases require careful choices to adjust the interaction strength of the polymer solutes with the stationary phase so that the polymer solutes elute out in a reasonable elution time. The process depends upon variations of the column temperature for precise control of the solute retention in the isocratic elution mode. Mixed solvent system of a polar and a less polar solvent are often employed to adjust the interaction strength [72].

2.8 Optical Activity in Polymers

Optical activity in biopolymers has been known and studied well before this phenomenon was observed in synthetic polymers. Homopolymerization of vinyl monomers does not result in structures with asymmetric centers (The role of the end groups is generally negligible). Polymers can be formed and will exhibit optical activity, however, that will contain centers of asymmetry in the backbones [73]. This can be a result of optical activity in the monomers. This activity becomes incorporated into the polymer backbone in the process of chain growth. It can also be a result of polymerization that involves asymmetric induction [74, 75]. These processes in polymer formation are explained in subsequent chapters. An example of inclusion of an optically active monomer into the polymer chain is the polymerization of optically active propylene oxide. (See Chap. 5 for additional discussion). The process of chain growth is such that the monomer addition is sterically controlled by the asymmetric portion of the monomer. Several factors appear important in order to produce measurable optical activity in copolymers [76]. These are: (1) Selection of comonomer must be such that the induced asymmetric center in the polymer backbone remains a center of asymmetry. (2) The four substituents on the originally inducing center on the center portion must differ considerably in size. (3) The location of the inducing center must be close to the polymer backbone. (4) The polymerization reaction must be conducted at sufficiently low temperature to insure stereo chemical selectivity. An example is a copolymerization of maleic anhydride with optically active l-α-methylbenzyl vinyl ether. The copolymer exhibits optical activity after the removal of the original center of asymmetry [77].

An example of an asymmetric induction from optically inactive monomers is an anionic polymerization of esters of butadiene carboxylic acids with (*R*)-2-methylbutyllithium or with butyllithium complexed with (−)methyl ethyl ether as the catalyst. (This type of polymerization reaction is described in Chap. 4) The products, tritactic polymers exhibit small, but measurable optical rotations [78]. Also, when benzofuran, that exhibits no optical activity, is polymerized by cationic catalysts like aluminum chloride complexed with an optically active co catalyst, like phenylalanine, an optically active polymer is obtained [77].

By contrast, an example of formation of enantioselective polymer from achiral monomers, where the chirality is inherent in the main chain is polymerization of 1,5-hexadiene with an optically active catalyst [77]. The catalyst precursors are (*R*,*R*) or (*S*,*S*)-[ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)zirconium (1,1′-by-1-naphtholate). The product is an optically active version of poly(methylene-1,3-cyclopentane):



This polymer is highly isotactic and contains 72% *trans* rings.

It was also observed that conjugated polymers that are also electrical conductors (see Chap. 10) exhibit optical activity that depends critically on their structural organization [78]. Thus, strong chiroptical properties can be obtained from substituted polythiophene [79] (Chap. 10) with optically active side chains, especially when the monomers are coupled within the polymer in a regioregular head-to-tail fashion. Actually, optical activity of these materials is only found when the polymers are aggregated at low temperature, in poor solvent, or in solution cast films. This contrasts with other optically active polymers, like polypeptides, poly(l-alkynes) and polyisocyanates that show an optically active conformation of the main chain in the absence of supramolecular association.

In addition, it was shown that a repetitive inversion of optical activity in films can be obtained by warming and cooling cycles, where the cooling rate determines the handedness of the associates [78]. A similar result concerning inversion of chirality has been found in solution, depending on the composition of a binary solvent mixture.

Review Questions

Section 2.1

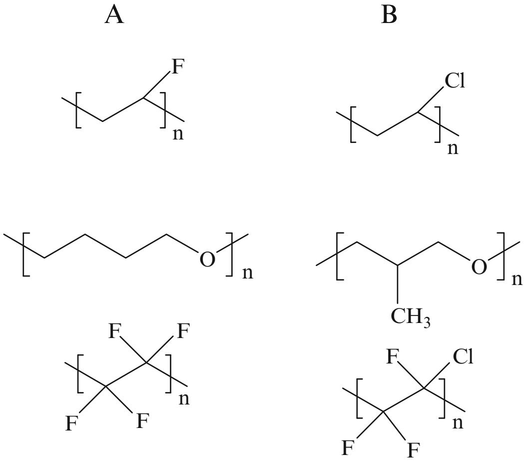
1. What are the secondary bond forces that influence the physical properties of macromolecules?

Section 2.1.1

1. Explain and illustrate dipole–dipole interactions in polymers and how do they affect the properties of polymeric materials. Can you give other examples?

Section 2.1.2

1. What are the induction forces?
2. Explain what type of chemical structures and chemical bonds in the backbones of the polymeric chains stiffen them and what type flexibilizes (or “softens”) them.
3. How do the pendant groups affect the melting points of polymers?
4. Does copolymerization raise or lower the melting point of a polymer?
5. Which polymer, A or B, would have a higher melting point? Explain



6. Explain what the induction forces of polymers and how they affect the physical properties of these materials?
7. Illustrate and explain why nylon 11 melts approximately 50°C higher than linear polyethylene
8. Why does poly(ethylene adipate) melt at a considerably lower temperature than does poly (ethylene terephthalate)?
9. What type of bonds in the polymeric chain tend to soften them?
10. Does copolymerization lower or raise the melting temperature of polymers? Explain

Section 2.2

1. Describe an amorphous state of polymers

Section 2.2.1

1. Describe the glassy state of polymers
2. What is the second order transition temperature? Are the send order transition temperatures of polymers absolute values or do they vary depending upon various conditions? Explain.
3. How can the transition to a glassy state be observed?
4. Explain structural recovery and the asymmetry of structural recovery.
5. What equation describes the asymmetry of structural recovery?
6. What is the Flory–Fox equation and what is it limited to?

Section 2.2.2

1. Explain the phenomenon of elasticity.
2. What natural structural arrangement of polymeric chains leads to rubber elasticity.
3. What is meant by the negative coefficient of expansion?

Section 2.2.2.1

1. Write the equation for the reactive force of an elastomer and explain what each term represents and define an ideal elastomer.
2. What is the entropy of elasticity? What is it proportional to?
3. What is the relationship between the retractive force of an elastomer and its temperature?
4. Write the equation for the work done in stretching a chain of an ideal elastomer and explain what each term represents.
5. Write the equation for a free energy change of a stretched elastomer.
6. Write the equation for the average energy per (stretched) chain
7. What is the free energy change for a stretched elastomer? Explain.

Section 2.2.2.2

1. Define a Newtonian liquid and a Hookian ideal elastic solid, and an ideal elastomer.
2. What is meant by viscoelasticity?
3. Explain what is meant by a yield point and a Bingham Newtonian fluid.
4. How is the viscosity of a molten polymer related to its temperature?
5. How is shear stress defined mathematically?
6. What is a thixotropic liquid?
7. What is the relationship Newtonian viscosity of amorphous polymers and their chain length?
8. What is shear creep compliance equal to ?
9. Why are shear thinning and thixotropy two different phenomena? Explain
10. What relationship describes flow behavior of liquids that deviate from Newtonian flow?
11. Write the equation for shear-stress-relaxation modulus for viscous fluids. Explain
12. What are the two important quantities in behavior of polymeric liquids?
13. Describe two techniques for measuring the viscosity of molten polymers.

Section 2.3

1. How does crystallinity of polymers that are formed from the melt differ from that of small molecules?
2. What are the two ways that crystal growth can take place in polymeric materials?
3. What type of polymers tend to crystallize?
4. What is the typical size of polymeric crystals formed from the melt?
5. What is a fringed micelle or a fringed crystallite model?
6. What is the folded chain lamella? An adjacent-reentry model? A switchboard or a nonadjacent-reentry model?
7. What is drawn fibrilar morphology? What is vitrification?

8. What are spherulites? How are they observed?
9. Explain the difference between a crystallite formed from the melt and a polymer crystal formed from a dilute solution

Section 2.3.1

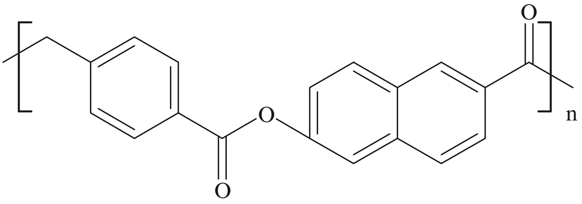
1. What are the three different interfacial free energies that are characteristics of crystals?
2. What equation described the dependence of the melting temperature of a polymer crystal upon its chain length? Explain and write the equation.
3. What is the first order transition temperature?

Section 2.3.2

1. How can one obtain information on the kinetics of crystallization
2. What is the Avrami equation and what are its drawbacks?

Section 2.4

1. What are mesophases ?
2. What is anisotropic behavior?
3. What are lyotropic and thermotropic liquid crystals?
4. Explain nematic, smectic, and cholesteric liquid crystal arrangements.
5. Which of the two polymers would you expect to exhibit liquid crystalline behavior? Explain.



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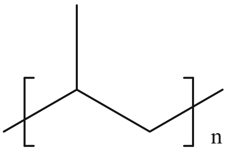

B

6. What is the difference between the main chain and side chain liquid crystals?

Section 2.5

1. What happens to the arrangement of the polymeric chains in films and fibers upon application of an external stress?
2. What is orientation and how does that benefit the properties of polymeric materials?

Section 2.6

1. What are the two stages of dissolution when a polymer dissolves in a solvent?
2. What is the heat of mixing of binary systems? Write equation.
3. What is the radius of gyration? Write equation
4. Define unperturbed dimensions and expansion factor

Section 2.6.1

1. What is the change in entropy of mixing, according to the Flory–Huggins theory? Explain and write the equation.
2. What is the change in the free energy of mixing according to the Flory–Huggings theory? Write equation.
3. What is the Flory temperature? write equation and explain what happens to a solution of a polymer below this temperature

Section 2.7

1. Define the degree of polymerization
2. What is the DP of polystyrene with molecular weight of 104,000 and poly(vinyl chloride) with molecular weight of 63,000?
3. What are the important features of chain-growth and step-growth polymerizations? Can you explain the difference between the two? Can you suggest an analytical procedure to determine by what mechanism a particular polymerization reaction takes place?
4. What is the DP of polystyrene with molecular weight of 104,000 and poly(vinyl chloride) with molecular weight of 630,000?
5. Explain the differences between thermosetting and thermoplastic polymers and define gel point.
6. Give the definitions of oligomer, telomer, and telechelic polymers
7. Why must statistical averages be used to express molecular weights of polymers?
8. What is number average molecular weight? What is the equation for number average molecular weight?
9. What is a weight average molecular weight? What is the equation for the weight average molecular weight?
10. In a mixture of two kinds of molecules there are ten of each in kind. The molecular weight of molecules A is 10,000 and the molecular weight of molecules B is 100,000. What is the number average molecular weight of the mixture and the weight average molecular weight?
11. What is the viscosity average molecular weight and how does it differ from the weight average molecular weight?
12. What is a molecular weight distribution? What is a monodisperse polymer and a polydisperse polymer?
13. What is the Mark–Houwink–Sakurada equation? Can you suggest a way to determine K and a constants experimentally for a given polymer?
14. Give the definitions and formulas for the relative viscosity, specific viscosity, reduced viscosity, inherent viscosity, and intrinsic viscosity.
15. Why is it necessary to extrapolate to zero (explain how this is done) in order to obtain intrinsic viscosity.
16. Discuss the various methods of molecular weight determination explain why a particular method yields a number of a weight average molecular weight, or, as in case of GPC, both.

Section 2.8

1. Discuss optical activity in polymers.

Recommended Reading

H. Sperling, *Introduction to Physical Polymer Science*, 2nd ed., Wiley, New York, 2006

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Chapter 3
Free-Radical Chain-Growth Polymerization

3.1 Free-Radical Chain-Growth Polymerization Process

Polymerizations by free-radical mechanism are typical free-radical reactions. That is to say, there is an ***initiation***, when the radicals are formed, a ***propagation***, when the products are developed, and a ***termination***, when the free-radical chain reactions end. In the polymerizations, the propagations are usually chain reactions. A series of very rapid repetitive steps follow each single act of initiation, leading to the addition of thousands of monomers.

This process of polymerization of vinyl monomers takes place at the expense of the double bonds, $-\mathrm{C}{=}\mathrm{C}- \rightarrow -\mathrm{C}{-}\mathrm{C}-$. Table 3.1 illustrates the steps in this process.

Formation of initiating radicals is the rate-determining step in the initiation reaction. The formation of initiating radicals can result, as shown in Table 3.1, from cleavages of compounds, such as peroxides, or from other sources. Actually, many reactions lead to formations of free radicals. The initiating radicals, however, must be energetic enough to react with the vinyl compounds. A linear correlation exists between the affinities of some radicals for vinyl monomers and the energy (calculated) required to localize a π electron at the β-carbon of the monomer [1]. By comparison to other steps in the polymerization process, initiation is a slow step and requires high energy of activation.

3.1.1 Kinetic Relationships in Free-Radical Polymerizations

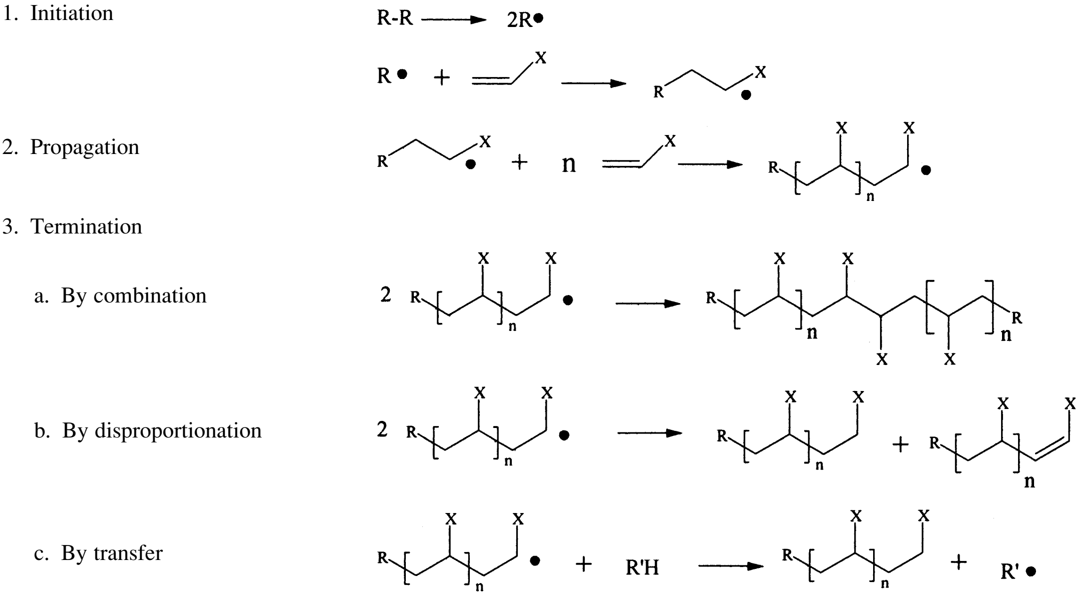
A kinetic scheme for typical free-radical polymerizations is pictured as follows [2]; the rate of propagation R_p is equal to the rate of polymerization R_{pol}, as all the monomer molecules (except one) are consumed during this step.

Initiation	$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}$	$\mathrm{d}[\mathrm{R}\bullet]/\mathrm{d}t = R_i = 2k_d[\mathrm{I}]$
	$\mathrm{R}\bullet + \mathrm{M} \xrightarrow{k_i} \mathrm{RM}\bullet$	$-\mathrm{d}[\mathrm{R}\bullet]/\mathrm{d}t = k_I[\mathrm{R}\bullet][\mathrm{M}]$
Propagation	$\mathrm{RM}\bullet + \mathrm{nM} \xrightarrow{k_p} \sim\mathrm{P}_{n+1}\bullet$	$R_P = k_P[\sum \mathrm{RM}_n\bullet][\mathrm{M}]$
Termination	$\sim\mathrm{P}_{n+1}\bullet + \sim\mathrm{P}_{m+1}\bullet \xrightarrow{k_t} \mathrm{polymer}$	$-\mathrm{d}[\mathrm{P}\bullet]/\mathrm{d}t = 2k_t[\mathrm{P}\bullet]^2$
Transfer	$\sim\mathrm{P}_n\bullet + \mathrm{S} \xrightarrow{k_{tr}} \mathrm{P}_n + \mathrm{S}\bullet$	
	$\mathrm{S}\bullet + \mathrm{nM} \rightarrow \mathrm{SM}_n\bullet$	

In the above shown kinetic scheme, M stands for the monomer concentration, I is the concentration of the initiator, and [R•] and [P•] mean the concentration of primary and polymer radicals,

A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_3,

Table 3.1 Illustration of a free radical polymerization



respectively. S stands for the chain transferring agent. R_I denotes the decomposition rate of the initiator and R_P the rate of polymerization. The rate constants, for the initiator decomposition is k_d, for the initiation reaction is k_I, for the propagation k_P, and for the termination is k_T. The above is based on an assumption that k_P and k_I are independent of the sizes of the radicals. This is supported by experimental evidence that shows that radical reactivity is not affected by the size, when the chain length exceeds dimer or trimer dimensions [3]. The reactions involved in a typical free-radical polymerization process, as stated above, are illustrated in Table 3.1

The equation for the rate of propagation, shown above in the kinetic scheme, contains the term [M•]. It designates radical concentration. This quantity is hard to determine quantitatively because its concentration is usually very low. A ***steady state*** assumption is, therefore, made to simplify the calculations. It is assumed that while the radical concentration increases at the very start of the reaction, it reaches a constant value almost instantly. This value is maintained from then on, and the rate of change of free-radical concentration is assumed to quickly become and remain zero during the polymerization. At steady state, the rates of initiation and termination are equal, or $R_i = R_t = 2k_i[\mathrm{M}\bullet]$ [4]. This assumption makes it possible to solve for [M•] and can then be expressed as:

$$[\mathrm{M}\bullet] = (k_d[\mathrm{I}]/k_t)^{1/2}$$

The rate of propagation is

$$R_P = k_P[\mathrm{M}](k_d[\mathrm{I}]/k_t)^{1/2}$$

The rate of propagation is approximately equal to the total rate of polymerization. The total rate can be designated as R_{pol}. Because all but one molecule are converted during the step of propagation, we can write:

$$R_P = k_P\left[\sum\nolimits_n \mathrm{RM_n}\right](\mathrm{M})$$

This rate of propagation applies if the kinetic chain length is large and if the transfer to monomer is not very efficient. The rate of monomer disappearance can be expressed as

$$-\,\mathrm{d}[\mathrm{M}]/\mathrm{d}t = R_i + R_p$$

Because many more molecules of the monomer are involved in the propagation than in the initiation step, a very close approximation is

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = R_{\mathrm{p}}$$

The average lifetime, τ, of a growing radical under steady state conditions can then be written as follows [3, 5],

$$\tau = k_P[M]/2k_t(R_P)$$

Not all primary radicals that form attack the monomer. Some are lost to side reactions. An initiator efficiency factor, f, is, therefore, needed. It is a fraction of all the radicals that form and can be expressed as:

$$f = \text{ initiating radicals/total number radicals that form.}$$

The rate of initiator decomposition and the rate equation can be expressed as

$$R_{\mathrm{I}} = 2fk_{\mathrm{d}}[\mathrm{I}] = k_{\mathrm{i}}\left[\sum \mathrm{RM_n}\bullet\right]^2$$

$$R_{\mathrm{P}} = k_{\mathrm{P}}[\mathrm{M}](k_{\mathrm{d}}[\mathrm{I}]f/k_{\mathrm{t}})^{1/2} = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t$$

According to the kinetic scheme, chain transfer does not affect the rate of polymerization but alters the molecular weight of the product. Also, it is important to define the average number of monomer units that are consumed per each initiation. This is the ***kinetic chain length***, and it is equal to the rate of polymerization per rate of initiation:

$$\text{kinetic chain length} = v = k_{\mathrm{P}}/k_{\mathrm{i}}$$

At steady state conditions, ν is also equal to k_p/k_t. The kinetic chain length can also be expressed as:

$$v = k_{\mathrm{p}}[\mathrm{M}]/2k_{\mathrm{t}}[\mathrm{M}\bullet]$$

By substituting the expression for [M•] the equation becomes:

$$v = k_{\mathrm{P}}[\mathrm{M}]/2(fk_{\mathrm{d}}k_{\mathrm{t}}[\mathrm{I}])^{1/2}Z$$

The ***number average degree of polymerization***, **DP**, is equal to 2 v, if the termination takes place by coupling. It is equal to v, if it takes place by disproportionation. (Terminations by coupling or disproportionation are discussed in the section on the termination reactions) Above kinetic relationships apply in many cases. They fail, however, to apply in all cases [2]. To account for it, several mechanisms were advanced. They involve modifications of the initiation, termination, or propagation steps. These are beyond the discussions in this book.

At steady state conditions,

$$R_{\mathrm{i}} = f\,\mathrm{I}[\mathrm{M}] = R_{\mathrm{t}} = k_{\mathrm{t}}\left[\sum\nolimits_{\mathrm{n}} \mathrm{RM_n}\bullet\right]^2$$

3.2 Reactions Leading to Formation of Initiating Free Radicals

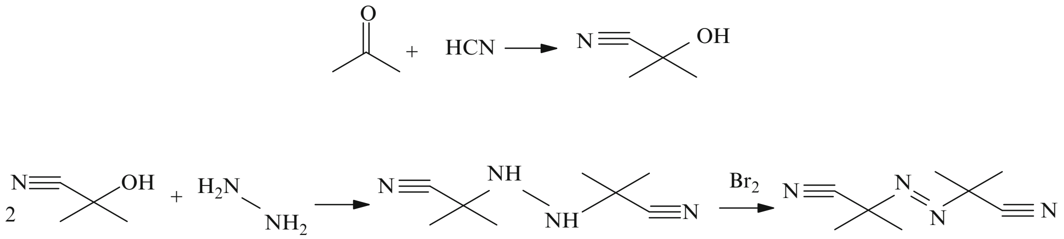
Initiating free radical can come from many sources. Thermal decompositions of compounds with azo and peroxy groups are common sources of such radicals. The radicals can also come from "redox" reactions or through various light induced decompositions of various compounds. Ionizing radiation can also be used to form initiating radicals.

3.2.1 *Thermal Decomposition of Azo Compound and Peroxides*

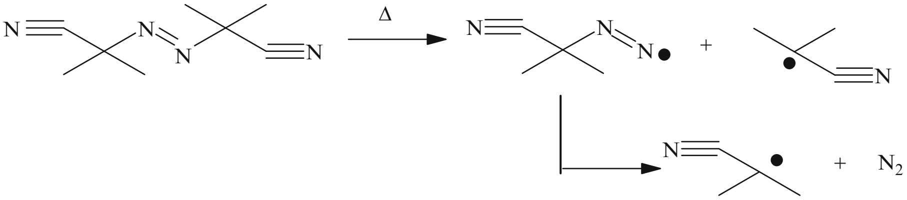
The azo compound and peroxides contain weak valence bonds in their structures. Heating causes weak bonds in these compounds to cleave and to dissociate into free radicals as follows:

$$\text{R-N=N-R} \xrightarrow{\Delta} 2\text{R}\bullet + \text{N}_2$$

For many azo compounds such dissociations occur at convenient elevated temperatures. One commonly used azo compound is α,α′-azobisisobutyronitrile. An original synthesis of this compound was reported to be as follows [3, 4]:



The final products of decomposition of this compound are two cyanopropyl radicals and a molecule of nitrogen:



As stated earlier, not all free radicals that form, however, initiate polymerizations. Some are lost to side reactions. Thus, for instance, some free radicals that form can recombine inside or outside the solvent cage, where the decompositions take place, to yield either tetramethylsuccinonitrile or a ketenimine [4, 5]:

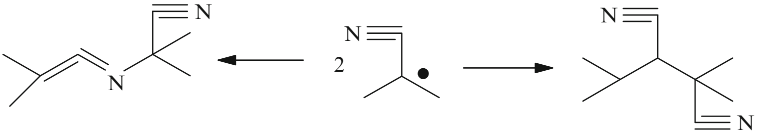


Table 3.2 Decomposition rates of some azonitrile initiators[a]

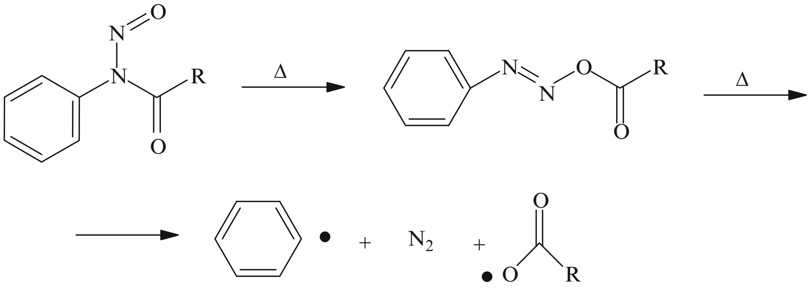
Compound	Solvent	T(°C)	$K_d{}^b(s^{-1})$
2,2′-azobisisobutyronitirle	Benzene	78.0	8×10^{-5}
2,2′-azobis-2-ethylpropionitrile	Nitrobenzene	100.0	1.1×10^{-3}
2,2′-azobis-2-cyclopropylpropionitrile	Toluene	50.0	8.2×10^{-5}
1,1′-azobiscyclohexanenitrile	Toluene	80.0	6.5×10^{-6}
2,2′-azobis-2-cyclohexylpropionitrile	Toluene	80.0	8.3×10^{-6}
1,1′-azobiscyclooctanenitrile	Toluene	45.0	1.5×10^{-4}

[a] From ref. [13], and from other sources in the literature

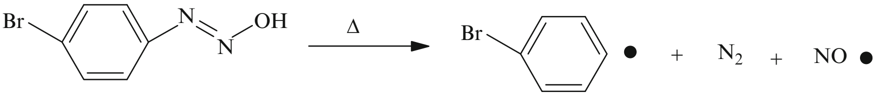
[b] $K_c = Ae^{(-E_a/RT)}$

Examples of other, fairly efficient, azo initiators include the following:

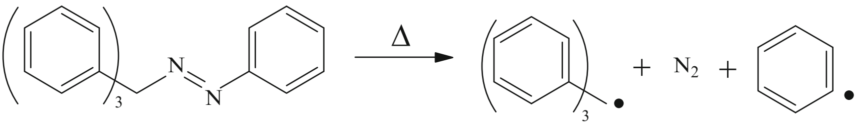
1. *N*-Nitrosoacylanilides,



2. Bromobenzenediazohydroxide,



3. Triphenylazobenzene,



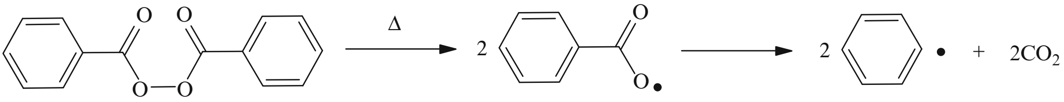
The triphenylmethyl radical shown above is resonance stabilized and unable to initiate polymerizations. The phenyl radical, on the other hand is a hot radical. It initiates polymerizations readily. Decomposition rates of some azonitrile initiators are listed in Table 3.2. There are also many peroxides available for initiating free-radical polymerizations. These can be organic and inorganic compounds. There are, however, many more organic peroxides available commercially than are the inorganic ones. The organic ones include dialkyl and diaryl peroxides, alkyl and aryl hydroperoxides, diacyl peroxides, peroxy esters, and peracids. Hydrogen peroxide is the simplest inorganic peroxide.

Syntheses, structures, and chemistry of various peroxides were described thoroughly in the literature [5]. Here will only be mentioned some properties of peroxides and their performance as they pertain to initiations of polymerizations. Decompositions of peroxides, such as the azo compounds, are also temperature dependent [6]. This means that the rates increase with temperature. The rates are also influenced by the surrounding medium, such as the solvents that imprison or "cage" the produced pairs of free radicals. Before undergoing a net translational diffusion out of the cage, one

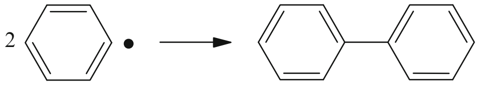
Table 3.3 Effect of substituents on decomposition of dibenzoylperoxide in benzene [10, 11]

Substituent	$K_i \times 10^3$	log K_1/K	$\sigma_i + \sigma_0$
p,p′-dimethoxy	7.06	0.447	0.536
p-methoxyy	4.54	0.255	0.268
p,p′-dimethyl	3.68	0.164	0.340
p,p′-di-*t*-butyl	3.65	0.161	0.394
Parent compound	2.52	0.000	0.000
p,p′-dichloro	2.17	−0.065	+0.454
m,m′-dichloro	1.58	−0.203	+0.746
m,m′-dibromo	1.54	−0.215	+0.782
p,p′-dicyano	1.22	−0.314	+1.300

or both of the radicals may or may not expel a small molecule. For instance, benzoyl peroxide can and often does decompose into a phenyl radical and carbon dioxide, as follows:



The resultant phenyl radicals can combine and yield new and completely inactive species:



The above-described recombination reactions of free radicals are some of the causes of inefficiency among initiators. The average time for recombination of free radicals inside a solvent cage and also the time for their diffusion out of the cage is about 10^{-10} s [7]. In addition, the efficiency of the initiator is affected by the monomer and by the solvent. It was shown that the viscosity of the medium is inversely proportional to the initiator efficiency because the more viscous the solution, the greater the cage-effect [8, 9].

Numerous lists are available in the literature that give the decomposition temperatures or the half-lives at certain elevated temperatures of many initiators [6]. Decompositions of peroxides may proceed via concerted mechanisms [10, 11] and the rates are structure dependent. This can be illustrated on benzoyl peroxide. The benzoyl groups, the two halves of this molecule, are dipoles. They are attached, yet they repel each other. Rupture of the peroxide link releases the electrostatic repulsion between the two dipoles. Presence of electron donating groups in the *para* position increases the repulsion, lowers the decomposition temperature, and increases the decomposition rate. The opposite can be expected from electron attracting groups in the same position [6]. The effect of substituents on the rate of spontaneous cleavage of dibenzoyl peroxide was expressed [11] in terms of the Hammett equation, $\log (K/K_O) = \rho\, \sigma$. This is shown in Table 3.3.

In addition, peroxides can cleave in two ways, ***heterolytically*** and ***homolytically***. Heterolytic cleavage of peroxides results in formation of ions,

$$\text{R}^{\oplus} + :^{\ominus}\text{O-O-R}' \rightleftharpoons \text{R-O-O-R}' \rightleftharpoons \text{R-O-O:}^{\ominus} + \text{R}'^{\oplus}$$

but homolytic cleavage results in formation of radicals:

$$\text{R-O-O-R}' \rightleftharpoons \text{R-O}\bullet + \bullet\text{O-R}'$$

Table 3.4 Decomposition of benzoyl peroxide in various solvents at 79.8°C [15]

Solvent	Approximate% decomposition in 4 h
Anisole	43.0
Benzene	50.0
Carbon tetrachloride	40.0
Chlorobenzene	49.0
Chloroform	44.0
Cyclohexane	84.0
Cyclohexene	40.0
Ethyl acetate	85.0
Ethylbenzene	46.0
Methyl benzoate	41.0
Methylene chloride	62.0
Nitrobenzene	49.0
Tetrachloroethylene	35.0
Toluene	50.0

In the gaseous phase, the cleavage is usually homolytic because it requires the least amount of energy [12]. In solution, however, the dissociation may be either one of the two, depending upon the nature of the R groups. Heterolytic cleavage may be favored, in some cases, if the two groups, R and R′, differ in electron attraction.

The same is true if the reaction solvent has a high dielectric constant. Solvation of the ions that would form due to heterolytic cleavage is also a promoting influence for such a cleavage:

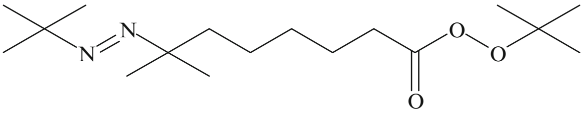
$$\mathrm{A{:}B} + 2\mathrm{S} \rightarrow \mathrm{SA{:}}^{\ominus} + \mathrm{BS}^{\oplus}$$

where, S represents the solvent.

In sum total, the types and the amounts of side reactions that can take place are a function of the structures of the peroxides, the stability of the formed radicals, the solvent, and the monomer that is being polymerized. The stability of the radicals that form can also affect the amount of radicals being captured by the monomers. Also, it was reported that while generally the character of free radicals is neutral, some of them are electrophilic (such as chloro) and others are nucleophilic (such as *t*-butyl). This tendency, however, is relatively slight when compared with positive and negative ions [15].

There is much information in the literature on the rates and manner of decomposition of many peroxides in various media. Beyond that, diagnostic tests exist that can aid in determining the decomposition rates of a particular peroxide in a particular media [13]. Table 3.4 is presented to show how different solvents affect the rate of decomposition of benzoyl peroxide into radicals.

Some initiators can function as both, thermal and photoinitiators. Such an initiator, for instance, is 2,2′-azobisisobutyronitrile. Also, Engel and coworkers [16] reported synthesis of an initiator that can function both as a thermal free radical initiator and a photoinitiator (see Sect. 3.2.4). It can be illustrated as follows:



The claimed advantage of this initiator is that it can be used to form block copolymers.

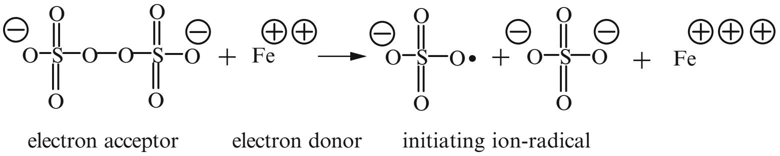
3.2.2 *Bimolecular Initiating Systems*

Decompositions of peroxides into initiating radicals are also possible through bimolecular reactions involving electron transfer mechanisms. Such reactions are often called ***redox*** initiations and can be illustrated as follows:

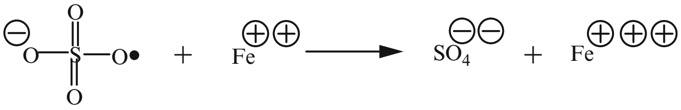
$$\underset{\text{electron donor}}{\mathrm{A}} + \underset{\text{electron acceptor}}{\mathrm{R\text{-}O\text{-}O\text{-}R'}} \longrightarrow \mathrm{A}^{\oplus} + \mathrm{RO}\bullet + {}^{\ominus}\mathrm{OR'}$$

where, A is the reducing agent and ROOR′ is the peroxide.

The above can be illustrated on a decomposition of a persulfate (an inorganic peroxide) by the ferrous ion:



Side reactions are possible in the presence of sufficient quantities of reducing ions:



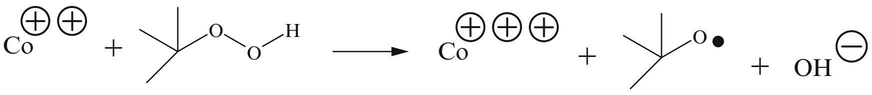
A redox reaction can also take place between the peroxide and an electron acceptor:

$$\mathrm{R\text{-}O\text{-}O\text{-}H} + \mathrm{Ce}^{\oplus\oplus\oplus\oplus} \longrightarrow \mathrm{R\text{-}O\text{-}O}\bullet + \mathrm{Ce}^{\oplus\oplus\oplus} + \mathrm{H}^{\oplus}$$

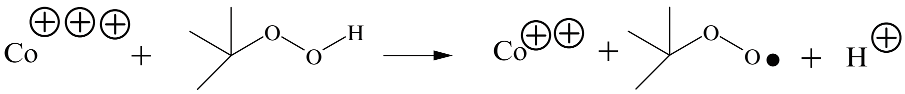
Side reactions with an excess of the ceric ion can occur as well:

$$\mathrm{R\text{-}O\text{-}O}\bullet + \mathrm{Ce}^{\oplus\oplus\oplus\oplus} \longrightarrow \mathrm{R}^{\oplus} + \mathrm{O_2} + \mathrm{Ce}^{\oplus\oplus\oplus}$$

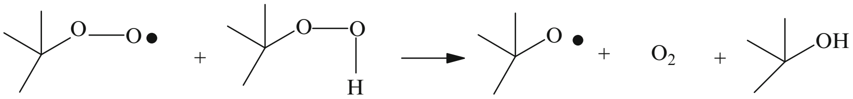
Another example is a redox reaction of *t*-butyl hydroperoxide with a cobaltous ion [17]:
The cobaltic ion that forms can act as an electron acceptor:

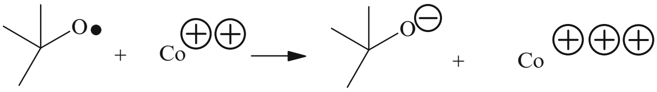


The cobaltic ion that forms can act as an electron acceptor:



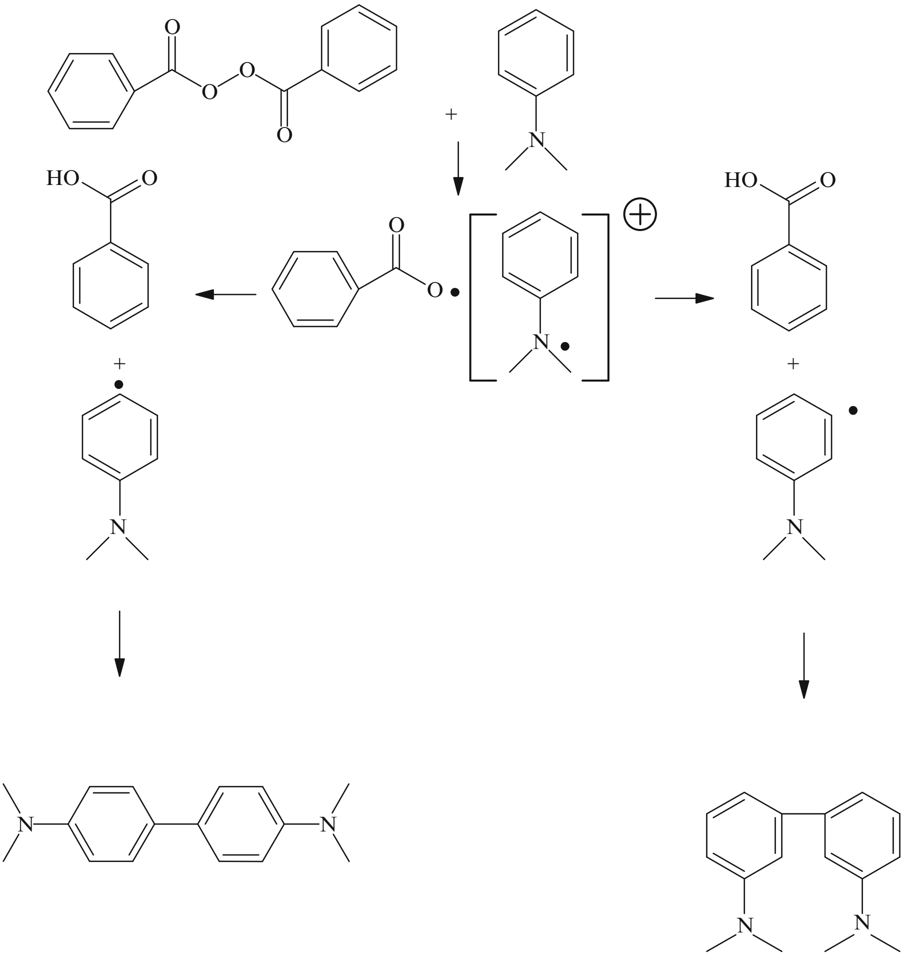
Side reactions can occur here too, such as:



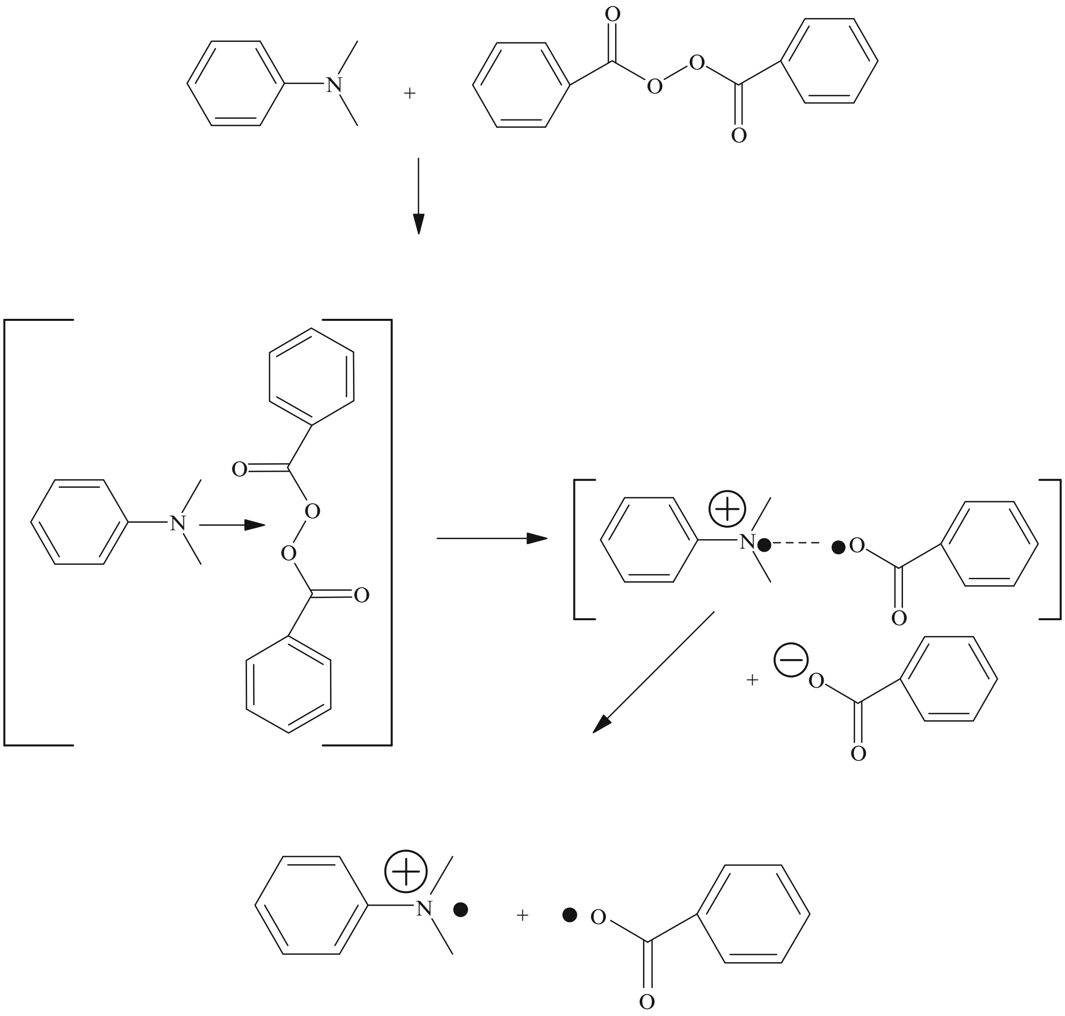


Nevertheless, cobaltous ions form efficient redox initiating systems with peroxydisulfate ions [18].

Tertiary aromatic amines also participate in bimolecular reactions with organic peroxides. One of the unpaired electrons on the nitrogen atom transfers to the peroxide link, inducing decomposition. No nitrogen, however, is found in the polymer. It is, therefore, not a true redox type initiation and the amine acts more like a *promoter* of the decomposition [19]. Two mechanisms were proposed to explain this reaction. The first one was offered by Horner et al. [19]:



A second mechanism, proposed by Imoto and Choe [20] shows the complex as an intermediate step:

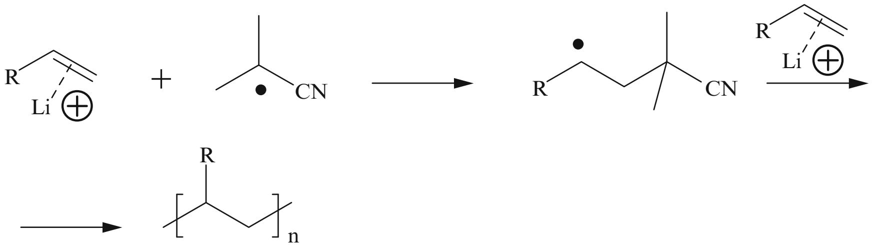


The dimethyl aniline radical-cation, shown above, undergoes other reactions than addition to the monomer. The benzoyl radical is the one that initiates the polymerizations.

Presence of electron-releasing substituents on diethyl aniline increases the rate of the reaction with benzoyl peroxide [21]. This suggests that the lone pair of electrons on nitrogen attack the positively charged oxygen of the peroxide link [22].

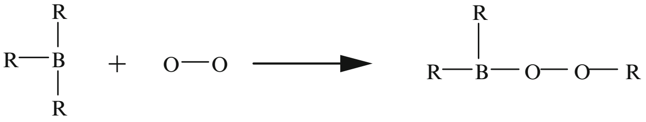
By comparison to peroxides, the azo compounds are generally not susceptible to chemically induced decompositions. It was shown [23], however, that it is possible to accelerate the decomposition of α,α′-azobisisobutyronitrile by reacting it with bis(-)-ephedrine-copper (II) chelate. The mechanism was postulated to involve reductive decyanation of azobisisobutyronitrile through coordination to the chelate [23]. Initiations of polymerizations of vinyl chloride and styrene with α,α′-azobisisobutyronitrile coupled to aluminum alkyls were investigated [24]. Gas evolution measurements indicated some accelerated decomposition. Also, additions of large amounts of tin tetrachloride to either α,α′-azobisisobutyronitrile or to dimethyl-α,α′-azobisisobutyrate increase the decomposition rates [25]. Molar ratios of $[SnCl_4]/[AIBN] = 21.65$ and $[SnCl_4]/[MAIB] = 19.53$ increase the rates by factors of 4.5 and 17, respectively. Decomposition rates are also enhanced by donor solvents, such as ethyl acetate or propionitrile in the presence of tin tetrachloride [25].

A bimolecular initiating system, based in 2,2′-azobisisobutyronitrile was reported by Michl and coworkers [26]. It consists of weakly solvated lithium in combination with the cyanopropyl radical (from AIBN). The combination can initiate polymerizations of olefins. The reaction was illustrated as follows:



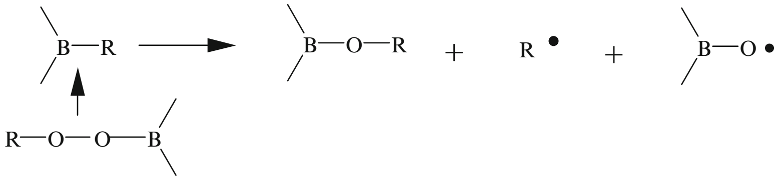
3.2.3 Boron and Metal Alkyl Initiators of Free-Radical Polymerizations

These initiators were originally reported a long time ago [27–29]. Oxygen plays an important role in the reactions [30, 31]. It reacts with the alkyl boride under mild conditions to form peroxides [32, 33]:



$$R_3B + O\text{—}O \longrightarrow R_2B\text{—}O\text{—}O\text{—}R$$

Initiating radicals apparently come from reactions of these peroxides with other molecules of boron alkyls [34, 35]. One postulated reaction mechanism can be illustrated as follows [35]:



Another suggested reaction path is [36]:

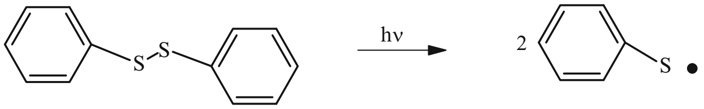
$$R_2B\text{-}O\text{-}O\text{-}R + 2R'_3B \rightarrow 2R\bullet + R'_2B\text{-}O\text{-}BR'_2 + R'_2B\text{-}O\text{-}R$$

Catalytic action of oxygen was observed with various organometallic compounds [35]. One example is dialkylzinc [37] that probably forms an active peroxide [38]. The same is also true of dialkylcadmium and of triethylaluminum [38]. Peroxide formation is believed to be an important step in all these initiations. Initiating radicals, however, do not appear to be produced from mere decompositions of these peroxides [35].

3.2.4 Photochemical Initiators

This subject is discussed in greater detail in Chap. 10, in the section on photo-cross-linking reactions of coatings and films. A brief explanation is also offered here because such initiations are used, on a limited scale, in a few conventional preparation of polymers.

Many organic compounds decompose or cleave into radicals upon irradiation with light of an appropriate wavelength [38, 39]. Because the reactions are strictly light and not heat induced, it is possible to carry out the polymerizations at low temperatures. In addition, by employing narrow wavelength bands that only excite the photoinitiators, it is possible to stop the reaction by merely blocking out the light. Among the compounds that decompose readily are peroxides, azo compounds, disulfide, ketones, and aldehydes. A photodecomposition of a disulfide can be illustrated as follows:



Today, many commercially prepared photoinitiators are available. Some consists of aromatic ketones that cleave by the Norrish reaction or are photoreduced to form free radicals. There are also numerous other two and three component photoinitiating systems. There are also those that decompose by irradiation with visible light and make it possible to initiate the reactions with longer wavelength light (see Chap. 10) Some examples of various photoinitiators are given in Chap. 10. Many others can be found in the literature.

As an example can be sited the work by Barner-Kowollik and coworkers studied the photoinitiation process in methyl methacrylate polymerization, using high-resolution electro spray-mass spectrometry [40]. The polymerization was conducted using a pulsed laser at temperatures ≤0°C in the presence of the photoinitiators 2,2-dimethoxy-2-phenylacetophenone, benzoin, benzil, benzoin ethyl ether, and 2,2-azobisisobutylnitrile. They identified the termination products, both combination and disproportionation with high accuracy. Both the benzoyl and acetal fragments generated as a result of 2,2-dimethoxy-2-phenylacetophenone photocleavage were found to initiate and highly likely terminate the polymerization. Both the benzoyl and ether fragments produced as a result of benzoin photocleavage were found to act as initiating and probable terminating species, indicating that the ether radical fragment does not act exclusively as a terminating species.

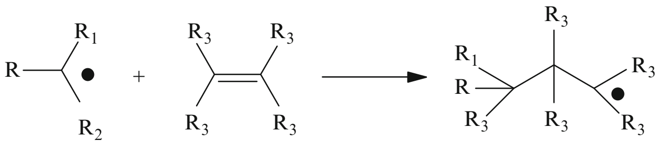
3.2.5 Initiation of Polymerization with Radioactive Sources and Electron Beams

Different radioactive sources can initiate free-radical polymerizations of vinyl monomers. They can be emitters of gamma rays, beta rays, or alpha particles. Most useful are strong gamma emitters, such as ^{60}Co or ^{90}Sr. Electron beams from electrostatic accelerators are also efficient initiators. The products from irradiation by radioactive sources or by electron beams are similar to but not identical to the products of irradiation by ultraviolet light. Irradiation by ionizing radiation causes the excited monomer molecules to decompose into free radicals. Ionic species also form from initial electron captures. No sensitizers or extraneous initiating materials are required. It is commonly accepted that free radicals and ions are the initial products and that they act as intermediate species in these reactions. There is still insufficient information, however, on the exact nature of all of these species [38, 39]. The polymerizations are predominantly by a free-radical mechanism with some monomers and by an ionic one with others [38, 39].

3.3 Capture of Free Radicals by Monomers

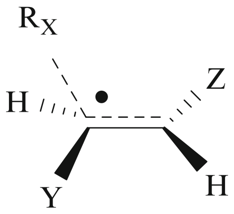
Once the initiating radical is formed, there is competition between addition to the monomer and all other possible secondary reactions. A secondary reaction, such as a recombination of fragments, as shown above, can be caused by the cage effect of the solvent molecules [41]. Other reactions can take place between a radical and a parent initiator molecule. This can lead to the formation of different initiating species. It can, however, also be a dead end as far as the polymerization reaction is concerned.

After the initiating radical has diffused into the proximity of the monomer, the capture of the free radical by the monomer completes the step of initiation. This is a straightforward addition reaction, subject to steric effects:



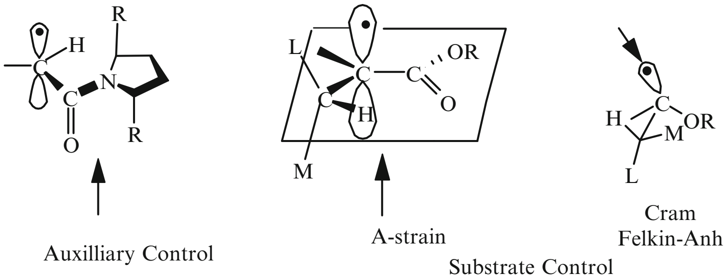
The unpaired electron of the radical is believed to be in the pure p-orbital of a planar, sp^2, carbon atom. Occasionally, however, radicals with sp^3 configuration appear to form [42–44].

Using quantum chemical calculations it was demonstrated that nucleophilic and electrophilic alkyl or aryl radicals attack alkenes following a tetrahedral trajectory [45, 46]:



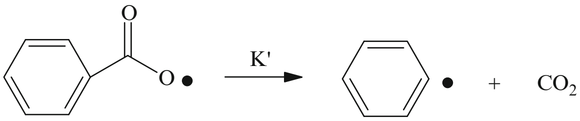
This means that only substituents Y at the attacked olefinic carbon exert large steric effects [47]. In addition to the steric effects, the rates of addition of strongly nucleophilic or electrophilic radicals are governed mainly by polar effects of the substituents R_x, Y, and Z [48]. In borderline cases, however, the stabilities of the adducts and products tend to dominate [47].

Also, it was demonstrated that acyclic radicals can react with high stereoselectivity [45]. In order for the reactions to be stereoselective, the radicals have to adopt preferred conformations where the two faces of the prochiral radical centers are shielded to different extents by the stereogenic centers. Giese and coworkers [49] demonstrated with the help of Electron Spin Resonance studies that ester-substituted radicals with stereogenic centers in β-positions adopt preferred conformations that minimize allylic strain [49] (shown below). In these conformations, large (L) and medium sized substituents (M) shield the two faces. The attacks come preferentially from the less shielded sides of the radicals. Stereoselectivity, because of A-strain conformation, is not limited to ester-substituted radicals [50]. The strains and steric control in reactions of radicals with alkenes can be illustrated as follows [50]:

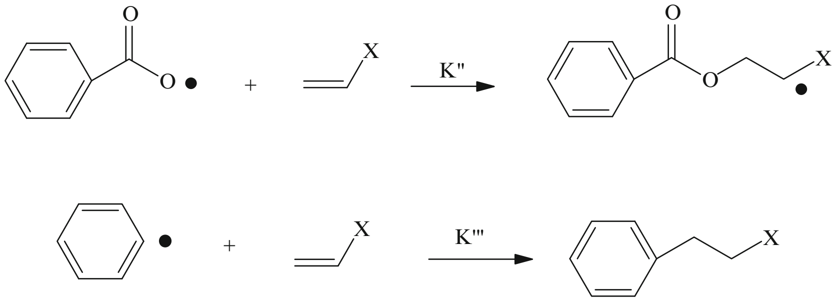


The above considerations can be illustrated on initiation by benzoyl peroxide, a commonly used initiating compound. The half-life of the initial benzoyloxy radicals from decompositions of benzoyl peroxide is estimated to be 10^{-4} to 10^{-5} s. Past that time, they decompose into phenyl radicals and carbon dioxide [49]. This is sufficient time for the benzoyloxy radicals to be trapped by fast-reacting monomers. Slow-reacting monomers, however, are more likely to react with the phenyl radicals that form from the elimination reaction. In effect, there are two competing reactions [50]:

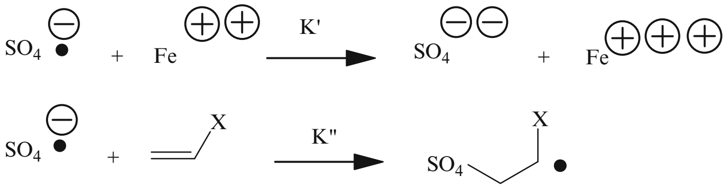
1. Decomposition of the free radical:



2. Two types of radicals can add to the monomer (where x represents any typical substituent of vinyl monomers, such as halogens, or esters, or aromatic groups, or nitriles, etc.):



The ratio of the rates of the two reactions, K''/K', (or K'''/K') depends upon the reactivity of the monomers. It is shown in Table 3.5 [51, 52]. The benzoyloxy radical is used in this table as an illustration. A similar comparison is possible for a redox initiating system. An initiating sulfate radical ion from a persulfate initiator can react with another reducing ion or add to the monomer:

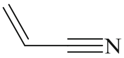
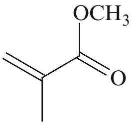
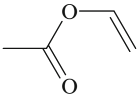
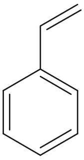
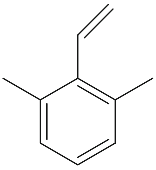


In Table 3.6 are shown the relative reaction rates of SO_4• ⊖ with some monomers at 25°C [53–57]. As explained, the rate of addition of a radical to a double bond is affected by steric hindrance from bulky substituents. Polar effect, such as dipole interactions also influence the rate of addition.

Forbes and Yashiro studied the addition of the initiating radials to methyl methacrylate in liquid supercritical carbon dioxide [58]. They demonstrated that the rate of addition of the initiating radicals to the monomers, k_{add} values, can be measured in liquid CO_2.

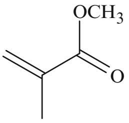
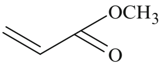
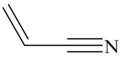
Phenyl or methyl groups located on the carbon atom that is under a direct attack by a free radical can be expected to interfere sterically with the approach. For instance, due to steric hindrance, *trans*-β-methylstilbene is more reactive toward a radical attack than is its *cis* isomer [58]. Yet, the *trans* isomer is more stable of the two. While 1,1-disubstituted olefins homopolymerize readily, the 1,2-disubstituted olefins are hard to homopolymerize [59]. Some exceptions are vinyl carbonate [61] and maleimide derivatives [62]. Also, perfluoroethylene and chlorotrifluoroethylene polymerize readily. Table 3.6 shows the relative reaction rates of SO_4• ⊖ with some monomers at 25°C [50].

Table 3.5 Relative reactivities of the benzoyloxy radical at 60°C

Monomer	Structure	K'/K'' (mol/L)
Acrylonitrile		0.12
Methyl methacrylate		0.30
Vinyl acetate		0.91
Styrene		2.50
2,5-dimethylstyrene		5.0

Addition to monomer/decomposition rates [51, 52]

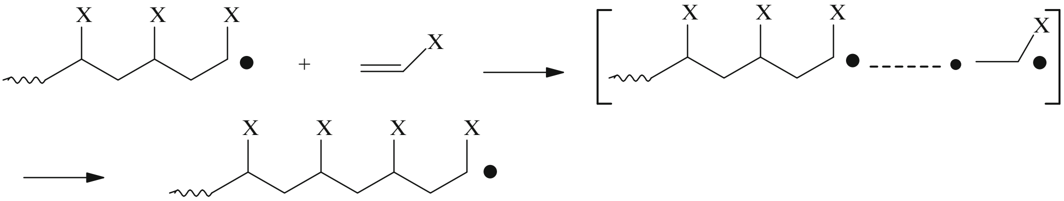
Table 3.6 Relative rates of reactions of the sulfate ion-radical with some monomers [51, 52]

Monomer	Structure	Relative rates K''/K'
Methyl methacrylate		7.7×10^{-3}
Methyl acrylate		1.1×10^{-3}
Acrylonitrile		3.9×10^{-4}

Homopolymerizations of diethyl fumarate by free-radical mechanism were reported [63]. The M_n was found to be 15,000. The same is true of homopolymerizations of several other dialkyl fumarates and also dialkyl maleates [64–66]. The polymerization rates and the sizes of the polymers that form decrease with increases in the lengths of linear alkyl ester groups. There is, however, an opposite correlation if the ester groups are branched. Also, the maleate esters appear to isomerize to fumarates prior to polymerization [66].

3.4 Propagation

The transition state in a propagation reaction can be illustrated as follows:



In the above transition state, the macroradical electron is localized on the terminal carbon. Also, the two π electrons of the double bond are localized at each olefinic carbon. Interaction takes place between p-orbital of the terminal atom in the active polymer chain with associated carbon of the monomer. This results in formation of σ-bonds [67].

The rate of the propagation reaction depends upon the reactivity of the monomer and the growing radical chain. Steric factors, polar effects, and resonance are also important factors in the reaction.

Another factor that can affect the rate of propagation is interaction between propagating radicals. Siegmann and Beuermann [60] studied the rate of propagation of 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl methacrylate and compared it to the rate of propagation of methyl methacrylate. They observed that k_p for 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl methacrylate polymerization is 1.9 times that of k_p for methyl methacrylate. They concluded that this higher rate is due to less interactions occurring between the propagating macroradicals.

Bowman and coworkers studied the impact of intermolecular and intramolecular interactions on the polymerization kinetics of monoacrylates [69]. They carried out polymerization studies in the presence of extensive amounts of solvent. This was an attempt to elucidate the effects of intermolecular interactions, such as bulk medium polarity, π–π stacking, and hydrogen bonding and characterize the contribution of intramolecular conformational effects to monomer reactivity. Solution polymerization kinetics of various monomers were measured in the presence of 95 wt% 1,4-dioxane. The results were compared to bulk polymerization kinetics. The studies revealed that aliphatic acrylates such as hexyl acrylate exhibit approximately two to threefold reduction in reactivity upon dilution. Monomers characterized by only hydrogen-bonding features such as hydroxyethyl acrylate exhibit an 8- to 12-fold reduction upon dilution. Monomers possessing only aromatic ring stacking interactions such as phenyl acrylate exhibit approximately a five to tenfold reduction upon dilution under similar conditions. Even at a concentration of 5 wt% monomer in 1,4-dioxane, there were approximately two to fivefold differences in reactivity observed between various acrylates. Bowman and coworkers attributed these reactivity differences between various acrylates, upon extensive dilution, solely to intramolecular interactions [69].

3.4.1 Steric, Polar, and Resonance Effects in the Propagation Reaction

The steric effects depend upon the sizes of the substituents. The resonance stabilization of the substituents has been shown to be in the following order [70]:

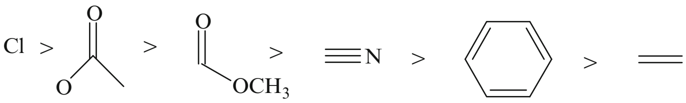
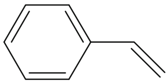
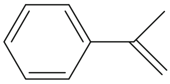
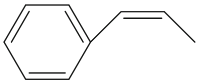
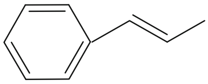
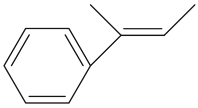
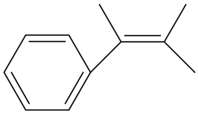
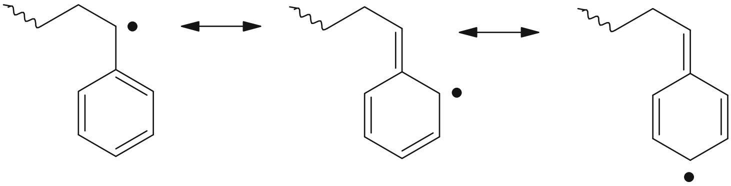


Table 3.7 Affinity of methyl radical for olefins[a] [56, 57, 67]

Monomer	Structure	Methyl affinity
Styrene		792
α-methyl styrene		92.6
cis-β-methyl styrene		40
Trans-β-methyl styrene		92.5
α,β-dimethyl styrene		66
α,β,β′-trimethyl styrene		20

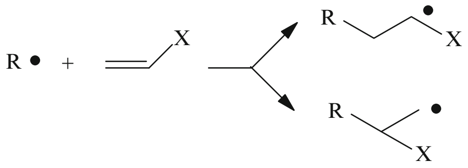
[a] From Carrick, Szwarc, Leavitt, Levy, and Stannett, by permission of American Chemical Society

The reactivities of the propagating polymer-radicals, however, exert greater influence on the rates of propagation than do the reactivities of the monomers. Resonance stabilization of the polymer-radicals is a predominant factor. This fairly common view comes from observations that a methyl radical reacts at a temperature such as 60°C approximately 25 times faster with styrene than it does with vinyl acetate [72]. In homopolymerizations of the two monomers, however, the rates of propagation fall in an opposite order. Also, poly(vinyl acetate)-radicals react 46 times faster with *n*-butyl mercaptan in hydrogen abstraction reactions than do the polystyrene-radicals [71]. The conclusion is that the polystyrene radicals are much more resonance stabilized than are the poly (vinyl acetate)-radicals. Several structures of the polystyrene-radicals are possible due to the conjugation of the unpaired electrons on the terminal carbons with the adjacent unsaturated groups. These are resonance hybrids that can be illustrated as follows:

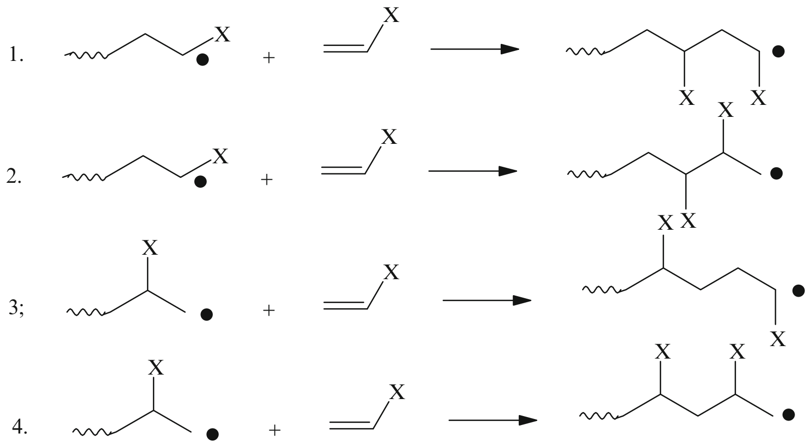


There is not such opportunity, however, for resonance stabilization of the poly(vinyl acetate) radicals because oxygen can accommodate only eight electrons. The effect of steric hindrance on the affinity of a methyl radical is illustrated in Table 3.7 [56, 57].

In vinyl monomers, both olefinic carbons are potentially subject to free-radical attack. Each would give rise to a different terminal unit:



The newly formed radicals can again potentially react with the next monomer in two ways. This means that four propagation reactions can occur:

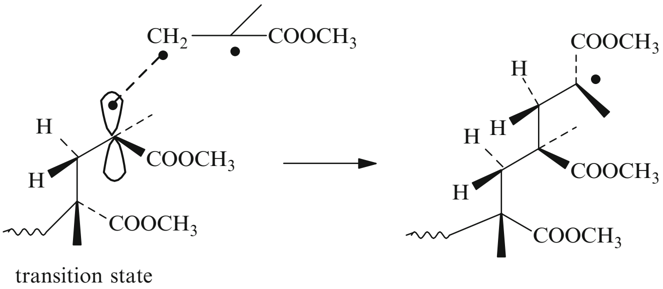


Contrary to the above shown four propagation modes, a “head to tail” placement shown in (3.1), strongly predominates. This is true of most free radical vinyl polymerizations. It is consistent with the localized energy at the α-carbon of the monomer. Also, calculations of resonance stabilization tend to predict head to tail additions [68].

The free-radical propagation reactions that correspond to conversions of double bonds into single bonds are strongly exothermic. In addition, the rates increase with the temperature. It is often assumed that the viscosity of the medium, or change in viscosity during the polymerization reaction does not affect the propagation rate or the polymer growth reaction. This is because it involves diffusion of small monomer molecules to the reactive sites. Small molecules, however, can also be impeded in their process of diffusion. This can impede the growth rate [50].

During chain growth, the radical has a great deal of freedom with little steric control over the manner of monomer placement. Decrease in the reaction temperature, however, lowers mobility of the species and increases steric control over placement. This is accompanied by an increase in stereoregularity of the product [70, 71]. The preferred placement is ***trans–trans***, because of lower energy required for such placement. As a result, a certain amount of syndiotactic arrangement is observed in polymerizations at lower temperatures [72]. *Trans–trans* configurations (with respect to the carbon atoms in the chains) yield zigzag backbones. This was predicted from observations of steric effects on small molecules [74, 75]. It was confirmed experimentally for many polymers, such as, for instance, in the formation of poly(1,2-polybutadiene) [74] and poly(vinyl chloride) [72]. Also, in the free-radical polymerizations of methyl methacrylate, syndiotactic placement becomes increasingly dominant at lower temperatures. Conversely, the randomness increases at higher temperatures [74]. The same is true in the free-radical polymerization of halogenated vinyl acetate [75].

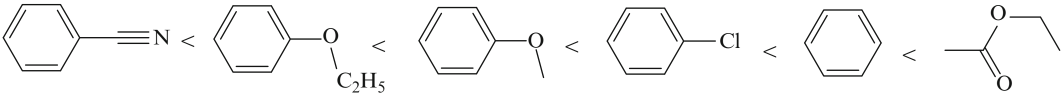
One proposed mechanism for the above is as follows. The least amounts of steric compression within macromolecules occur during the growth reactions if the ultimate and the penultimate units are *trans* to each other. Also, if the lone electrons face the oncoming monomers during the transition states [80, 81], as shown below, syndiotactic placement should be favored:



While the above model explains the formation of syndiotactic poly(methyl methacrylate), possible interactions between the free radicals on the chain ends and the monomers are not considered. Such interactions, however, are a dominant factor in syndiotactic placement, if the terminal carbons are sp^2 planar in structures [75].

3.4.2 *Effect of Reaction Medium*

There were some early reports that reaction media influences the polymerizations of vinyl chloride in aliphatic aldehydes at 50°C [80, 81]. This was not confirmed in subsequent studies [82–84]. Subsequently, the rate of polymerization was shown to be influenced by the pH of the reaction medium in polymerizations of monomers such as methacrylic acid (MAA) [85, 88]. Also, the rate of polymerization and solution viscosities increase in polymerizations of acrylamide and acrylic acid with an increase in water concentration [83]. It is not quite clear whether this is due to increases in the speeds of propagations or due to decreases in the termination rates. In the free-radical polymerization of vinyl benzoate, the rate of propagation varies in different solvents in the following order [88, 89]:



Similarly, the rate of photopolymerization of vinyl acetate is affected by solvents [88]. In most cases, however, the rate of polymerization is proportional to the square root of the initiator concentration and to the concentration of the monomer [5].

De Sterck and coworkers [90] studied solvent effect on tacticity of methyl methacrylate in free-radical polymerization. They observed that solvents CH_3OH and $(CF_3)_3COH$, which are H-bonded with the carbonyl oxygens and are located on the same side of the backbone of the growing polymer radical hinder the formation of isotactic poly(methyl methacrylate) to some extent. Methanol is less effective in reducing the isotacticity because of its small size and also because of the relatively loose hydrogen bonds with the carbonyl oxygens.

There is a controversial suggestion that the solvent affects the propagation step in some reactions by forming "hot" radicals [91]. These radicals are supposed to possess higher amounts of energy. At the moment of their formation, they obtain surplus energy from the heat of the reaction and from the activation energy of the propagation reaction. This is claimed to provide the extra energy needed to activate the next chain propagation step. The surplus energy may affect the polymerization kinetics if the average lifetime of the hot radicals is sufficient for them to react with the monomer molecules. This surplus energy is lost by the hot radicals in collisions with monomer and solvent molecules.

There is a difference in the rate constants of propagation for hot and ordinary radicals so two different reaction schemes were written [91]:
Propagation by ordinary radicals:

$$\mathrm{R}\bullet + \mathrm{M} \rightarrow \mathrm{RM}\bullet \quad (k_2)$$

Propagation by hot radicals:

$$\mathrm{R}^* + \mathrm{M} \rightarrow \mathrm{RM}^* \quad (k_2{}^*)$$

Energy transfer processes:

$$\mathrm{R}^* + \mathrm{Solvent} \rightarrow \mathrm{R}\bullet + \mathrm{Solvent} \quad (k_3'{}^*)$$

where, R* is the symbol for hot radicals.

The rate expression for the polymerization is then written as follows [92]:

$$-\,\mathrm{d}[\mathrm{M}]/\mathrm{d}t = K_{\mathrm{X}}X^{0.5}[\mathrm{M}] \times [\mathrm{I} + 1/(\gamma + \gamma' + \mathrm{S}/[\mathrm{M}])]$$

where, $K_x = k_2(2k_1f/k_4)^{1/2}$, $\gamma = k_1{*}/k_2{*}$ and $\gamma' = k_3{*}/k_2{*}$, S = solvent, [M] = monomer

In comparing free-radical polymerizations of ethyl acrylates in benzene and in dimethyl formamide at 50°C [218] the rates were found to be proportional to the square roots of the initiator concentration. They were not proportional, however, to the concentrations of the monomer. This was interpreted in terms of hot radicals [93].

Similar results, however, were interpreted by others differently. For instance, butyl acrylate and butyl propionate polymerizations in benzene also fail to meet ideal kinetic models. The results, however, were explained in terms of termination of primary radicals by chain transferring (see Sect. 3.5 for explanation of chain transferring).

3.4.3 Ceiling Temperature

For most free-radical polymerization reactions, there are some elevated temperatures at which the chain-growth process becomes reversible and depropagation takes place:

$$\mathrm{M}_{\mathrm{n}+1} \xrightarrow{k_{\mathrm{d}}\mathrm{p}} \mathrm{M}_{\mathrm{n}}\bullet + \mathrm{M}$$

where, $k_{\mathrm{d\cdot p}}$ is the rate constant for depropagation or depolymerization. The equilibrium for the polymerization–depolymerization reaction is temperature dependent. The reaction isotherm can be written:

$$\Delta F = \Delta F^0 + RT\ln K$$

In the above equation ΔF^0 is the free energy of polymerization of both, monomer and polymer, in appropriate standard states [88]. The standard state for the polymer is usually solid (amorphous or partly crystalline). It can also be a one molar solution. The monomer is a pure liquid or a one molar solution. The relationships of monomer concentration to heat content, entropy, and free energy are shown by the following expression. This applies over a wide range of temperatures [5].

$$\ln[\mathrm{M}] = \Delta H^0{}_\mathrm{P}/RT_\mathrm{c} - \Delta S^0{}_\mathrm{P}/R$$

In the above equation, T_c is the ***ceiling temperature*** for the ***equilibrium monomer concentration***. It is a function of the temperature of the reaction. Because the heat content is a negative quantity, the concentration of the monomer (in equilibrium with polymer) increases with increasing temperatures. There are a series of ceiling temperatures that correspond to different equilibrium monomer concentrations. For any given concentration of a monomer in solution, there is also some upper temperature at which polymerization will not proceed. This, however, is a thermodynamic approach. When there are no active centers present in the polymer structure, the material will appear stable even above the ceiling temperature in a state of metastable equilibrium.

The magnitude of the heat of polymerization of vinyl monomers is related to two effects: (1) Steric strains that form in single bonds from interactions of the substituents. These substituents, located on the alternate carbon atoms on the polymeric backbones, interfere with the monomers entering the chains. (2) Differences are in resonance stabilization of monomer double bonds by the conjugated substituents [70].

Most 1,2 disubstituted monomers, as stated earlier, are difficult to polymerize. It is attributed to steric interactions between one of the two substituents on the vinyl monomer and the β-substituent on the ultimate unit of the polymeric chain [94]. A strain is also imposed on the bond that is being formed in the transition state.

The propagation reaction usually requires only an activation energy of about 5 kcal/mol. As a result, the rate does not vary rapidly with the temperature. On the other hand, the transfer reaction requires higher activation energies than does the chain-growth reaction. This means that the average molecular weight will be more affected by the transfer reaction at higher temperature. When allowances are made for chain transferring, the molecular weight passes through a maximum as the temperature is raised. At temperatures below the maximum, the product molecular weight is lower because the kinetic chain length decreases with the temperature. Above the maximum, however, the product molecular weight is also lower with increases in the temperature. This is due to increase in the transfer reactions. The above assumes that the rate of initiation is independent of the temperature. The relationship of the kinetic chain length to the temperature can be expressed as follows [5]:

$$\mathrm{d}\ln v/\mathrm{d}T = (E_\mathrm{P} - 1/2E_\mathrm{T} - 1/2E_\mathrm{I})/RT^2$$

where, E_P, E_T, and E_I are energies of propagation, termination, and initiation, respectively. A large E_I means that if the temperature of polymerization is raised, the kinetic chain length decreases. This is affected further by a greater frequency of chain transferring at higher temperatures. In addition, there is a possibility that disproportionation may become more significant.

3.4.4 Autoacceleration

When the concentrations of monomers are high in solution or bulk polymerizations, typical auto-accelerations of the rates can be observed. This is known as the ***gel effect*** or as the ***Trammsdorff effect***, or also, as the ***Norrish–Smith effect*** [66]. The effect has been explained as being caused by a decrease in the rate of termination due to increased viscosity of the medium. Termination is a reaction that requires two large polymer-radicals to come together and this can be impeded by viscosity. At the same time, in propagation the small molecules of the monomer can still diffuse for some time to the radical sites and feed the chain growth.

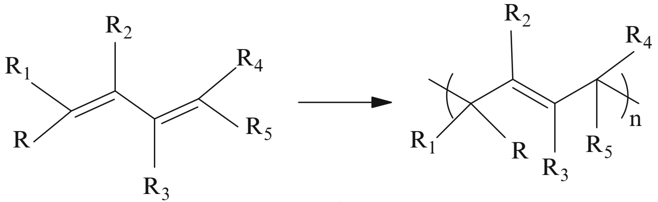
One should not mistake an acceleration of the polymerization reaction due to a rise in the temperature under nonisothermal conditions for a true gel effect from a rise in viscosity. The gel effect can occur when the temperature of the reaction is kept constant.

A critical analysis of the gel effect suggests that the situation is complicated. In some polymerizations, three different stages appear to be present when $R_P/[M][I]^{1/2}$ is plotted against conversion or against time [95]. The plot indicates that during the first stage there is either a constant or a declining rate and during the second stage there is autoacceleration. During the third stage, there is again a constant or a declining rate [95].

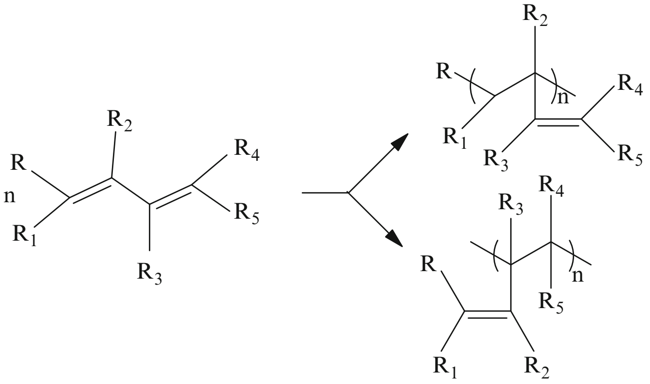
Numerous publication made a substantial case for associating and/or attributing the gel effect to entanglement of polymerizing chain radicals, resulting in a marked reduction in the termination rate parameter, k_T. This was often done by using the assumption that in the neighborhood of the gel effect k_T is controlled by polymer self-diffusion, which in turn exhibits entangled polymer dynamics. O'Neil et al. [96], however, argued against that opinion. They carried out a series of experiments involving bulk polymerizations of methyl methacrylate and styrene and feel that their data contradicts this widely held belief that the gel effect onset is related to the formation of chain entanglements. The experimental conditions used were such that they tended to delay or eliminate the formation of chain entanglement. These conditions were high initiator and/or chain transferring agent concentrations and additions of low molecular weight polymers prior to the reactions. The results indicated that the gel effect occurs readily in the absence of entanglement and that delaying the onset of entanglements does not necessarily delay the onset of the gel effect. Also, critical examination of the molecular weights produced in these experiments indicated values that were too low for entanglement formation in solution (polymer plus monomer) and sometimes even in bulk polymer, not only at the onset but also throughout the gel effect [96]. O'Neil et al. [96], found that even under conditions where entanglements are likely to exist, the gel effect onset does not correlate with polymer molecular weight of the chains produced in a manner consistent with entanglement arguments. Whether the kinetics during the gel effect may be affected by entanglements was left uncertain.

3.4.5 Polymerization of Monomers with Multiple Double Bonds

Polymerizations of monomers with multiple double bonds yield products that vary according to the locations of these bonds with respect to each other. Monomers with conjugated double bonds, such as 1,3-butadiene and its derivatives, polymerize in two different ways. One way is through one of the double bonds only. Another way is through both double bonds simultaneously. Such 1,4 propagation is attributable to the effect of conjugation and hybridization of the C_2–C_3 bond that involves *sp*^{2} hybrid orbitals [97]. All three modes of propagation are possible in one polymerization reaction so that the product can, in effect, be a copolymer. The 1,4, 1,2, and 3,4, placement in propagations can be illustration as follows:



1,4-placement

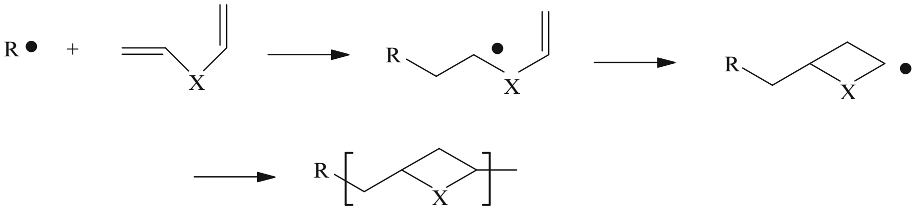


1,2 and 3,4 placements

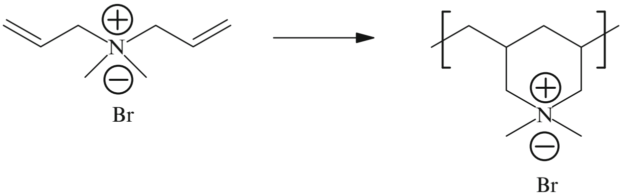
The polymerizations and copolymerizations of various conjugated dienes are discussed in Chap. 6.

3.4.5.1 Ring Forming Polymerization

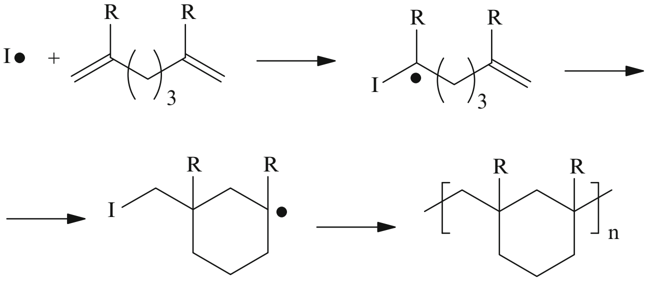
Propagation reactions of unconjugated dienes can proceed by an intra-intermolecular process. This usually results in ring formation or in ***cyclopolymerization***. It can be illustrated as follows:



where, X can designate either a carbon or a heteroatom. An example of such a polymerization is a free-radical polymerization of quaternary diethyldiallylamine [98]:

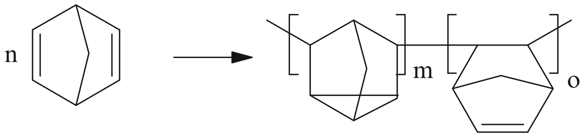


Another example is a polymerization of 2,6-disubstituted 1,6-heptadiene [103]:

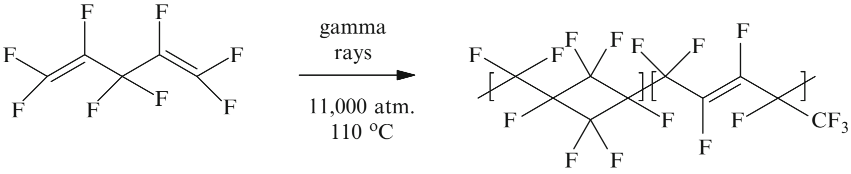


where, R=$COOC_2H_5$, $COOCH_3$, or COOH.

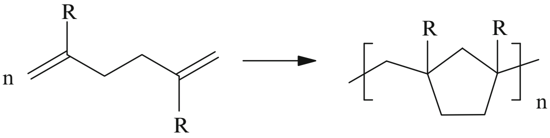
The intra-intermolecular propagations can result in ring structures of various sizes. For instance, three-membered rings can form from ***transanular*** polymerizations of bicycloheptadiene [100, 101]:



Four-membered rings form in free-radical polymerization of perfluoro-1,4-pentadiene [103]. The size of the ring that forms depends mainly on the number of atoms between the double bonds:



Formation of many five-membered rings is also known. One example is a polymerization of 2,3-dicarboxymethyl-1,6 hexadiene [98]:

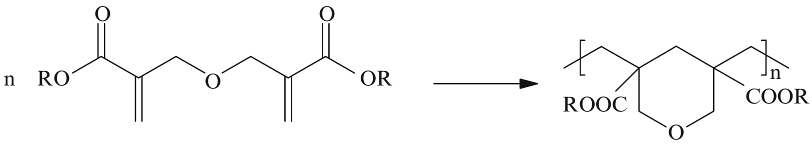


where, R=$COOCH_3$.

The polymer that forms, shown above, is cross-linked, but spectroscopic analysis shows that 90% of the monomer placement is through ring formation [104]. Formations of six-membered rings are also well documented. Two examples were shown above in the polymerization of a quaternary diethyldiallylamine and in the polymerization of 2,6 disubstitued, 1,6-heptadiene. Many other 1,6-heptadienes yield linear polymers containing six-membered rings [105].

This tendency to propagate intra-intermolecularly by the unconjugated dienes is greater than can be expected from purely statistical predictions [106]. Butler suggested that this results from interactions between the olefinic bonds [107–109]. Ultraviolet absorption spectra of several unconjugated diolefins does show bathochromic shifts in the absorption maxima relative to the values calculated from Woodward's rule [102, 104]. This supports Butler's explanation [107, 109].

A RAFT type of controlled/living polymerization (see Sect. 3.14.4) was applied to cyclopolymerization of *t*-butyl (hydroxyethyl) acrylate ether dimer [108]. The polymerizations, carried out in xylene at 70°C, yielded polymers with six-membered tetrahydropyran repeat units:



3.5 The Termination Reaction

The termination process in free-radical polymerization is caused, as was shown early in this chapter, by one of three types of reactions: (1) a second order radical-radical reaction, (2) a second order radical-molecule reaction, and (3) a first order loss of radical activity.

The first reaction can be either one of combination or of disproportionation. In a combination reaction, two unpaired spin electrons, each on the terminal end of a different polymer-radical, unite to form a covalent bond and a large polymer molecule. In disproportionation, on the other hand, two polymer-radicals react and one abstracts an atom from other one. This results in formation of two inactive polymer molecules. The two differ from each other in that one has a terminal saturated structure and the other one has a terminal double bond. Usually, the atom that is transferred is hydrogen.

It was suggested [111] that a basic rule of thumb can be applied to determine which termination reaction predominates in a typical homopolymerization. Thus, polymerizations of 1,1-disubstituted olefins are likely to terminate by disproportionation because of steric effects. Polymerizations of other vinyl monomer, however, favor terminations by combination unless they contain particularly labile atoms for transferring. Higher activation energies are usually required for termination reactions by disproportionation. This means that terminations by combination should predominate at lower temperatures.

For a polymer radical that simply grows by adding monomeric units and still possesses an active center after the growth, the number of monomeric units (r) added to a radical center during the time interval t, according to Tobita [112], conforms to the following Poisson distribution:

$$p(r) = \mathrm{e}^{-\theta}\theta^{r}/r$$

where θ is the expected number of monomeric units added to a radical center, given by

$$\theta = k_{\mathrm{p}}[\mathrm{M}]t$$

where k_{p} is the propagation rate coefficient and [M] is the monomer concentration. If the number of the added monomeric units, r, is large enough, one can approximate that $r \cong \theta$. For bimolecular termination reactions that are independent of chain length, the required time for bimolecular termination between a particular radical pair is also given by the following most probable distribution [112]:

$$p_{\mathrm{t}}(\theta_{\mathrm{t}}) = \xi \exp\left(-\xi\theta_{\mathrm{t}}\right)$$

where $\xi = k_{\mathrm{t}}/(k_{\mathrm{p}}[\mathrm{M}]vN_{\mathrm{A}})$, and k_{t} is the bimolecular termination rate coefficient. The imaginary time for chain stoppage by bimolecular termination must be considered for all radical pairs that exist in the reaction medium [112].

The third type of a termination reaction is chain transferring. Premature termination through transferring results in a lower molecular weight polymer than can be expected from other termination reactions. The product of chain transferring is an inert polymer molecule and, often, a new free radical capable of new initiation. If, however, the new radical is not capable of starting the growth of a new chain, then this is ***degenerative chain transferring***. It is also referred to as a ***first-order termination reaction***. The molecules that accept the new radical sites (participate in chain transferring) can be any of those present in the reaction medium. This includes solvents, monomer molecules, inactive polymeric chains, and initiators.

The ease with which chain transferring takes place depends upon the bond strength between the labile atoms that are abstracted and the rest of the molecule to which they are attached. For instance, chain transferring in methyl methacrylate polymerization to the solvent occurs in the following order [115]:

$$\text{benzene} < \text{toluene} < \text{ethyl benzene} < \text{cumene}$$

The rate of a chain transferring reaction is,

$$R_{\mathrm{tr}} = k_{\mathrm{tr}}[\mathrm{M}\bullet][\mathrm{XA}]$$

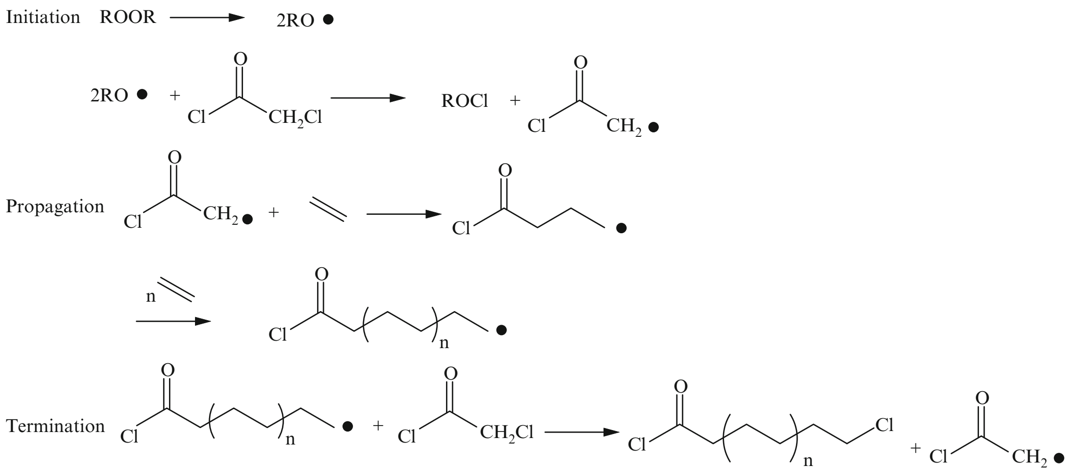
where, k_{tr} is the chain transferring constant in a reaction:

$$M\bullet + X - A \xrightarrow{K_{tr}} M - X + A\bullet$$

Examples of molecules that have particularly labile atoms and contribute readily to chain-transferring are mercaptans and halogen compounds, such as chloroform, carbon tetrachloride, etc.

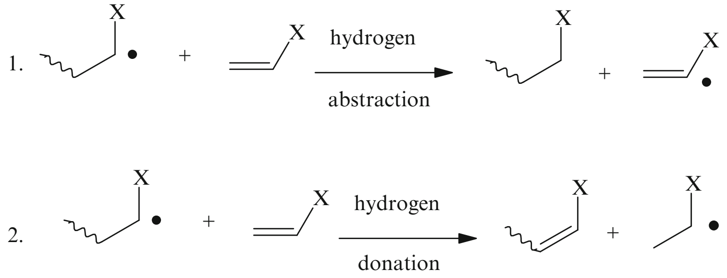
A polymer that was prematurely terminated in its growth by chain transferring may be a ***telomer***. In most cases of telomer formation, the newly formed radical and the monomer radical are active enough to initiate new chain growth. Thus, the life of the kinetic chain is maintained.

An illustration of a ***telomerization reaction*** can be free-radical polymerization of ethylene in the presence of chloroacetyl chloride:

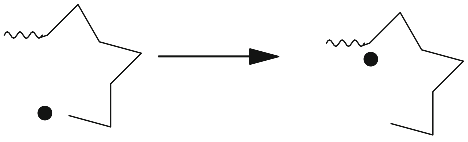


Chain transferring is affected by temperature but not by changes in the viscosity of the reaction medium [115]. When a transfer takes place to a monomer, it is independent of the polymerization rate [116, 117]. When, however, transfer takes place to the initiator, the rate increases rapidly [118].

A chain transferring reaction to a monomer can be illustrated as follows:



A transfer reaction can also occur from the terminal group of the polymer-radical to a location on the polymeric backbone. This is known as ***backbiting***:



The new free-radical site on the polymer backbone starts chain growth that results in formation of a branch. The same reaction can take place between a polymer-radical and a location on another polymer chain. In either case, fresh chain growth results in formation of a branch.

Whether chain transferring can take place to an initiator depends upon the initiator's chemical structure. It was believed in the past that chain transferring to α,α′-azobisisobutyronitrile does not occur. Later it was shown that chain transferring to this initiator does occur as well, at least in the polymerizations of methyl methacrylate [118, 119].

The amount of chain transferring that takes place to monomers is usually low because the reaction requires breaking strong carbon-hydrogen bonds. Monomers, however, such as vinyl chloride and vinyl acetate have fairly large chain transferring constants. In the case of vinyl acetate, this is attributed to the presence of an acetoxy methyl group. This explanation, however, cannot be used for vinyl chloride.

The chain transferring constants, are usually defined as:

$$C_{\mathrm{M}} = k_{\mathrm{tr,M}}/k_{\mathrm{p}} \quad \text{for monomers}$$

$$C_{\mathrm{S}} = k_{\mathrm{tr,S}}/k_{\mathrm{p}} \quad \text{for solvents}$$

$$C_{\mathrm{I}} = k_{\mathrm{tr,I}}/k_{\mathrm{P}} \quad \text{for initiators,}$$

The values can be found in handbooks and other places in the literature. Presence of chain transferring agents in a polymerization reaction requires redefining the degree of polymerization to include the chain termination terms. The number average degree of polymerization has to be written as follows:

$$\overline{\mathrm{DP}} = \frac{R_{\mathrm{p}}}{(R_{\mathrm{t}}/2) + k_{\mathrm{tr,M}}[\mathrm{M}\bullet][\mathrm{M}] + k_{\mathrm{tr,s}}[\mathrm{M}\bullet][\mathrm{S}] + k_{\mathrm{tr,I}}[\mathrm{M}\bullet][\mathrm{I}]}$$

It can also be expressed in terms of the chain transferring constants as follows:

$$1/\overline{\mathrm{DP}} = 2R_{\mathrm{P}}/R_{\mathrm{I}} + C_{\mathrm{M}} + C_{\mathrm{S}}[\mathrm{S}]/[\mathrm{M}] + C_{\mathrm{I}}[\mathrm{I}]/[\mathrm{M}]$$

This can also be written in still another form:

$$1/\overline{\mathrm{DP}} = k_{\mathrm{t}}R_{\mathrm{P}}/k_{\mathrm{P}}{}^{2}[\mathrm{M}]^{2} + C_{\mathrm{M}} + C_{\mathrm{S}}[\mathrm{S}]/[\mathrm{M}] + C_{\mathrm{I}}k_{\mathrm{t}}R_{\mathrm{P}}{}^{2}/k_{\mathrm{P}}{}^{2}fk_{\mathrm{d}}[\mathrm{M}]^{3}$$

When a polymerization reaction is conducted in a concentrated solution, or in complete absence of a solvent, the viscosity of the medium increases with time, (unless the polymer precipitates out). This impedes all steps in the polymerization process, particularly the diffusions of large polymer-radicals [54]. The decreased mobility of the polymer-radicals affects the termination process. It appears that this is common to many, though not all, free-radical polymerizations. All molecular processes in the termination reactions are not fully understood, particularly at high conversions [119] This is a complex process that consists of three definable steps. These can be pictured as follows. First, two polymer radicals migrate together by means of translational diffusion. Second, the radical sites reorient toward each other by segmental diffusion. Third, the radicals overcome the small chemical activation barriers and react. The termination reaction is, therefore, diffusion controlled. At low concentrations, this will be segmental diffusion while at medium or high concentrations it will be translational diffusion.

Present theories of terminations suggest that at intermediate conversions, terminations are dominated by interactions between short chains formed by transfer and entangled long chains [121].

When terminations are diffusion controlled, most termination events involve two highly entangled chains whose ends move by the “reaction-diffusion” process [119]. In this process, terminations occur because of the propagation-induced diffusion of the chain ends of growing macroradicals. This means that the rates of terminations depend upon the chain lengths [113].

Diffusion theories have been proposed that relate the rate constant of termination to the initial viscosity of the polymerization medium. The rate-determining step of termination, the segmental diffusion of the chain ends, is inversely proportional to the microviscosity of the solution [123]. Yokota and Itoh [124] modified the rate equation to include the viscosity of the medium. According to that equation, the overall polymerization rate constant should be proportional to the square root of the initial viscosity of the system.

The number average termination rate constants in a methyl methacrylate polymerization were measured with an in-line ESR spectrometer. This was done by observing the radical decay rates [120]. The results are in disagreement with the concept of termination by propagation-diffusion that is expected to be dominant at high conversion rates. Instead, the termination rate constants decrease dramatically in the posteffect period at high conversions. Actually, a fraction of the radicals were found trapped during the polymerization. Thus, there are two types of radicals in the reaction mixture, trapped and free radicals. In the propagations and termination reactions, the two types of radical populations have very different reactivities [120].

Shipp and coworkers [120] described a method for analyzing the chain length dependence of termination rate coefficients of the reacting radicals in low conversion free radical polymerizations. Their method involves comparing experimental molecular weight distributions of polymers formed in pulsed laser photolysis experiments with those predicted by kinetic simulation. The method is enabled by direct measurements of the concentration of radicals generated per laser pulse. Knowledge of the radical concentrations should mean that the only unknowns in the simulations are the termination rate coefficients. They concluded that the analysis demonstrates the need for chain length dependent termination rate constants in describing polymerization kinetics.

Free-radical photopolymerizations (see Chap. 10) of multifunctional acrylic monomers result in cross-linked polymeric networks. The kinetic picture of such polymerizations varies from ordinary linear polymerization because the diffusion of free radicals and functional groups becomes severely restricted. This causes growing polymer chains to rapidly cyclize and cross-link into clusters (microgels). The clusters become linked up into networks. Many free radicals become trapped, but terminations take place by combinations and by chain transferring. The cumulative chain length in such polymerizations can be calculated from the following equation [125]:

$$v = \frac{x n_{\mathrm{m0}}}{n_{\mathrm{rg}}}$$

where, χ is the conversion of functional groups and n_{m0} is the initial number of functional groups and n_{rg} is the total number of radicals generated.

3.6 Copolymerization

If more than one monomer species is present in the reaction medium, a copolymer or an interpolymer can result from the polymerization reaction. Whether the reaction products will consist of copolymers or just a mixture of homopolymers of both, however, depends largely upon the reactivity of the monomers. A useful and a simplifying assumption in kinetic analyses of free-radical copolymerizations is that the reactivity of polymer radicals is governed entirely by the terminal monomer units [52]. For instance, a growing polymer radical that contains a methyl methacrylate terminal unit, is

Table 3.8 Some reactivity ratios [132, 136]

Monomer 1	Monomer 2	r_1	r_2
Styrene	Butadiene	0.78	1.39
Styrene	Methyl methacrylate	0.52	0.46
Styrene	Vinyl acetate	55.0	0.01
Vinyl acetate	Vinyl chloride	0.23	1.68
Methyl acrylate	Vinyl chloride	9.00	0.083

considered, in terms of reactivity, as a poly(methyl methacrylate) radical. This assumption although not always adequate [52] can be used to predict satisfactorily the behavior of many mixtures of monomers. Based on this assumption, the copolymerization of a pair of monomers involves four distinct growth reactions and two types of polymer radicals.

3.6.1 Reactivity Ratios

In a reaction of two monomers, designated as M_1 and M_2, four distinct reactions can be written as follows:

$$1.\ \sim M_1\bullet + M_1 \xrightarrow{k_{11}} \sim M_1M_1\bullet$$

$$2.\ \sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim M_1M_2\bullet$$

$$3.\ \sim M_1\bullet + M_2 \xrightarrow{k_{21}} \sim M_1M_2\bullet$$

$$4.\ \sim M_2\bullet + M_2 \xrightarrow{k_{22}} \sim M_2M_2\bullet$$

The ratios of k_{11}/k_{12} and k_{22}/k_{21} are called ***monomer reactivity ratios***. They can be written as follows:

$$r_{\mathbf{1}} = k_{\mathbf{11}}/k_{\mathbf{12}} \quad r_{\mathbf{2}} = k_{\mathbf{22}}/k_{\mathbf{21}}$$

The relationship can be express in terms of the ratio of the monomers, $[M_1]/[M_2]$ that end up in the formed polymer, R_p:

$$R_p = R_m(r_{12}R_m + 1)/(r_{21} + R_m)$$

where, R_m is equal to $[M_1]/[M_2]$. Table 3.8 illustrates a few typical reactivity ratios taken from the literature. Many more can be found [128].

These reactivity ratios represent the relative rates of reactions of polymer radicals with their own monomers vs. that with the comonomers. When $r_1 > 1$, the radical $\sim M_1\bullet$ is reacting with monomer M_1 faster than it is with the comonomer M_2. On the other hand, when $r_1 < 1$, the opposite is true. Based on the ***r values***, the composition of the copolymers can be calculated from a ***copolymerization equation*** [52] shown below:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left[\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}\right]$$

In an ideal copolymerization reaction,

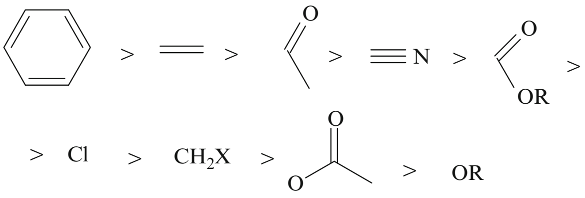
$$k_{11}/k_{12} = k_{22}/k_{21} \text{ and } r_1 r_2 = 1$$

If r_1 and r_2 values are equal to or approach zero, each polymer radical reacts preferentially with the other monomer. This results in an alternating copolymer, regardless of the composition of the monomer mixture. That is, however, a limiting case. In the majority of instances, $r_1 \times r_2$ is greater than zero and less than one. When the polymer radicals react preferentially with their own monomer, and $r_1 \times r_2 > 1$, then mainly a mixture of homopolymers forms and only some copolymerization takes place.

Reactivity of vinyl monomers is very often determined experimentally by studying copolymerizations. Values of many free-radical reactivity ratios have been tabulated for many different monomer pairs [126]. Also, the qualitative correlations between copolymerization data and molecular orbital calculations can be found in the literature [136].

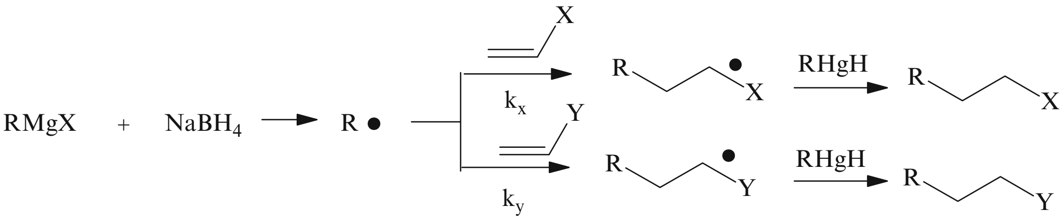
Some general conclusion about monomer reactivity toward attacking radicals was drawn by Mayo and Walling [130]:

1. The alpha substituents on a monomer have the effect of increasing reactivity in the following order.



2. The effect of a second alpha substituent is roughly additive.

Giese and coworkers [131–136] developed a special technique for studying the effects of the substituents upon the relative reactivity of vinyl monomers toward free radicals. Briefly it is as follows. Free radicals are produced by reducing organomercury halides with sodium borohydride. The radicals undergo competitive additions to pairs of various substituted olefins. The adducts are in turn trapped by hydrogen transfers from the formed organomercury hydrides. Relative quantities of each product are then determined



This method was applied in copolymerization of acrylonitrile and methyl acrylate [129]. It showed that the ratios of the rate constants for each of the two monomers are independent of their concentrations.

Copolymerization reactions are affected by solvents. One example that can be cited is an effect of addition of water or glacial acetic acid to a copolymerization mixture of methyl methacrylate with acrylamide in dimethyl sulfoxide or in chloroform. This causes changes in reactivity ratios [131]. Changes in r values that result from changes in solvents in copolymerizations of styrene with methyl methacrylate are another example [133, 134]. The same is true for styrene acrylonitrile copolymerization [132]. There are also some indications that the temperature may have some effect on the reactivity ratios [135], at least in some cases.

3.6.2 *Q and e Scheme*

Though molecular orbital calculations allow accurate predictions of reactivity ratios [133], many chemists also rely upon the Price–Alfrey ***Q–e* equations** [140]. These are based on: (1) the polarity of the double bonds of the monomers or measures of the propagating chain ends, (2) mesomerism of the substituents with the double bonds or with the chain ends, and (3) the steric hindrance of the substituents. This relationship is expressed in the following equation [149]:

$$\mathrm{K}_{12} = \mathrm{P}_1\mathrm{Q}_2^{-e_1e_2}$$

it can also be written as follows:

$$\log \mathrm{K}_{12} = \log \mathrm{Q}_1 + \log \mathrm{Q}_2 - 0.4343e_1e_2$$

where K_{12} represents the rate constant for the reaction of the propagating radical ~M_1• with monomer M_2, P_1 represents the general reactivity of the polymer radical with the terminal unit of monomer M_1, Q_1 and Q_2 are the reactivities of the monomer M_1 and M_2, and e_1 and e_2 are measures the polar characters of the monomers.

It is possible to calculate the Q and e values from r_1 and r_2, or, conversely, r values can be obtained from the Q and e values. The relationship is as follows [136]:

$$r_1 = k_{11}/k_{12} = \mathrm{Q}_1/\mathrm{Q}_2 \exp[-e_1(e_1 - e_2)]$$

$$r_2 = k_{22}/k_{21} = \mathrm{Q}_2/\mathrm{Q}_1 \exp[-e_2(e_2 - e_1)]$$

The Q and e scheme is based on a semiempirical approach. Nevertheless, some attempts were made to develop theoretical interpretations. Thus, Schwann and Price [141] developed the following relationship:

$$Q = \exp(-q/RT)$$

$$e = \varepsilon/(\gamma DRT)^{\mathbf{1/2}}$$

In the above equation, q represents the resonance of stabilization (kcal/mol), ε is the electrical charge of the transition state, and γ is the distance between the centers of the charge of the radical and the monomer, D stands for the effective dielectric constant of the reaction field. The values of q and e are derived by calculation. In addition, more rigorous molecular orbital calculations [138] show a relationship between Q and the localized energy of a monomer, and between e and the electron affinity. Also, a scale of Q and e values was deduced from essentially molecular orbital considerations [143]. In addition, a Huckel treatment of the transition state for the monomer–radical reaction in a free-radical copolymerization was developed [142]. The resulting reactivity ratios compared well with those derived from the Q and e scheme. This scheme is regarded by some as a version of the molecular orbital approach [145]. Nevertheless, the scheme should only be considered as an empirical one. The precision of calculating Q and e values can be poor because steric factors are not taken into account. It is good, however, for qualitative or semiquantitative results.

A revised reactivity scheme was proposed by Jenkins, that he called U,V scheme [148]. It is claimed to be more accurate and also capable of application to both copolymerizations and to transfer reactions. The scheme retains much of the format of the Q and e scheme. In this one, the intrinsic radical reactivity is quantified by reference to the rate of reaction of the radical with styrene monomer.

The original approach for this scheme was based on copolymerizations of styrene with acrylonitrile and with other acrylic monomers [149]. In developing a more general approach, however, Jenkins concluded that while in principle, a general procedure involves fewer assumptions, in practice much of the utility is lost. He proposed that it is convenient in practice to employ k_{is}: from styrene copolymerizations.

In writing the original scheme for styrene copolymerization with acrylic monomers in benzene, Jenkins introduced the term "*S*" to denote styrene σ_{p} represents the Hammett sigma constant for a substituent in the *para* position. In his revised scheme, he still uses k_{is} and writes it as follows:

$$\log r_{12} = \log k_{1\mathrm{s}} + u_2 + v_2$$

The term k_{11} is substituted from both sides of the equation to yield:

$$\log r_{12} = \log k_{1\mathrm{s}} - u_2\sigma_1 - v_2$$

The above equation represents a postulate on the same bases as does the *Q* and *e* scheme. This scheme contains an assumption that the intrinsic reactivity of a radical is measured by the value of $k_{1\mathrm{s}}$ and its polarity σ_1 (or π_1). Thus,

$$\log r_{12} - \log k_{1\mathrm{s}} = -u_2\sigma_1 - v_2$$

It follows that $r_{\mathrm{s}2} = -v_2$ and $\sigma_1 = \pi_{\mathrm{S}} = u_{\mathrm{S}} = v_{\mathrm{S}} = 0$. The final equation becomes:

$$\log r_{12} = \pi_1(u_1 - u_2) + (v_1 + v_2)$$

k_{is} represents the intrinsic reactivity of the styrene polymer radical (assuming that it is monomer 1)
v_2 represents the intrinsic reactivity of monomer 2
σ_1 represents the polarity of the polymer radical derived from monomer 1, and
u_2 represent polarity of monomer 2

Whether this scheme is applicable to general copolymerizations is not clear at this point.

3.6.3 Solvent Effect on Copolymerization

It was reported by Barb in 1953 that solvents can affect the rates of copolymerization and the composition of the copolymer in copolymerizations of styrene with maleic anhydride [145]. Later, Klumperman also observed similar solvent effects [145]. This was reviewed by Coote and coworkers [145]. A number of complexation models were proposed to describe copolymerizations of styrene and maleic anhydride and styrene with acrylonitrile. There were explanations offered for deviation from the terminal model that assumes that radical reactivity only depends on the terminal unit of the growing chain. Thus, Harwood proposed the "bootstrap model" based upon the study of styrene copolymerized with MAA, acrylic acid, and acrylamide [146]. It was hypothesized that solvent does not modify the inherent reactivity of the growing radical, but affects the monomer partitioning such that the concentrations of the two monomers at the reactive site (and thus their ratio) differ from that in bulk.

Hutchinson and coworkers investigated [147] effects of solvent on free-radical copolymer composition and propagation kinetics in copolymerizations of styrene with three methacrylates, 2-hydroxyethyl methacrylate, glycidyl methacrylate, and *n*-butyl methacrylate Three different solvents, *n*-butanol, toluene, and *N*,*N*-dimethylformamide were used. They found that all three solvents effected the composition of styrene-2-hydroxyethyl methacrylate copolymer. Liang and Hutchinson [147] also observed variations in monomer reactivity ratios with solvent polarity. Butanol was the only one that affected styrene butyl methacrylate copolymer composition. None of the solvents appeared to effect the composition of the styrene–glycidyl methacrylate copolymer.

3.7 Terpolymerization

A quantitative treatment of terpolymerization, where three different monomers are interpolymerized, becomes complex. Nine growth reactions take place [155]:

Reaction	Rate
$\sim M_1\bullet + M_1 \xrightarrow{K_{11}} \sim M_1M_1\bullet$	$R_{11} = k_{11}[M_1\bullet][M_1]$
$\sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim M_1M_2\bullet$	$R_{12} = k_{12}[M_1\bullet][M_2]$
$\sim M_1\bullet + M_3 \xrightarrow{k_{13}} \sim M_1M_3\bullet$	$R_{13} = k_{13}[M_1\bullet][M_3]$
$\sim M_2\bullet + M_1 \xrightarrow{k_{22}} \sim M_2M_1\bullet$	$R_{21} = k_{21}[M_2\bullet][M_1]$
$\sim M_2\bullet + M_2 \xrightarrow{k_{22}} \sim M_2M_2\bullet$	$R_{22} = k_{22}[M_2\bullet][M_2]$
$\sim M_2\bullet + M_3 \xrightarrow{k_{23}} \sim M_2M_3\bullet$	$R_{23} = k_{23}[M_2\bullet][M_3]$
$\sim M_3\bullet + M_1 \xrightarrow{k_{31}} \sim M_3M_1\bullet$	$R_{31} = k_{31}[M_3\bullet][M_1]$
$\sim M_3\bullet + M_2 \xrightarrow{k_{32}} \sim M_3M_2\bullet$	$R_{32} = k_{32}[M_3\bullet][M_2]$
$\sim M_3\bullet + M_3 \xrightarrow{k_{33}} \sim M_3M_3\bullet$	$R_{33} = k_{33}[M_3\bullet][M_3]$

There are six reactivity ratios in copolymerizations of three monomers [148]:

$$r_{12} = k_{11}/k_{12} \quad r_{13} = k_{11}/k_{13} \quad r_{21} = k_{22}/k_{21}$$

$$r_{23} = k_{22}/k_{23} \quad r_{31} = k_{33}/k_{31} \quad r_{32} = k_{33}/k_{32}$$

The rates of disappearance of the three monomers are given by

$$-\,d[M_1]/dt = R_{11} + R_{21} + R_{31}$$

$$-\,d[M_2]/dt = R_{12} + R_{22} + R_{32}$$

$$-\,d[M_3]/dt = R_{13} + R_{23} + R_{33}$$

By assuming steady state conditions for the three radicals, $M_1\bullet$, $M_2\bullet$, and $M_3\bullet$ it is possible to write:

$$R_{12} + R_{13} = R_{21} + R_{31}; \quad R_{21} + R_{23} = R_{12} + R_{32}; \quad R_{31} + R_{32} = R_{13} + R_{23}$$

An equation for terpolymer composition was developed from the rate expressions by expressing the steady state with the relationships [94]:

$$R_{12} = R_{21}; \quad R_{23} = R_{32}; \quad R_{31} = R_{13}.$$

$$\begin{aligned} d[M_1]/d[M_2]/d[M_3] = {} & [M_1]\{[M_1] + [M_2]/r_{12} + [M_3]/r_{13}\} \\ & /[M_2]r_{21}/r_{12}\{[M_1]/r_{21} + [M_2] + [M_3]/r_{23}\} \\ & /[M_3]r_{31}/r_{13}\{[M_1]/r_{31} + [M_2]/r_{32} + [M_3]\} \end{aligned}$$

It is claimed that this ***terpolymerization composition equation*** is often in good agreement with experimental results. Other, more complicated equations also exist, but apparently they yield results that are similar to those obtained from the above shown expression [94, 149].

One example of other equations is an early theoretical relationship for terpolymerization that was written by Alfrey and Goldfinger [150].

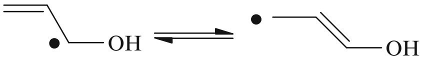
$$\frac{a}{b} = \frac{A[A/(r_{31}r_{21}) + B/(r_{21}r_{32}) + C/(r_{31}r_{23})][A + B/r_{12} + C/r_{13}]}{B[(A/(r_{12}r_{31}) + B/(r_{12}r_{32}) + C/(r_{32}r_{13})][B + A/r_{21} + C/r_{23}]}.$$

$$\frac{a}{c} = \frac{A[A/(r_{31}r_{21}) + B/(r_{21}r_{32}) + C/(r_{31}r_{23})][A + B/r_{12} + C/r_{13}]}{C[A/(r_{13}r_{21}) + B/(r_{23}r_{12}) + C/(r_{13}r_{23})][C + A/r_{13} + B/r_{32}]}$$

where a, b, and c are the quantities of each monomer found in the resultant terpolymer and A, B, and C are the quantities of the monomer in the feed system. Needless to say, a copolymerization of four or even more monomers becomes progressively more difficult to treat rigorously.

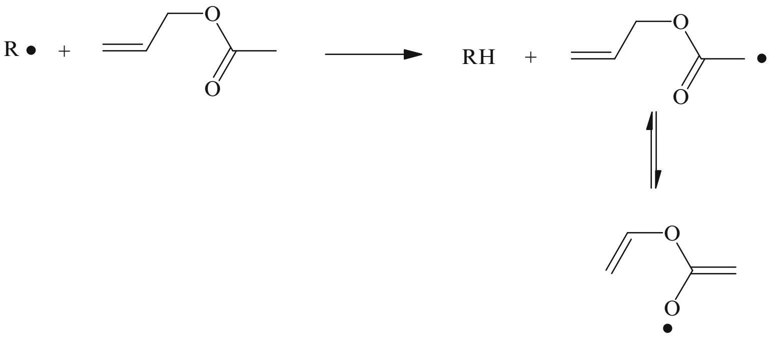
3.8 Allylic Polymerization

Compounds possessing allylic structures polymerize by free-radical mechanism only to low molecularweight oligomers. In some cases the products consist mostly of dimers and trimers. The DP for poly(allyl acetate), for instance, is only about 14. This is due to the fact that allylic monomer radicals are resonance-stabilized to such an extent that no extensive chain propagations occur. Instead, there is a large amount of chain transferring. Such chain transferring essentially terminates the reactions [151]. The resonance stabilization can be illustrated on an allyl alcohol radical:



The hydrogen transfer takes place from the allylic hydrogen, as shown on allyl acetate:

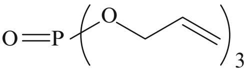
Hydrogen transfer can also take place to the acetate moiety:



The above described chain transferring is called ***degradative chain transferring***. Other monomers, such as methyl methacrylate and methacrylonitrile, also contain allylic carbon–hydrogen bonds. They fail to undergo extensive degradative chain transferring, however, and do form high-molecular-weight polymers. This is believed to be due to lower reactivity of the propagating radicals that form from these monomers [5].

Yamasaki et al. [152], reported that they successfully performed the radical polymerization of allylbiguanide hydrochloride in a concentrated, acid solution using either hydrochloric acid or phosphoric acid in the presence of a radical initiator at 50°C. The polymer was precipitated from the reaction solution through the addition of an excess amount of acetone. The molecular weight average of the product was 10,340–113,200, with a low polydispersity 1.04–1.68.

In spite of degradative chain transferring, polyallyl compounds can be readily polymerized by a free-radical mechanism into three-dimensional lattices. High DP is not necessary to achieve growth in three dimensions. An example of such polyallyl compounds is triallyl phosphate:



Many other polyallyl derivatives are offered commercially for use in cross-linked films and are described in the trade literature.

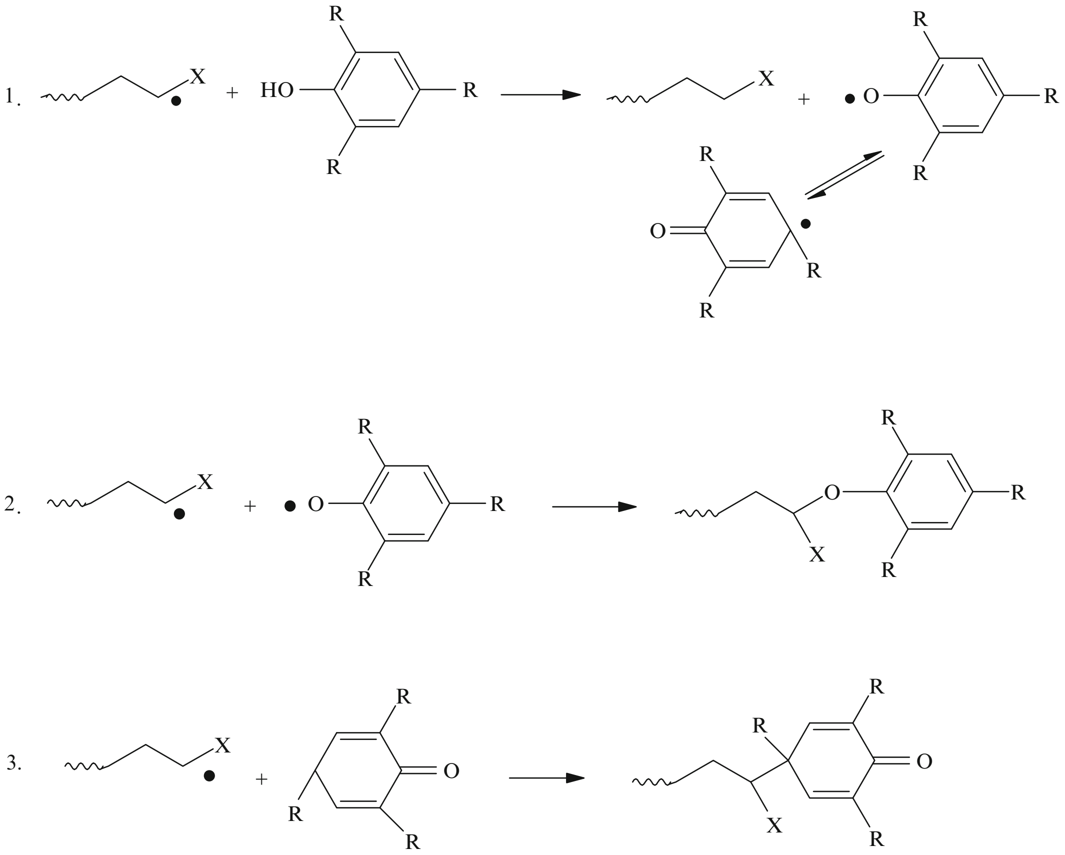
3.9 Inhibition and Retardation

Free-radical polymerizations are subject to inhibition and retardation from side reactions with various molecules [54]. Such polymerization suppressors are classified according to the effect that they exert upon the reaction. ***Inhibitors*** are compounds that react very rapidly with every initiating free radical as it forms. This prevents any polymerization reaction from taking place until the inhibitor is completely consumed in the process. The reactions of inhibitors with initiating radicals result in formations of new free radicals. The newly formed free radicals, however, are too stable to initiate chain growths. As a result, well-defined induction periods exist. After the inhibitors are used up, polymerizations proceed at normal rates.

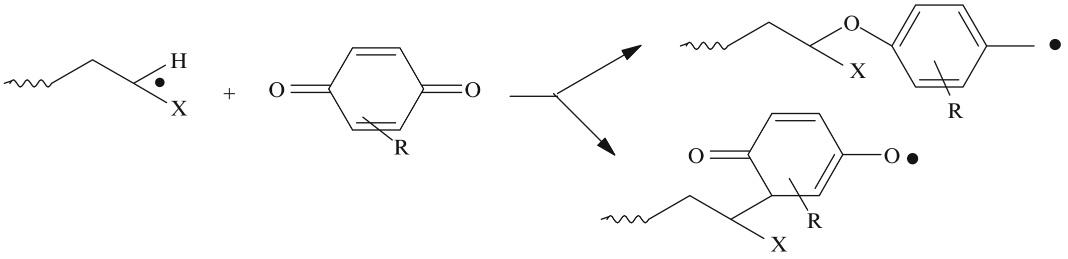
Retarders are compounds that also react with initiating radicals. They do not react, however, as energetically as do the inhibitors, so some initiating radicals escape and start chain growth. This affects the general rate of the reaction and slows it down. There is no induction period and retarders are active throughout the course of the polymerization.

The efficiency of an inhibitor depends upon three factors: (1) the chain transfer constant of an inhibitor with respect to a particular monomer, (2) the reactivity of the inhibitor radical that forms, (3) the reactivity of the particular monomer.

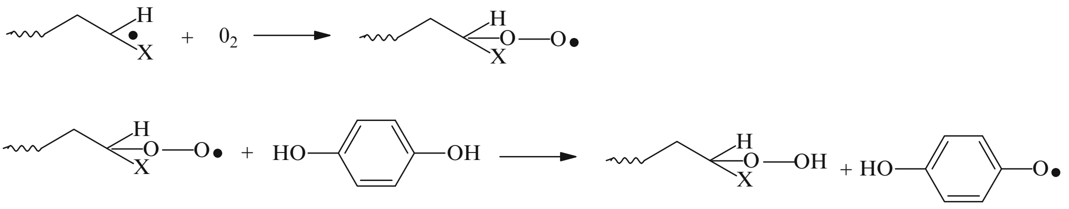
Phenols and arylamines are the most common chain transfer inhibitors. The reaction of phenols, though not fully elucidated, is believed to be as follows [153]



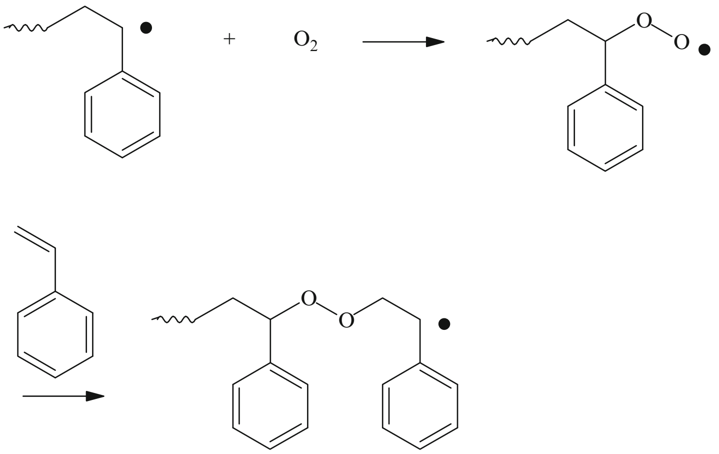
Quinones are effective inhibitors for many polymerization reactions. The reaction occurs either at an oxygen or at a ring carbon [153–156]:



The reaction, however, is not always strict inhibition. Thus, for instance, hydroquinone acts as an efficient inhibitor for the methyl methacrylate radical but only as a retarder for the styrene radical [155]. Hydroquinone is often employed as an inhibitor; it requires, however, oxygen for activity [156, 157]:



Oxygen, however, can also act as a comonomer in a styrene polymerization:



It causes marked retardation, however, in the polymerizations of methyl methacrylate [158]. The same is true of many other free-radical polymerizations.

The ability of phenols to inhibit free-radical polymerizations appears to increase with the number of hydroxyl groups on the molecules [157]. The locations of these hydroxyl groups on the benzene rings in relationships to each other is important. For instance, catechol is a more efficient inhibitor than is resorcinol [158].

Aromatic nitro compounds can act as strong retarders. Their effect is proportional to the quantity of the nitro groups per molecule [160, 161].

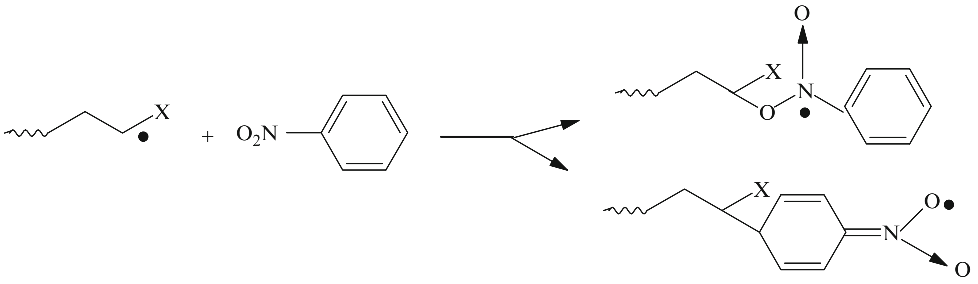


Figure 3.1 illustrates the effect of inhibitors and retarders on free-radical polymerization [162]. The equation that relates rate data to inhibited polymerizations is

$$2R_{\mathrm{P}}{}^2k_{\mathrm{t}}/k_{\mathrm{P}}{}^2[\mathrm{M}]^2 + R_{\mathrm{P}}[\mathrm{Z}]k_{\mathrm{z}}/k_{\mathrm{P}}[\mathrm{M}] - R_{\mathrm{i}} = 0$$

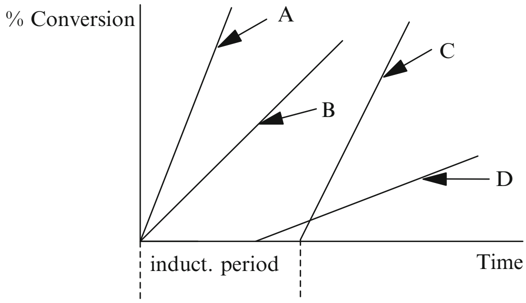


Fig. 3.1 Illustration of the effects of inhibitors and retarders. (A) Normal polymerization rate, (B) effect of a retarder, (C) effect of an ideal inhibitor, and (D) effect of a non ideal inhibitor. The time between A and C is the induction period caused by an ideal inhibitor

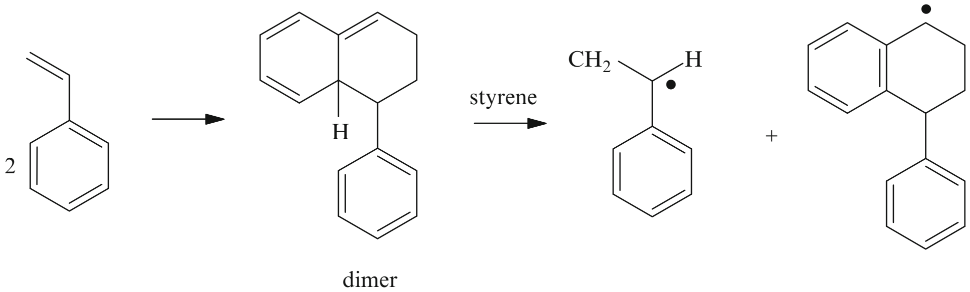
where Z is the inhibitor or the retarder in chain-growth termination:

$$\sim M_n\bullet + Z \xrightarrow{k_Z} \sim M_n + Z\bullet(\text{and/or} \sim M_n Z\bullet)$$

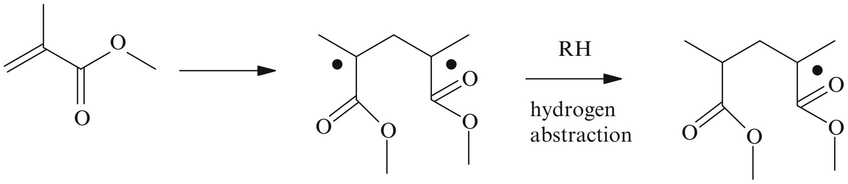
To simplify the kinetics it is assumed that Z• and ~M_nZ• do not initiate new chain growth and do not regenerate Z upon termination.

3.10 Thermal Polymerization

A few monomers, such as styrene and methyl methacrylate, will, after careful purification and presumably free from all impurities, polymerize at elevated temperatures. It is supposed that some ring-substituted styrenes act similarly. The rates of such thermal self-initiated polymerizations are slower than those carried out with the aid of initiators. Styrene, for instance, polymerizes only at a rate of 0.1% per hour at 60°C and only 14% at 127°C. The rate of thermal polymerization of methyl methacrylate is only about 1% of the rate for styrene [163, 164]. Several mechanisms of initiation were proposed earlier. The subject was reviewed critically [165]. More recently, the initiation mechanism for styrene polymerization has been shown by ultraviolet spectroscopy to consist of an initial formation of a Diels–Alder dimer. The dimer is believed to subsequently transfer a hydrogen to a styrene molecule and as in doing so form a free radical [166]:

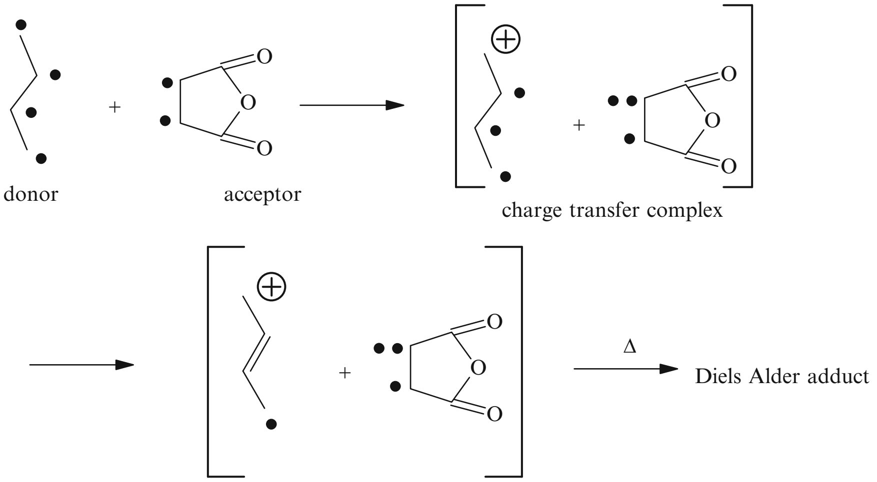


Thermal polymerization of methyl methacrylate, on the other hand, appears to proceed through an initial dimerization into a diradical [167]. This is followed by a hydrogen abstraction from any available source in the reaction mixture.

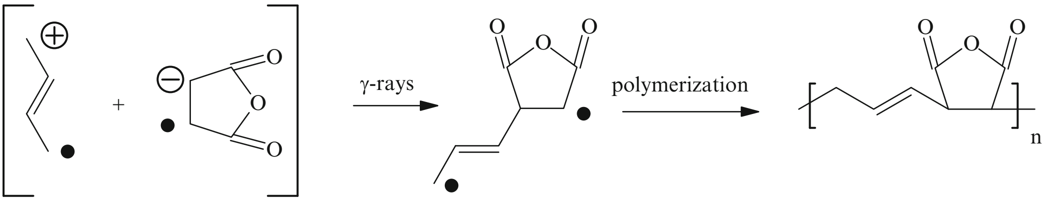


3.11 Donor–Acceptor Complexes in Copolymerization

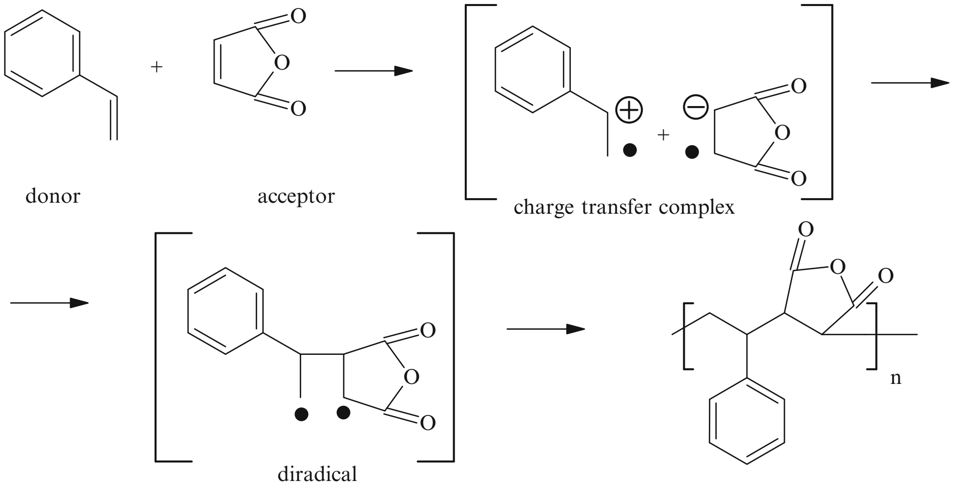
Polar interactions of electron donor monomers with electron acceptor monomers lead to strong tendencies toward formations of alternating copolymers. Also, some alternating copolymerizations might even result from compounds that by themselves are not capable of conventional polymerization. An example is copolymerization of dioxene and maleic anhydride. Two reaction mechanisms were proposed. One suggests that the interactions of donor monomers with acceptor radicals or acceptor monomers with donor radicals lead to decreased energies of activation for cross-propagations [168]. The transition state is stabilized by a partial electron transfer between the donor and acceptor species [169]. The second mechanism suggests that the interactions result in formations of charge-transfer complexes [170]. An electron is completely transferred from the donor monomer to the acceptor monomer. After the transfer, the complex converts to a diradical that subsequently polymerizes by intermolecular coupling. For instance, while many believe that the Diels–Alder reaction takes place by a concerted mechanism, the intermediate was postulated by some to be a charge-transfer complex. An electron is transferred from the donor to the acceptor and a charge-transfer complex forms [171]. This can be illustrated on a Diels–Alder reaction between butadiene and maleic anhydride:



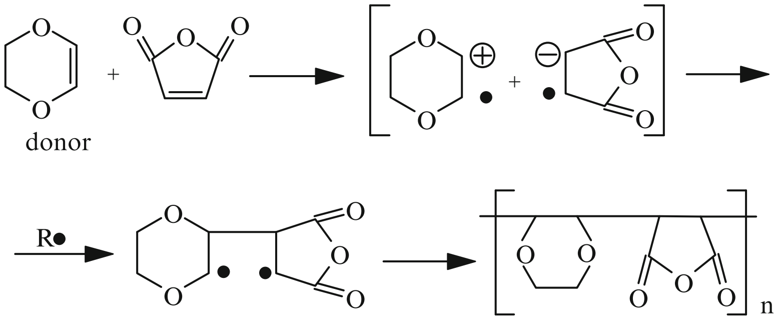
If the reaction mixture is irradiated with high energy radiation, such as gamma rays, instead of being heated, an alternating copolymer forms. The complex converts to a diradical [1, 171] that homopolymerizes:



Alternating copolymerization of styrene with maleic anhydride is also explained by donor acceptor interactions [171]. A charge-transfer complex is seen as the new monomer, a diradical, which polymerizes through coupling [171–174].



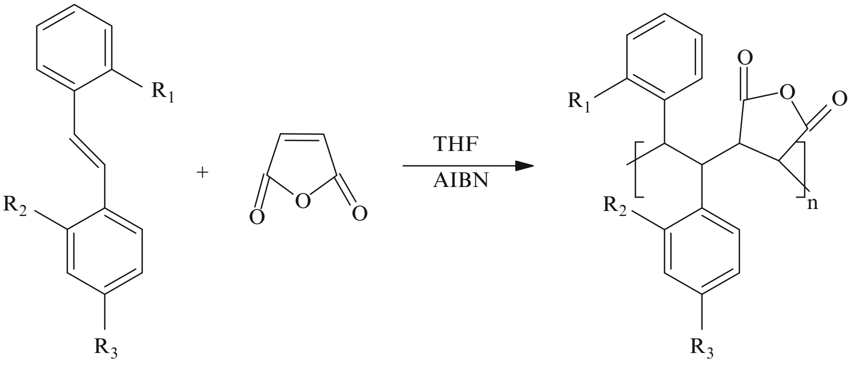
Charge-transfer complexes are also claimed to be the intermediates in free-radical alternating copolymerization of dioxene or vinyl ethers with maleic anhydride [176–179]:



where, R• is a polymerization-initiating radical. Here, a third monomer can be included to interpolymerize with the complex that acts as a unit. The product is a terpolymer [176, 177]. A diradical intermediate was also postulated in sulfur dioxide copolymerizations and terpolymerizations with bicycloheptene and other third monomers [173]. These third monomers enter the copolymer chain as block segments, while the donor–acceptor pairs enter the chains in a one-to-one molar ratio. This one-to-one molar ratio of the pairs is maintained, regardless of the overall nature of the monomer mixtures.

The propagation and termination steps in the above reactions are claimed [175, 181–183] to be related. As stated, an interaction and coupling between two diradicals is a propagation step. When such interactions result in disproportionations, however, they are termination steps. This means the charge-transfer mechanisms are different from conventional free-radical polymerizations. They involve interactions not only between growing polymer-radicals and monomers but also between polymer-radicals and complexes. In addition, the polymer radicals react with each other [175, 181–184].

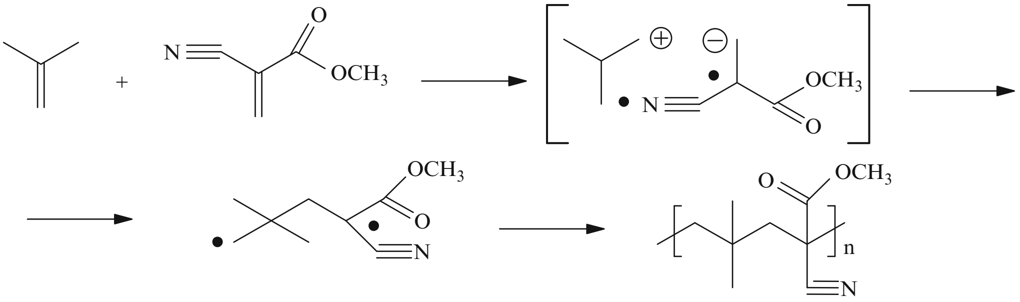
Li and Turner [185], reported copolymerization of maleic anhydride with *trans*-stilbene:



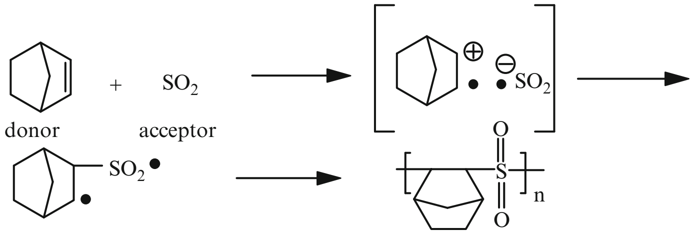
where, R_1, R_2, and R_3 are either methyl groups or hydrogens

The stability of charge-transfer complexes depends upon internal resonance stabilization. This degree of stabilization determines how easily the diradicals open up [183]. Consequently, the stability also determines how the copolymerization occurs. It can occur spontaneously, or under the influence of light or heat, or because of an attack by an initiating free radical.

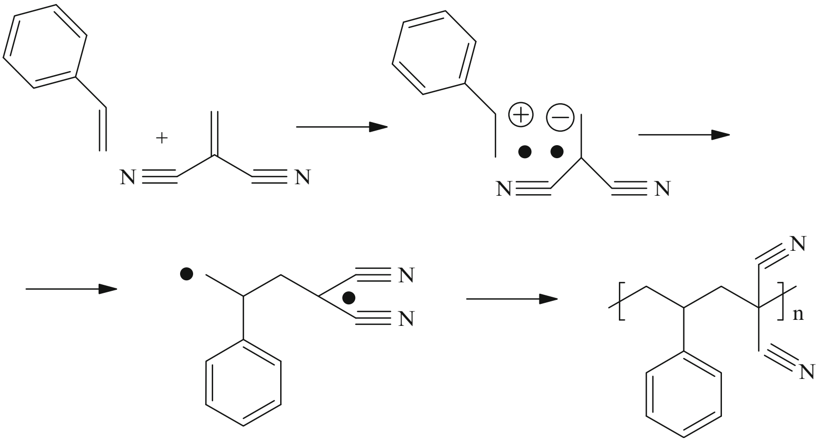
There are many examples of spontaneous reactions. When, for instance, isobutylene is added to methyl α-cyanoacrylate, a spontaneous copolymerization in a 1:1 ratio takes place at room temperature. This was explained by the following scheme [175, 181–183]:



The same happens when sulfur dioxide is added to bicycloheptene at −40°C [184].



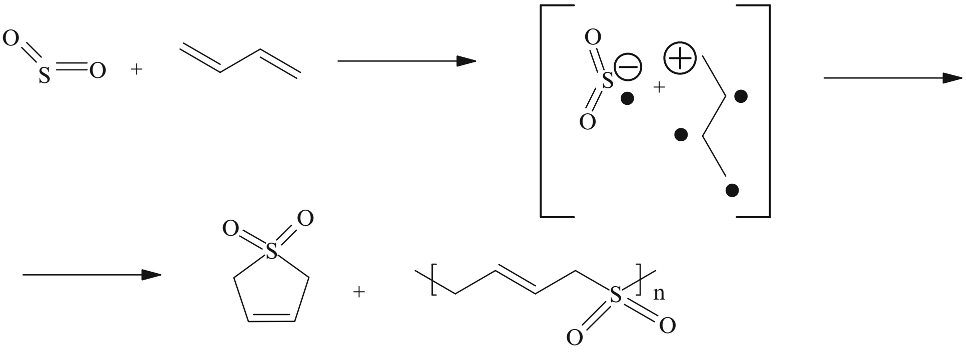
Another example is a room temperature 1:1 copolymerization of vinylidene cyanide with styrene [185]:



Still another example is a reaction of 1,3 dioxalene with maleic anhydride [183].

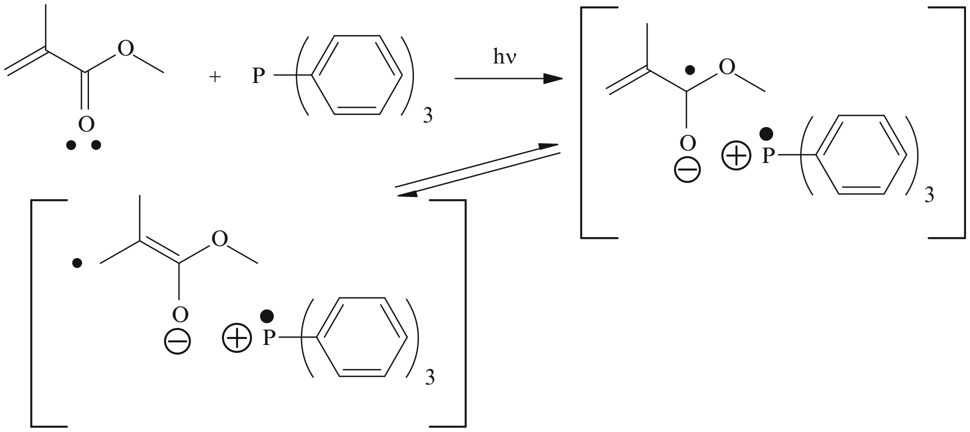
Examples of stable complexes are reactions of sulfur dioxide with styrene [175], or vinyl ethers with maleic anhydride [184], also α-olefins with maleic anhydride [179–181]. Also, a reaction of *trans*-stilbene with maleic anhydride [182], In these reactions charge-transfer complexes form. They are stable and their existence can be detected by spectroscopic means. Additional energy, such as heat or a free-radical attack, converts them to diradicals and polymerizes them into alternating copolymers [175, 185–191].

Examples of intermediates between the two extremes in stability are reaction products of sulfur dioxide with conjugated dienes [192]. In this case, the reaction results in formation of mixtures of alternating copolymers and cyclic adducts:



The yield of the polymer increases at the expense of the cyclic structure when heat or radiation is applied. A free-radical attack has the same effect [192].

If donor–acceptor interactions and subsequent polymerizations occur upon irradiation with ultraviolet light, the reactions can be very selective. An example is a triphenylphosphine interaction with acrylic monomers [193]:



This reaction does not occur, however, between triphenylphosphine and styrene or vinyl acetate [193].

The nature and the amount of solvent can influence the yield and the composition of the copolymers in these copolymerizations. Thus, copolymerization of phenanthrene with maleic anhydride in benzene yields a 1:2 adduct. In dioxane, however, a 1:1 adduct is obtained. In dimethyl formamide, no copolymer forms at all [193]. Another example is a terpolymerization of acrylonitrile with 2-chloroethyl vinyl ether and maleic anhydride or with *p*-dioxene-maleic anhydride. The amount of acrylonitrile in the terpolymer increases with an increase in the π-electron density of the solvent in the following order [194]:

$$\text{xylene} \gg \text{toluene} \gg \text{benzene} > \text{chlorobenzene} \gg \text{chloroform}.$$

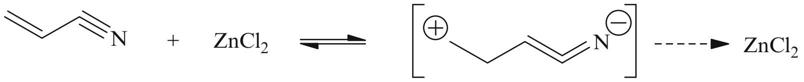
The ratio of maleic anhydride to the vinyl ether in the product remains, however, equimolar.

Whether the concept of charge-transfer complexes in copolymerizations is fully accepted is not certain. Much of the accumulated evidence, to date, such as UV and NMR spectroscopy, does support it in many systems [195]. Further support comes from the strong tendencies to form alternating copolymers over a wide range of feed compositions, and also from high reaction rates at equimolar feed compositions [171]. On the other hand, as shown above, it was claimed in the past that copolymerization of styrene with maleic anhydride involves charge-transfer complexes [171, 181–183]. This, however, is now contradicted in a publication of a study of radical copolymerization of maleic acid with styrene. The reaction was carried out in a dioxane solution at 70°C. The authors reported that UV spectroscopy fails to show presence of a charge transfer and formation of a complex between the two monomers in the copolymerization system [196].

3.12 Polymerization of Complexes with Lewis Acids

Some polar vinyl monomers such as methyl methacrylate or acrylonitrile interact and complex with Lewis acids. They subsequently polymerize at a faster rate and to a higher molecular weight than can be expected otherwise. The effective Lewis acids are $ZnCl_2$, $AlCl_3$, $Al(C_2H_5)_2Cl$, $AlCl_2(C_2H_5)$, $SnCl_4$, and some others [197–199]. Complexes can form on an equimolar basis and undergo homopolymerizations after application of heat. A free-radical attack or irradiation with ultraviolet light or with gamma rays is also effective [198].

It was proposed [198–201] that the greater reactivity is due to delocalization of the electrons of the complexed molecules:



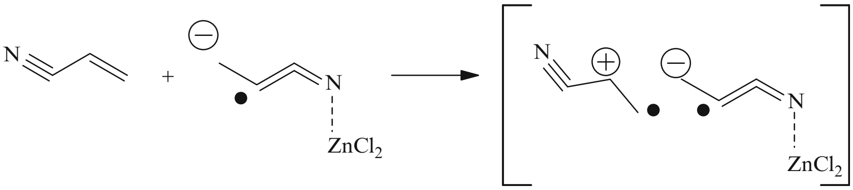
Molecular orbital calculations support this [200, 201]. Polymerizations can also be carried out with less than stoichiometric ratios of the Lewis acids to the monomers. As an illustration, coupling of an acrylic or a methacrylic monomer with a Lewis acid can be shown as follows [203, 204]

$$\mathrm{aM} + \mathrm{MeX}_n \rightleftharpoons (\mathrm{M})_\mathrm{a} ------ \mathrm{MeX_n}$$

where, $\mathrm{MeX_n}$ represents a Lewis acid.

Vinyl pyridine and vinyl imidazole also form complexes with zinc chloride. Here, conjugation with the metal salt results in a super delocalizability and leads to spontaneous thermal polymerization [203, 204].

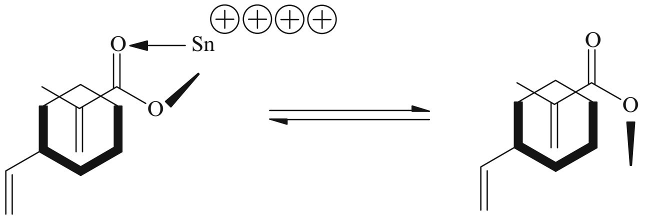
The increased reactivity toward polymerization by some monomers, even in the presence of less than equimolar amounts of Lewis acids, was suggested to be due to one of two possibilities. It may be due to greater reactivity of the portion of the monomer that complexes toward the growing chain end. It may also be due to formation of new complexes between uncomplexed monomer and complexed ones [171]:



The picture is more complicated when the Lewis acids are used in combinations with donor–acceptor monomers. The donor–acceptor complexes are believed to form first and then react with Lewis acids according to the following scheme [203, 204]:

$$a\mathrm{M}_1 + b\mathrm{M}_2 + \mathrm{MeX_n} \rightleftharpoons \left[a\left(\mathrm{M}_1\right) ---- \mathrm{MeX}_n\right] + b\mathrm{M}_2 \rightleftharpoons \left[\mathrm{MeX_n} ---- b\left(\mathrm{M}_2\right)\right] + a\mathrm{M}_1$$

A structure of methyl methacrylate and styrene complexed with $\mathrm{SnCl_4}$ was shown to be as follows [204]:



In formations of ternary complexes, the acceptor vinyl compound must have a double bond conjugated to a cyano or to a carbonyl group. Such acceptors are acrylonitrile, methacrylonitrile, acrylic and methacrylic esters and acids, methyl vinyl ketone, acrylamide, etc. Donor monomers are styrene, α-methyl styrene, butadiene, 2–3-dimethyl butadiene, isoprene, chloroprene, etc.

One proposed mechanism [171, 204] is that such charge-transfer polymerizations are in effect homopolymerizations of the charge-transfer complexes $[D \oplus A\_ \ldots MeX_n]$. In other words, the metal halide is complexed with the electron acceptor monomer and acts as an acceptor component.

The above opinion, however, is not universal. Others hold that the increased susceptibility to ultraviolet radiation or to initiating radicals [205] is due to increased reactivity of the propagating radicals of complexed monomers toward incoming uncomplexed ones.

Arguments against the ternary complex mechanism are as follows: (1) the physical evidence that proves the existence of the ternary molecular complexes is weak; (2) the ternary molecular complexes can have no bearing on the copolymerizations because the equilibrium concentration of the complexed monomers is low, compared to the uncomplexed ones [206].

A third opinion is that a complex of an acceptor monomer with a Lewis acid copolymerizes alternately with the donor monomer and with an uncomplexed acceptor monomer [207, 208]. This presumably takes place according to the conventional chain-growth polymerization scheme of radical copolymerization. The alternate placement of monomers is due to highly enhanced values of cross-propagation constants. It results from complexing acceptor monomers with Lewis acids. Such a mechanism fails to explain satisfactorily the completely alternating incorporation of monomers and the inefficiency of chain-transfer reagents. It also fails to explain the spontaneous initiation of alternating copolymerization.

Kabanov suggested [209] that during the primary free-radical formation of the Lewis acid–monomer complex, both the uncomplexed and the complexed monomers may participate in chain propagation. This would result in appearance of complexed propagating radicals besides the usual ones. In the complexed ones, the last unit carrying the valence is a ligand of coordination complex:

$$\sim M\bullet \ldots\ldots MeX_n$$

It excludes, however, all electron transfer reactions that may take place due to ultraviolet light irradiation.

3.13 Steric Control in Free-Radical Polymerization

In free-radical polymerization reactions, the propagating radical chain has a great amount of freedom. Atactic polymers, therefore, are usually formed. Some control that the reaction conditions exercise over the propagating species increases at lower temperatures due to lower mobilities. This leads to increased syndiotactic placement, as was discussed in the section on propagation. Special techniques, however, such as the use of canal complexes can be employed to form stereoregular polymers by free-radical mechanism. Urea and thiourea were used originally for such purposes [210, 211]. Monomers such as butadiene or others form complexes within the voids, or canals of the crystal lattices of these compounds. Brief exposure to high energy radiation initiates chain growth. In the canals, the monomer molecules are held in fixed positions, so chain growth is restricted in one direction only. Steric control is exercised because in these fixed positions the monomer molecules tend to align uniformly. It was suggested that in the canal complexes the monomers are not just lined up end to end, but packed in an overlapping arrangement. For molecules such as isobutylene or vinylidene chloride, it may be possible for the monomers to lie directly on top of each other, resembling a stack of coins. Such stacking greatly facilitates reactions between guest molecules [210, 211].

Polymerizations in thiourea canal complexes yields high melting crystalline *trans*-1,4 polybutadiene, 2,3-dimethylbutadiene, 2,3-dichlorobutadiene, and 1,3-cyclohexadiene. Cyclohexadiene monoxide, vinyl chloride, and acrylonitrile also form stereoregular polymers. On the other hand, polymerizations of isobutylene and of vinylidene chloride fail to yield stereospecific polymers.

Sodium montmorillonite can also be used to polymerize polar monomers between the lamellae. Here too, the organization of monomer molecules within the monolayers influences the structure of the resultant polymers [212, 213]. Poly(methyl methacrylate) formed in sodium montmorillonite is composed of short, predominantly isotactic stereosequences [211]. The percentage of isotactic component increases with an increase in the ion exchanging population on the surface of the mineral and is independent of the temperature between 20 and 160°C. In this way, it is possible to vary the population of isotactic triads at will up to 50% composition [205].

Perhydrotriphenylene also forms channel-like inclusions with conjugated dienes. Polymerization of these dienes yields some steric control [216, 218].

Uemura and coworkers [217] carried out radical polymerizations of vinyl monomers (styrene, methyl methacrylate, and vinyl acetate) within various nanochannels of porous coordination polymers. They studied the relationships between the channel size and polymerization behaviors, such as monomer reactivity, molecular weight, and stereostructures. They reported that in these polymerization systems, the polymer-growing radicals were remarkably stabilized by efficient suppression of the termination reactions within the channels, resulting in relatively narrow molecular weight distributions. A significant nanochannel effect on the polymer stereoregularity was also seen, leading to a clear increase of isotactic placement in the resulting polymers.

There were attempts at controlling steric placement by a technique called ***template polymerization***. An example is methyl methacrylate polymerization in the presence of isotactic poly(methyl methacrylate) [208, 209]. Thus template polymerization is a process of polymerizing a monomer in the presence of a polymer, usually from a different monomer. The presence of template polymers, however, only results in accelerating the rates of polymerizations [219].

3.14 Controlled/"Living" Free-Radical Polymerization

Living polymerizations are chain-growth reactions where the propagating centers on the growing chains do not terminate and do not undergo chain transfer. Such polymerizations are noted for preparations of polymers with controlled molecular weights, desired end groups and low polydispersities. In addition, the preparations of polymers with predetermined molecular weights and narrow molecular weight distributions require fast initiations and fast exchanges between sites of variable activities and variable lifetimes. Such chain-growth reactions, ionic in nature, are discussed in Chap. 4. In typical homogeneous free radical polymerizations, however, bimolecular terminations between two growing radicals cannot be avoided and, therefore, typical living free radical polymerization cannot be fully realized. Also, in conventional free radical polymerizations, the initiations are slow, while high-molecular-weight polymers form shortly after the start of the reactions. As the reactions progress, polydispersities increase, while the molecular weights actually decrease. It is possible, however, to adjust conditions of some radical polymerizations in such a way that polymers with controlled molecular weights and relatively low polydispersities form [220, 221]. These are not true living polymerization as such because termination reactions do occur. They possess, however, some characteristics that are similar to living polymerizations and are referred to by many as ***controlled/"living"*** polymerizations. Such reactions yield polymers with controlled molecular weights, exhibit increase in molecular weight with conversion, yield narrow molecular weight distributions, and can be used to form copolymers. Some examples of such polymerizations include nitroxyl radical-mediated polymerizations of styrene [222–225], atom transfer polymerizations controlled by ruthenium-(II)/aluminum [226, 227] or by copper/bipyridine complexes [228], Co (II)-mediated polymerizations of methacrylates and acrylates [229], and polymerization of styrene using a degenerative transfer method [230], as well as others. Some features are unusual for radical processes and the radical nature of some of these reactions might be questioned, as for instance, polymerizations catalyzed by transition metals. Evidence has been presented, however, that strongly indicates radical nature in at least in atom transfer polymerizations [231]. The evidence, however, is not unambiguous.

Some initial attempts at producing “living” polymerizations made use of ***iniferters.*** This term appears to come from the word ***inifer***, a bifunctional compound that brings about both initiation and chain transfer. “Living” cationic polymerizations make use of inifers to form block copolymers. This is discussed in Chap. 9. The term iniferter was proposed by Otsu and Yoshida in 1982 [232]. Iniferters used in controlled/living free-radical polymerizations are sulfur-centered free radicals that can be generated from sulfur-containing molecules such as dithiocarbamates. The radicals react reversibly with growing polymeric chain ends, thereby controlling the concentration of the radical species. Many of these sulfur centered radicals, however, can also initiate new polymer chains. This can lead to uncontrolled growth. To overcome these difficulties, other approaches were also developed [233].

Deactivation of growing radicals with stable radicals can be carried out with the aid of various nitroxyl radicals, protected phenoxy radicals, dithiocarbamate, trityl, and benzhydryl derivatives. Growing radicals can also be deactivated with nonradicals in the presence of organometallic compounds that form stabilized hyper-coordinated radicals. The polymerizations with the aid of reversible degradative chain transferring are unique in that they requires very rapid and “clean” chain transfers without side reactions. The enhanced control of polymerization process relies on reduction in the ratio of the rate of termination to that of propagation, due to low instantaneous concentration of growing radicals. This means that initiation and propagation reactions must proceed at similar rates due to application of the initiators resembling polymer end groups in their dormant state. Also, in these polymerization reactions, there must be a low proportion of chains marked by uncontrolled termination and/or transfer due to relatively low molecular weights.

Homogenous controlled/“living” free radical polymerizations are based, therefore, on the reversible deactivations of growing radicals. Early, Matyjaszewski divided such polymerizations into three classes [240, 241]. These were:

1. Deactivations of growing radicals with stable radicals by reversible formations of dormant covalent species, followed by homolytic cleavages:

$$P\bullet + R\bullet \underset{\text{act.}}{\overset{\text{deact.}}{\rightleftarrows}} P\text{—}R$$

2. Reversible deactivations of growing radicals with “nonradical” species by formation of dormant persistent radicals:

$$P\bullet + X^* \underset{\text{act.}}{\overset{\text{deact.}}{\rightleftarrows}} (P\text{—}X)$$

3. Reversible degenerative transfers based on thermodynamically neutral exchange reactions between growing radicals and transfer agents:

$$P_n\bullet + P_1\text{—}R \overset{k_{tr}}{\rightleftarrows} P_1\bullet + P_n\text{—}R$$

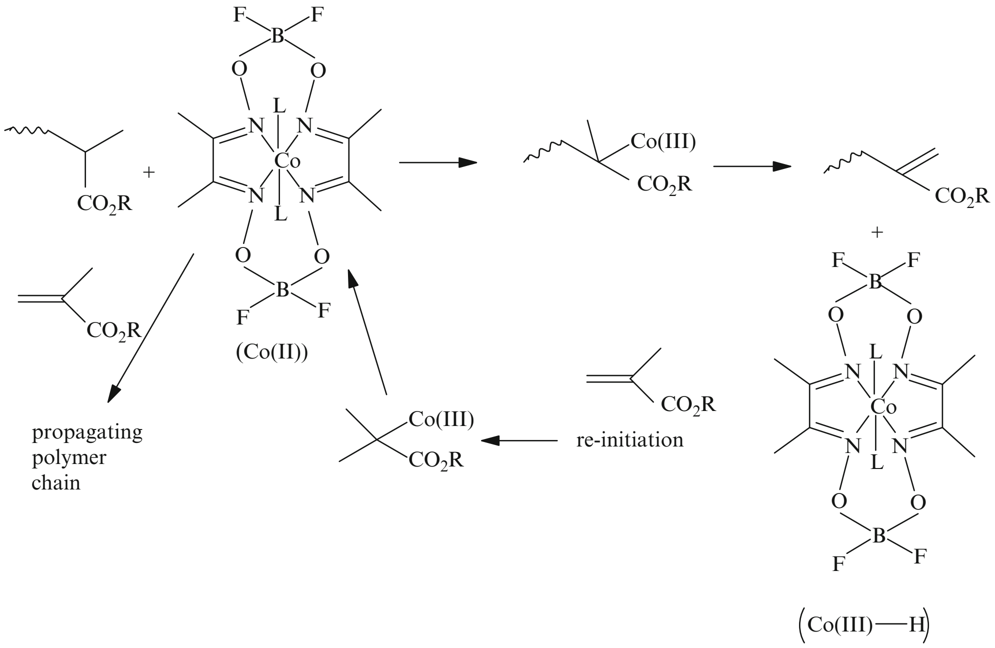
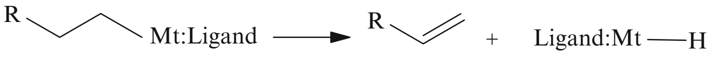


Fig. 3.2 Cobalt mediated controlled/"living" polymerization

3.14.1 Cobalt Mediated Polymerizations

Catalytic chain transfer polymerizations can utilize metals such as low spin cobalt(II) compounds as chain transferring agents. The mechanism is believed to involve repeated disturbing of each propagating step by abstraction of hydrogen atoms from the propagating polymers. This yields chains with unsaturated terminal units and hydrogen transfer agent adducts, Co(III)–H. Subsequent transfers of hydrogens to the growing chains result in reinitiating the processes [241]. The β-hydrogen abstractions from the growing radicals and the formations of metal hydrides [229] can be illustrated as follows:

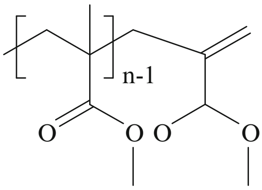


where Mt = Co

This catalytic cycle for a cobalt mediated polymerization, using bis-dimethyl-glyoximate cobalt boron fluoride catalyst was illustrated Haddleton et al. [233, 234]. A similar illustration of the process is shown in Fig. 3.2. The affinities of metals for hydrogen abstractions, and/or their abilities to lose electrons depend on their oxidation states and the nature of their ligands. Such reactions can, therefore, be suppressed. This can be done by choosing high oxidation state metals, ligands that protect the metal from the abstraction of the P–H atoms, and by controlling the position of the oxidation–reduction equilibrium.

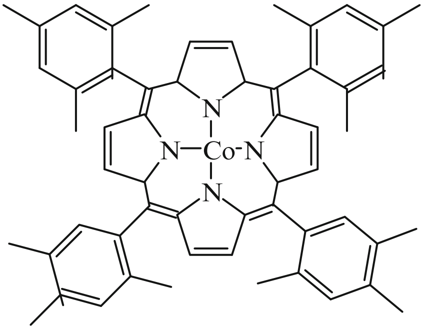
$$
\begin{gathered}
\mathrm{R}\text{—}\ \mathrm{Co}+++\mathrm{Ln} \rightleftharpoons \mathrm{R}\bullet+\bullet\mathrm{Co}++\mathrm{Ln} \\
\mathrm{RM_x}+\mathrm{Co}++\mathrm{Ln} \rightleftharpoons \mathrm{RM_x}\text{—}\mathrm{Co}+++\mathrm{Ln}
\end{gathered}
$$

The metal cobalt(II) is usually chelated. This can be cobalt porphyrin, cobalt phthalocyanin, or cobalt oxime, as well as others. The polymer molecules that form have, as stated earlier, terminal double bonds and can be illustrated as follows,



The cobalt hydride in turn reacts with a new monomer molecules to regenerate the Co(II) [235].

One publication describes a chain transferring agents that can be used in controlled polymerization of methacrylate monomers where reductive elimination of cobalt hydride from the neighboring methyl group deflects further chain growth [236]. The agent was illustrated as follows:

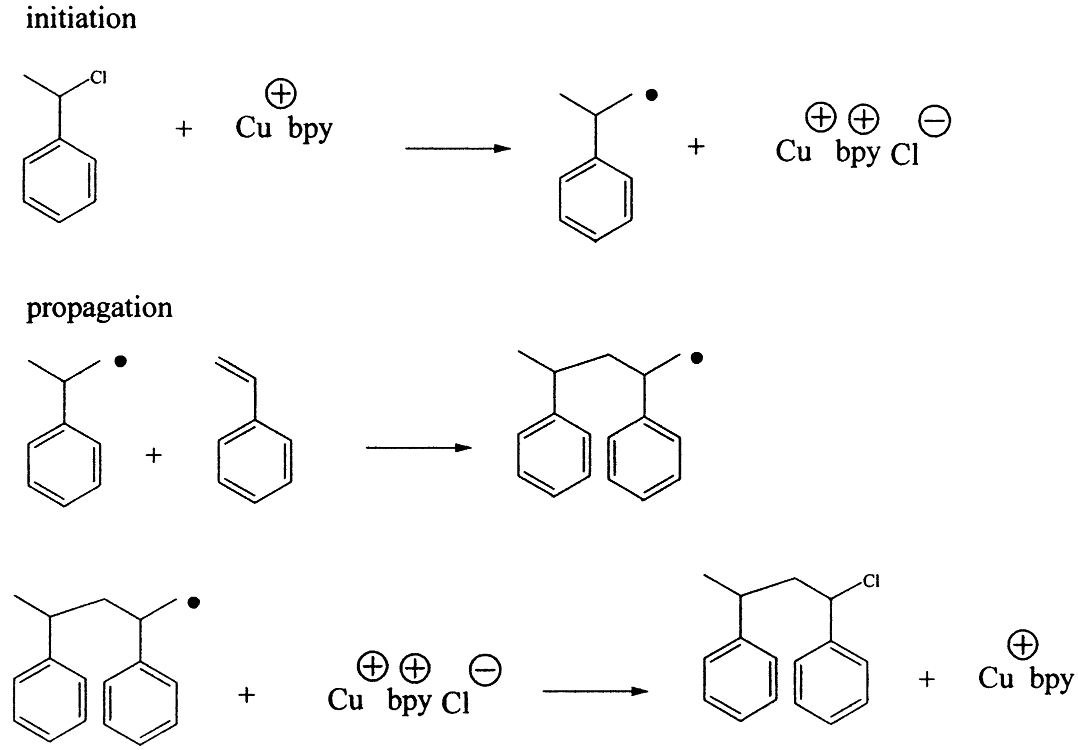


A described example is a reaction conducted at 60°C in deoxygenated benzene, using neopentylcobalt with tetramesityl-porphyrin ligand and methyl acrylate monomer [236]. A slow polymerization yields 66% conversion in 38 h. The product is a narrow molecular weight distribution polymer of $M_n = 144{,}000$. The polymerization is even slower with less hindered phenyl substituents on the porphyrin ligand. Both homopolymers and block copolymers can be formed.

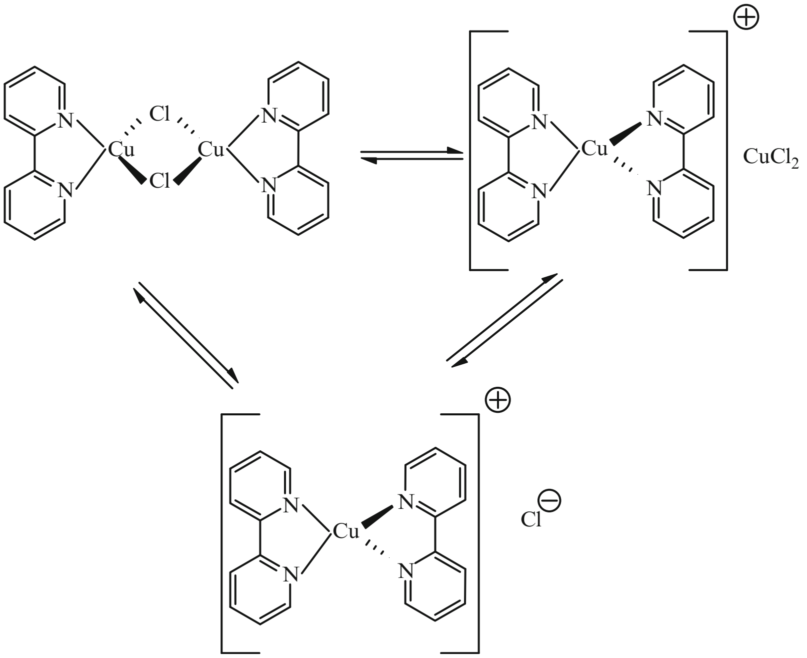
Catalytic chain transfer by a cobalt(ll) porphyrin in radical polymerization of MAA in water was studied by Wayland and coworkers [237]. Cobalt tetrasulfonatophenylporphyrin was found by them to be exceptionally effective in the catalytic chain transfer for the radical polymerization of MAA in water. A remarkable feature of this process is that the increase in the degree of polymerization, with conversion requires that more monomer be consumed in chain growth of the existing macromonomers than in initiation and propagation of new chains through chain transfer to monomer. Reinitiation of oligomer olefins and chain growth are significant inherent reactivity features of the cobalt^{++}-porphyrin catalyzed chain transfer process.

3.14.2 Atom Transfer Radical Polymerizations

Atom transfer radical polymerizations (ATRP) were reported simultaneously by two groups: (1) Matyjaszewski et al. [218] and (2) Sawamoto and coworkers [226]. Matyjaszewski et al. utilized a Cu/bipyridine complex as a ***halogen transfer agent*** that functions between dormant and active polymer chains. Formation of polymers with predetermined molecular weight of up to $M_n \approx 10$ [5] and polydispersity as narrow as 1.05 was reported [238, 239]. This type of polymerization appears to offer the possibility of preparing a broad range of polymeric materials [240–242]. The reactions proceed under conditions that could make the process commercially attractive. Thus, for instance, by using nonionic surfactants, such as poly(oxyethylene oleyl ethers) it is possible to prepare polymers from butyl methacrylate, methyl methacrylate, styrene, and butyl acrylate in aqueous emulsions. In addition, by using multidentate ligand such as tris[(2-dimethyl-amino)ethyl]amine the atom transfer polymerizations can be made to proceed rapidly at room temperature [242, 243]. The atom transfer polymerization reaction can be illustrated as follows:



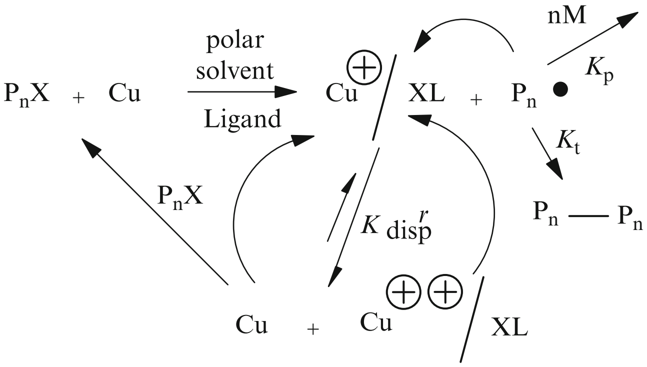
Polymerizations of styrene using 2,2′-dipyridyl as the ligand indicated that they proceed first order with respect to the concentration of initiator, and 0.4 and 0.6 orders with respect to the concentration of Cu(l) halide and ligand [218, 229]. The copper bipyridyl complexes mentioned above were pictured by Haddleton et al. [233, 234] as follows:



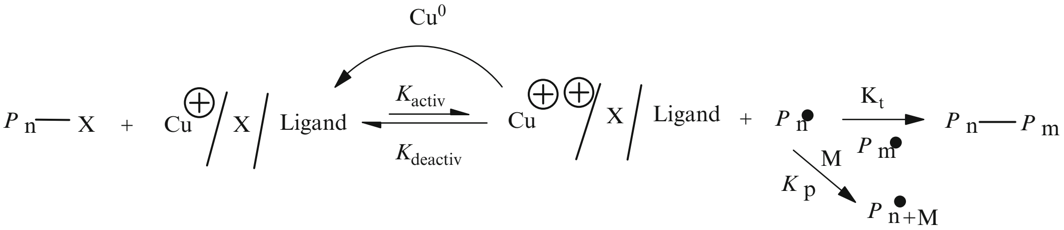
Recently, Matyjaszewski has summarized the mechanism of these polymerizations [245].

Matyjaszewski and coworkers [246–250] reported that small amounts of air present in the reaction mixture can be consumed by addition of sufficient amounts of an appropriate reducing agent, such as tin(II) 2-ethylhexanoate or ascorbic acid. In this process, the cuprous ions are initially oxidized by oxygen to the cupric ions, but then in turn reduced by the reducing agent. The cuprous ions activate the reaction. There is an induction period until all the oxygen is consumed. This is referred to as ***(ARGENT) ATRP***. Also, they have subsequently reported that polymerizations of 2-(dimethylamino)ethyl methacrylate does not require any addition of a reducing agent as the tertiary amine group presumably serves as an internal one [251].

In addition, Percec and coworkers [253] reported that polymerizations in polar solvents in conjunction with copper and appropriate ligands allow ultrafast syntheses of high-molecular-weight polymers at ambient temperature. The process is referred to as ***Single Electron Transfer-Living Radical Polymerization (SET-LRP).*** The mechanism proposed is based on disproportionation of cuprous ions to cupric ions and metallic copper. This is catalyzed by the polar solvents and the appropriate ligands. The proposed mechanism can be illustrated as follows:



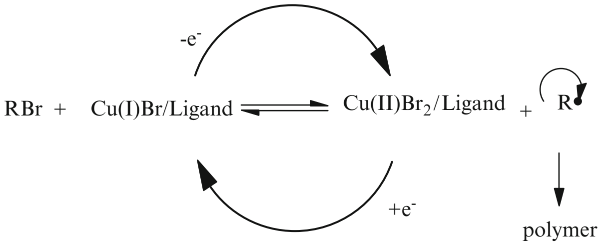
The work by Percec and coworkers included an investigation of various solvents and ligands for the catalyst activity and their ability to disproportionate the cuprous ion. They demonstrated that addition of 10 mol% of phenol as ligand leads to spontaneous disproportionation to metallic copper and cupric ions [253]. An alternative to the proposed Percec’s mechanism was proposed by Matyjaszewski [254]. According to this mechanism, metallic copper acts as a reducing agent for the cupric ions and yields active cuprous ions that catalyze the polymerization. This mechanism is similar to one proposed for the reactions that utilize ascorbic acid or tin based reagents to reduce cupric ions to cuprous ones [255, 256]. The mechanism can be illustrated as follows:



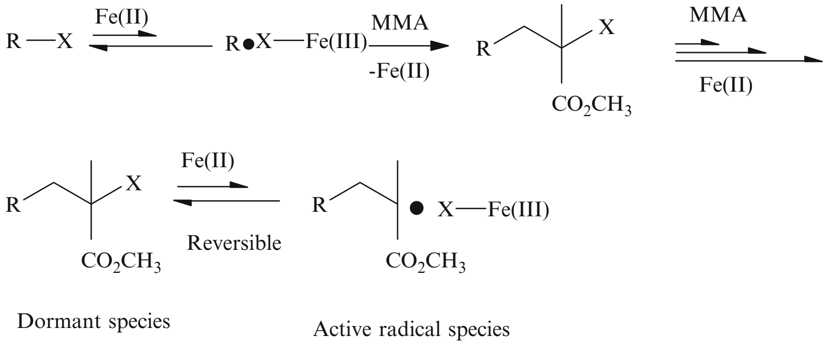
Haddleton and coworkers [256] investigated use of toluene as a solvent with phenol as an additive for use in living/controlled polymerizations. They demonstrated a direct relationship between the reaction time and the amount of phenol added. The optimum amount found by them is 20 equivalents of phenol with respect to the initiator. Their products were narrow molecular weight polymers with MWD ranging between 1.05 and 1.25.

Removal of copper from ATP products can sometimes be a problem [257]. Honigfort and coworkers reported that they found that when the ligands were supported on Janda Jel (see Chap. 10) resins, easy removal of the catalyst complex was possible from the reaction mixture. The Janda Jel ligands were used in ATRP of methyl methacrylate, styrene, and 2-(dimethylamino)ethyl methacrylate. The methyl methacrylate and 2-(dimethylamino)ethyl methacrylate polymerizations proceeded quickly to high conversion (>90%) and were well controlled. The styrene polymerization, however, was found by them to be sluggish and proceeded only to 63% conversion. After polymerizations were complete, the catalyst ligand complex was easily removed by filtration. Zhu and coworkers [257] claim to have a simple and effective method for purification of an ATP product using catalyst precipitation and microfiltration. The method relies on the precipitation of the Cu + Br ligand catalyst complex by the additions of Cu++Br$_2$. The precipitate thus formed is effectively retained by a 0.14-µm PTFE filter, resulting in up to 99.9% of the catalyst being removed from the polymer. The resulting clear polymer filtrate contains little residual copper, down to 10 ppm.

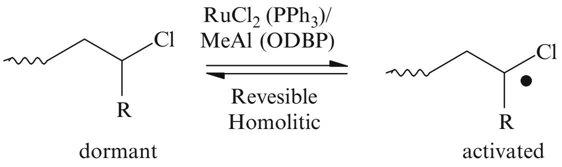
Matyjaszewski and coworkers developed a process [255] for an electrochemically mediated ATRP. They use applied voltage to drive the production of Cu + ions that catalyze the polymer formation. Because the rate of the reaction is controlled by a redox equilibrium between cuprous and cupric ions, electrochemistry permits the regulation of the concentration of each species.



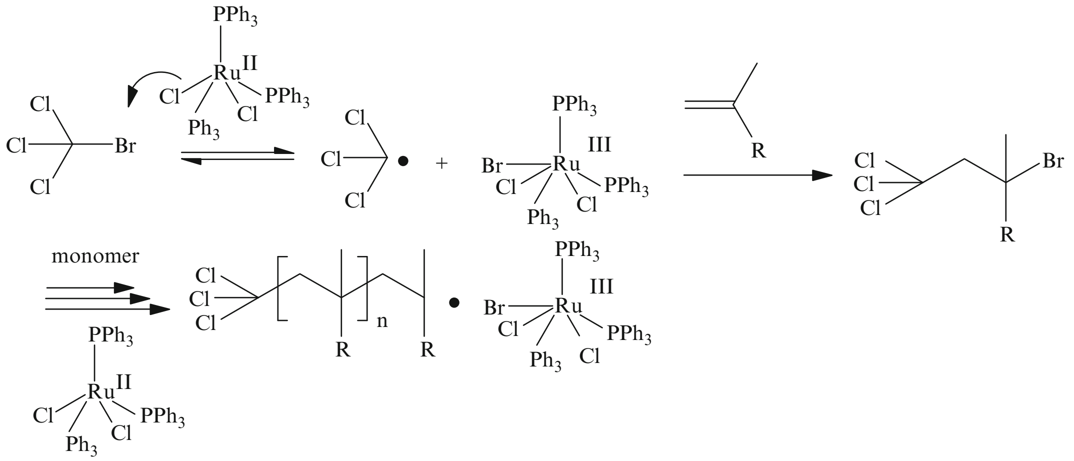
A similar ATP process is one that uses iron(II) bis(triphenylphosphine)-dichloride[$FeCl_2(PPh_3)_2$]. It induces "living" polymerization of monomers such as methyl methacrylate in conjunction with organic halides as initiators in the presence and in the absence of $Al(O^iPr)_3$ in toluene at 80°C. The molecular weight distributions of the products are 1.1–1.3 [269]. The following mechanism is visualized [269]:



The ATP process developed by Sawamoto and coworkers [226], uses an initiating system consisting of carbon tetrachloride, dichlorotri(triphenyl-phosphine)-ruthenium (II) and methylaluminum bis(2,6-di-*tert*-butylphenoxide) to polymerize methyl methacrylate [226]. The polymerization involves reversible and homolytic cleavages of carbon-halogen terminal groups assisted by transition metal complexes [226].



The ruthenium(II) complexes interact with CCl_4 and are oxidized in the process to become Ru(III) and radicals CCl_3• that add to molecules of methyl methacrylate. The polymerization proceeds via repetitive additions of methyl methacrylate molecules to the radical species that are repeatedly generated from the covalent species with carbon-halogen terminal groups [226]. Suwamoto also reported [226] that addition of a halogen donor, Ph_3C–Cl aids the shift of the equilibrium balance to dormant species. The reaction of polymerization can be illustrated as follows:



Klumperman and coworkers [259] observed that while it is lately quite common to treat living radical copolymerization as being completely analogous to its radical counterpart, small deviations in the copolymerization behavior do occur. They interpret the deviations on the basis of the reactions being specific to controlled/living radical polymerization, such as activation—deactivation equilibrium in ATRP. They observed that reactivity ratios obtained from atom transfer radical copolymerization data, interpreted according to the conventional terminal model deviate from the true reactivity ratios of the propagating radicals.

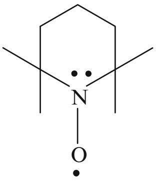
Velazquez and coworkers [260], developed a kinetic model incorporating effects of diffusion-controlled reactions on atom-transfer radical polymerization. The reactions considered to be diffusion-controlled are monomer propagation, bimolecular radical termination, chain transfer between propagating radicals and catalyst, and transfer to small molecules. Model predictions indicate that a diffusion-controlled propagation reduces the “living” behavior of the system, but a diffusion-controlled termination enhances its livingness. Also, diffusion-controlled transfer between chains and catalyst is the same in the forward and in the reverse directions. The “livingness” of the system is enhanced, but if one of them is kept unchanged the other is increased, and the “livingness” of the system is reduced. When diffusion-controlled termination is important, their simulations show that the overall effect of diffusion-controlled phenomena in ATRP is to enhance the livingness of the system.

Preparation of gradient copolymer of styrene and *n*-butyl acrylate was reported by the use of ATRP [261]. ***Gradient copolymers*** are copolymers with sequence distributions varying in a well-defined order as functions of chain lengths. It is suggested that gradient copolymers have the potential of outperforming block and alternating copolymers in some instances [261].

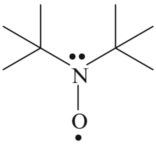
3.14.3 Nitroxide-Mediated Radical Polymerizations

A nitroxide mediated polymerization of styrene was first reported in 1985 [262]. This reaction, however, was studied extensively only since 1993. The monomer conversion rates vs. temperatures are much slower than they are in conventional styrene polymerization. Also, the polydispersities of the products are not as narrow as obtained in anionic polymerization but, generally, the polydispersities produced by this process are proportional to the molecular weights of the polymers produced. In fact, a linear relationship between polydispersity and the molecular weight of the polystyrene product was demonstrated [263].

After the initial nonstationary period, typical alkene polymerizations in the presence of alkoxyamines proceed according to the first order kinetics with the molecular weights increasing with conversion. The dispersity of the products and the contribution of the nonstationary periods depend upon the temperature, the particular initiating system and on the nature of the monomers. Styrene polymerizations can be carried out in the presence of stable nitroxyl radicals, such as the 2,2,6,6-tetramethylpiperydinyl-1-oxy radical, commonly referred to as ***TEMPO*** [264] or ditertiary butyl nitroxide, referred to as ***DTB N.***

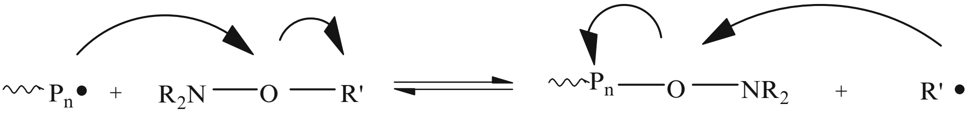


TEMPO

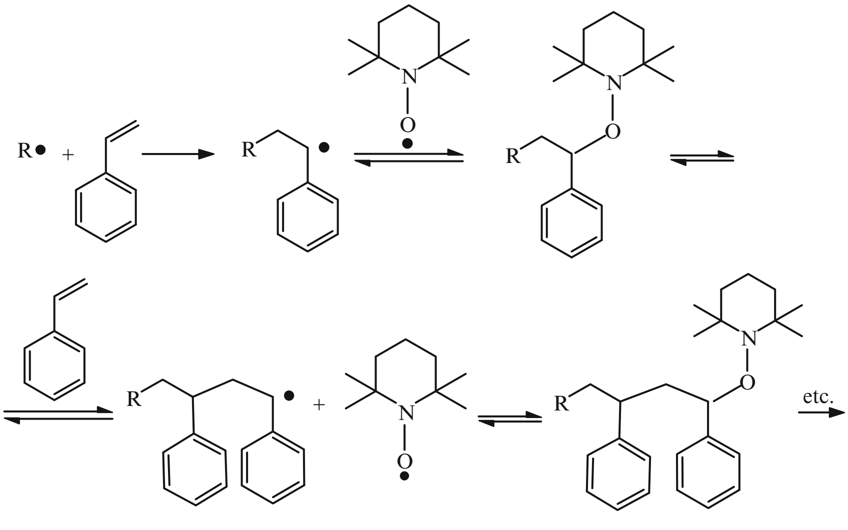


DTBN

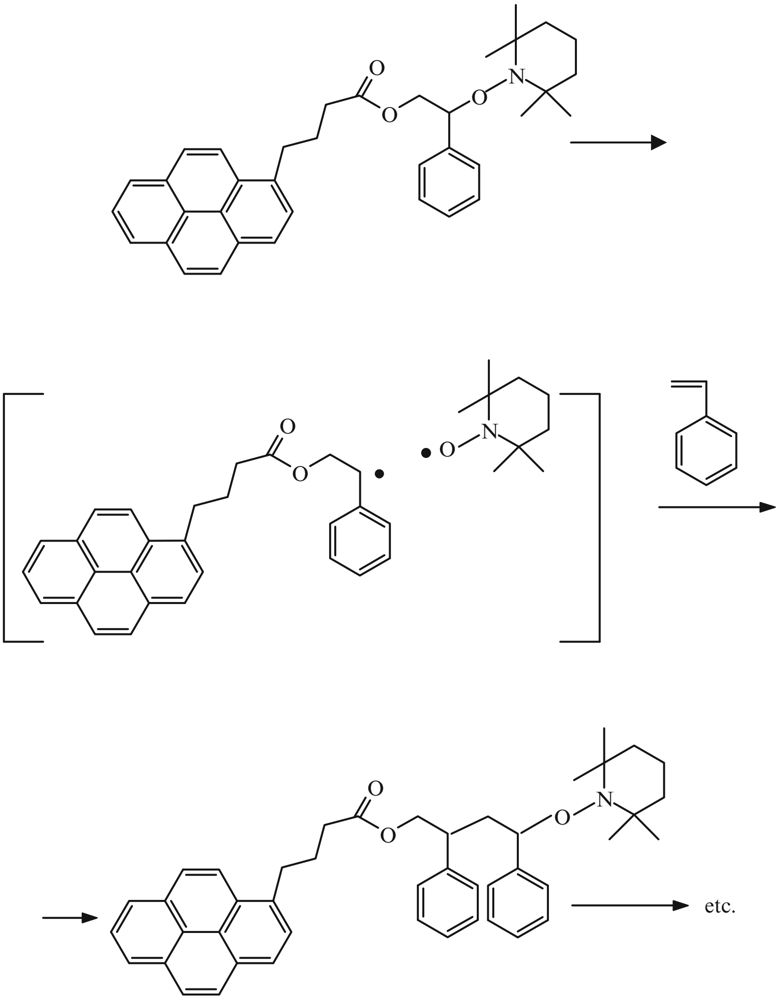
Such radicals are incapable of initiating polymerizations by additions to the double bonds, but react selectively with growing radicals to form reversibly covalent species [265]. In addition, the reactions of growing radicals with dormant species occur via degenerative transfer:



The position of the equilibrium constant in reactions with TEMPO depends on the nature of the radical, the solvent and the temperature. These polymerizations can be initiated by either bimolecular initiators or by unimolecular ones. The bimolecular initiators utilize common free radical sources such as benzoyl peroxide or azobisisobutyronitrile to start the reaction. The carbon-centered initiating radicals that form in turn react with TEMPO. This can be illustrated as follows:



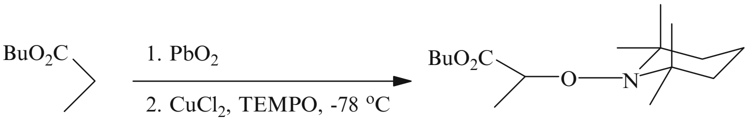
Various descriptions of different unimolecular initiators can be found in the literature. A presence of α-methyl groups on the alkoxyamines appears to be essential [266]. These compounds yield, upon dissociation, both stable radicals and initiating ones and can be shown as follows [267].



The optimal amount of the radical initiator depends on the efficiency of the initiation. Ideally the concentration of the radicals generated from the initiator should be slightly higher than the concentration of the scavenger.

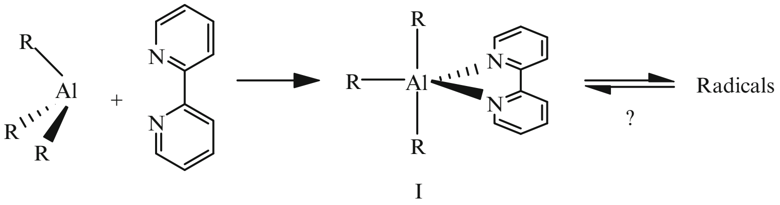
At higher temperatures, such as 120°C, the polymerizations of styrene tend to exhibit ideal behavior. Also, at higher temperatures narrower molecular weight distributions are obtained, indicating sufficiently high exchange rates.

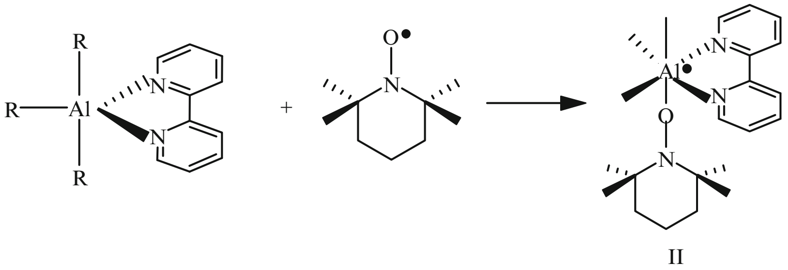
A low-temperature method for the preparation of unimolecular initiators was reported [268]. In this method, oxidation is used to generate carbon radicals in the presence of nitroxide traps such as TEMPO.

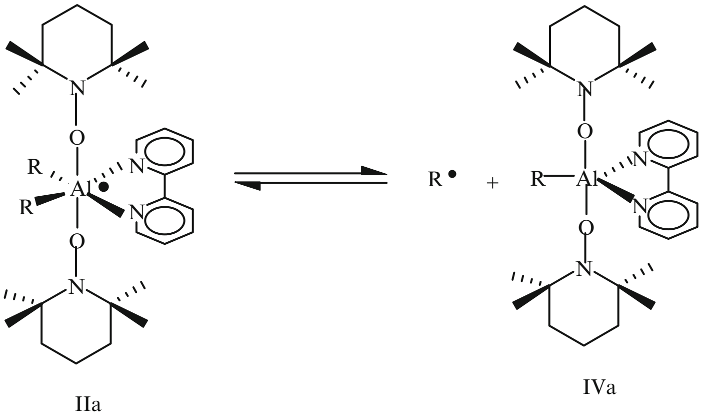


A variation in controlled/"living" polymerization of vinyl acetate by the use of a bidentate ligand, 2,2′-bipyridyl and TEMPO composition in 2:1.2 ratio that was reported by Mardare and Matyjaszewski [267]. The following mechanism was proposed.

(1) Pentacoordinated complexes (I) are formed at a molar ratio of 1.1



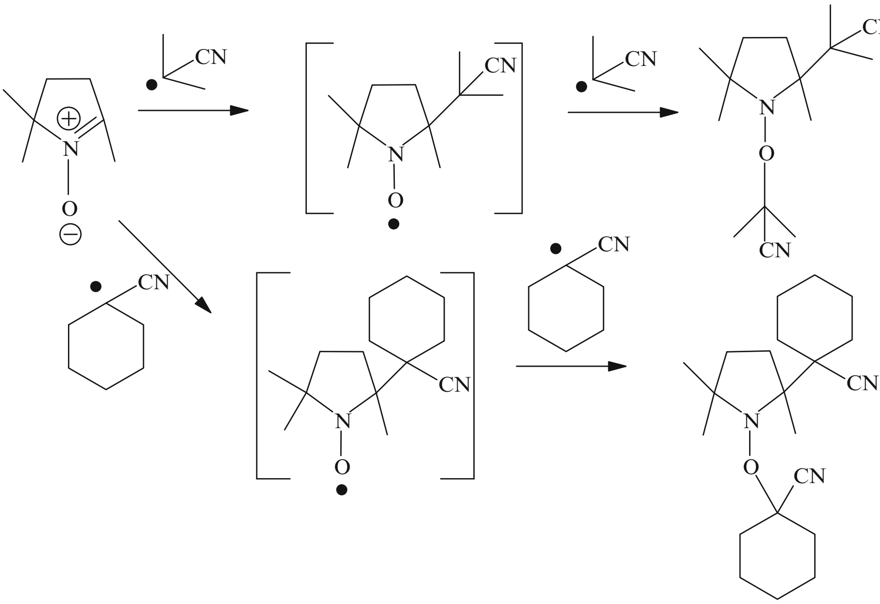




(2) The irreversible attacks by TEMPO on the pentacoordinated complexes, (Al(iBu)$_3$):BPy (I), lead to relatively stable and delocalized radicals(II). TEMPO also reacts with some short-lived radicals present at stage (1) to form alkoxyamines and pentacoordinated complexes of type IV. The radicals II could be in equilibrium with tiny amounts of very reactive radicals R• capable of initiations and subsequent propagations.

Aldabbagh and coworkers [269] reported that carrying out the nitroxide-mediated polymerization in supercritical carbon dioxide allows improved control of the reaction.

Nesvadba and coworkers [270] used nitrones in controlled radical polymerization of vinyl monomers. This was the beginning of the in situ **NMP** concept. The alkoxyamines were prepared by reaction of free radicals obtained from decomposition of azo-initiators, such as azobisisobutyronitrile or l,1′-azobis(cyclohexanecarbonitrile) with selected nitrones:



The alkoxyamines were utilized in radical polymerization of acrylates and styrene in bulk or in solution between 100 and 145°C. Low molecular weight polymers, 3,000–14,000 g/mol formed rapidly with polydispersity, M_w/M_n between 1.2 and 3.4. High styrene conversion was observed together with a low polydispersity.

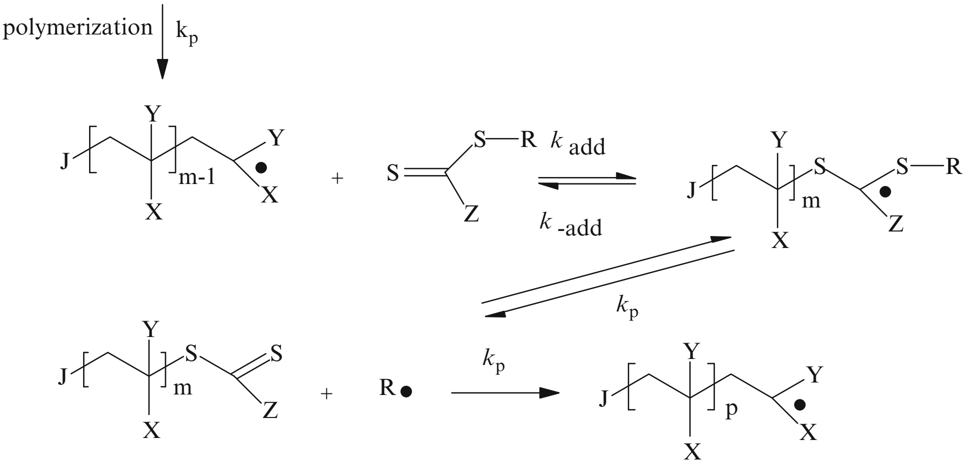
Subsequently, nitroxides and parent alkoxyamines were formed directly in the polymerization medium (in situ **NMP**) by reaction of the nitrone with the free radical initiators [270]. Two types of reactions were carried out. One was a reaction before monomer addition and the other one after the addition. In either case, a prereaction was systematically carried out at temperatures ranging from 60 to 80°C. This was followed by polymerizations at 130°C. The in situ-formed nitroxides and alkoxyamines controlled the radical polymerizations of *n*-butyl acrylate yielding, however, low molecular weight polymers, of $M_n < 10{,}000$ and M_w/M_n equal to 1.65–2.0.

A patent was issued to Wertmer and coworkers [271] for controlled radical (co)polymerization of vinyl monomers mediated by nitrones substituted by longer alkyl groups that contained as much as 18 carbon atoms. The nitrone was simply heated in the presence of peroxide and a monomer, such as styrene at 130°C for 24 h. High-molecular-weight polystyrene, $M_n = 98{,}000$–$146{,}000$ was formed. The ratio of M_w/M_n, however, was not disclosed

Recently, Grubbs and coworkers [272] have synthesized an active alkoxyamine by reaction of 2-methyl-2-nitrosopropane with 1-bromoethylbenzene, catalyzed by ligated CuBr in the presence of metallic copper. A purified alkoxyamine was used to initiate the radical polymerization of styrene and isoprene. Well-defined low polydispersity polymers formed with $M_w/M_n = 1.14$ for polystyrene and 1.28 for polyisoprene. Subsequently, Grubbs and coworkers [273] used this alkoxyamine and successfully controlled the radical polymerization of *n*-butyl acylate at 125°C. Lower ratio of M_w/M_n was observed when the alkoxyamine was preheated at temperatures up to 125 for 30 mm prior to adding the monomer. This prereaction was needed for an excess of free nitroxide to be formed in situ and for polymerization to be controlled.

3.14.4 Reversible Addition-Fragmentation Chain Transfer Polymerization

Another type of "living"/controlled radical polymerization involves ***reversible addition-fragmentation chain transfer***. It was named, therefore, ***RAFT polymerization***. Great versatility and effectiveness was shown for the process [274]. The process is said to be compatible with a very wide range of monomers including functional monomers containing such functional groups as acids, acid salts, and hydroxyl or tertiary amine groups. The conditions of polymerization are those used in conventional free-radical polymerizations. They can be carried out in bulk, solution, emulsion and suspension (see Sect. 3.16). The usual azo or peroxide initiators are employed [274]. The reaction was originally illustrated as follows [274]:

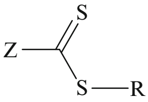


The RAFT process depends upon rapid addition—fragmentation equilibrium reaction between propagating (P_n•) as well as intermediate radicals, and chain activity and dormancy, as shown below in the reaction scheme. The concentrations of each of the species within the equilibrium is dependent on the relative rate coefficients for addition of a propagating radical to the RAFT agent (K_{add}) and fragmentation of the formed intermediate radical (K_{frag}). This equilibrium applies correctly only for polymeric chains that are present in significant concentrations after an initialization period. During the initiation period there are mainly shorter chains present. The important part of this equilibrium is the relatively stable radical intermediates.

It was reported that RAFT-mediated polymerization reactions typically contain anomalies, such as an "inhibition" period and rate retardation. The rate retardations or reductions in the polymerization rates apparently occur in the presence of RAFT agents, and are not observed when RAFT agents are absent. Examples are dithiobenzoate-mediated polymerization reactions [275].

Tonge and coworkers [276] investigated the reactions of short-chain species during the initial period of cumyl dithiobenzoate mediated polymerization of styrene at 84°C. Using electron spin resonance and hydrogen and carbon NMR spectroscopies they were able to demonstrate that the reactions are very specific during the initial stages. There is a strong preference to add single monomer species. This is followed by fragmentation and release of shorter radicals prior to formation of longer chains.

The effectiveness RAFT agents were investigated by Moad and coworkers [277]. These RAFT agents, such as thiocarbonylthio compounds, depend in effectiveness on the nature of the group, Z and R (shown below) that modify the reactivity of the thiocarbonyl group toward free radical addition. R is the free radical leaving group [277]:



These RAFT agents are based on the structure [S=C(Ph)S–R] [277] They found that the effectiveness of these agents also depends upon the nature of the monomer and on the polymerization conditions. For the polymerization of styrene, methyl methacrylate, butyl acrylate, and methyl acrylate at 60°C, the effectiveness of R decreases in the following order [277]:

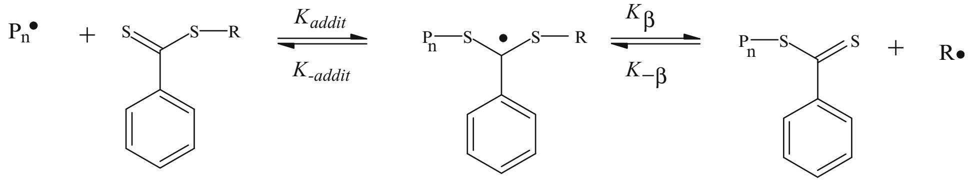
$$R = C(\text{alkyl})_2CN \sim C(CH_3)_2Ar > C(CH_3)_2C(=O)O(\text{alkyl}) > C(CH_3)_2C(=O)NH(\text{alkyl}) > \\ C(CH_3)_2CH_2C(CH_3)_3 \geqslant C(CH_3)HPh > C(CH_3)_3 \sim CH_2Ph$$

In addition, among the above compounds, only when R=$C(CH_3)_2CN$ or $C(CH_3)_2Ph$ did these thiocarbonylthio compounds yield polymers with narrower polydispersities in batch polymerizations. Also, only these compounds allowed molecular weight control that may be expected from a living polymerization. The reaction mechanism was proposed by Moad and coworkers as follows [277]:

initiation

$$\text{initiator} \longrightarrow I^{\bullet} \xrightarrow{M} \; \xrightarrow{M} P_n^{\bullet}$$

chain transfer

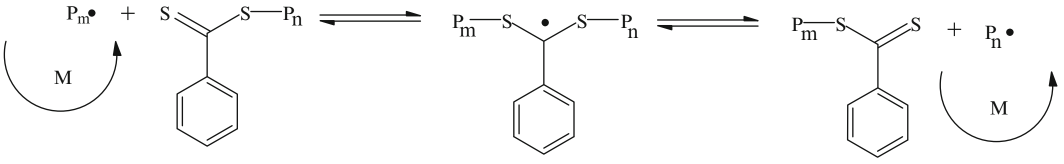


2 3 4

reinitiation

$$R\bullet \xrightarrow[K_i]{M} R{-}M\bullet \xrightarrow[K_p]{M} P_m\bullet$$

chain equilibration



termination

$$P_n\bullet + P_m\bullet \xrightarrow{K_t} \text{dead polymer}$$

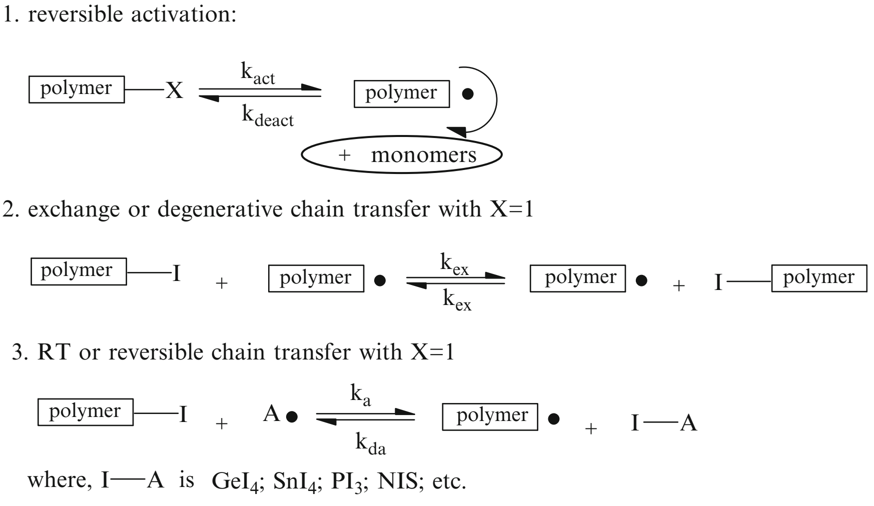
Moad and coworkers concluded [277] that a major factor that determines the transfer coefficient of dithiobenzoate derivatives is the way the intermediate 3 (see the above in equation) partitions between starting materials and products. This in turn is determined by the relative ability of the leaving group R• and by the propagating radical. Steric factors and radical stability of R• are also important. They conclude that more stable, more electrophilic, and bulkier radicals are better leaving groups. The partitioning of R• between the monomers (to reinitiate) or by adding to polymeric RAFT can also have a significant effect on the rate of consumption of RAFT agent [277].

Vana and coworkers [278] studied conversion vs. time and molecular weight distributions in conjunction with the kinetic scheme for the RAPT process. In particular, conditions leading to inhibition and rate retardation were examined to act as a guide to optimizing the reaction. They demonstrated that there is an inhibition period of considerable length. It is induced by either slow fragmentation of the intermediate RAFT radicals appearing in the preequilibrium or is due to slow reinitiation of the leaving group radicals from the initial RAFT agent. The absolute values of the rate coefficients governing the core equilibrium of the RAFT process (at a fixed value of the equilibrium constant) are found to be crucial in controlling the polydispersity of the resulting M_w/M_n values. Higher interchange frequency effects narrower distributions. They also demonstrated that the size of the rate coefficient controlling the addition reaction of propagating radicals to polymer-RAFT agent, K_β, is mainly responsible for optimizing the control of the polymerization. The fragmentation rate coefficient, $K-_\beta$, of the macro RAFT intermediate radical, on the other hand, may be varied over orders of magnitude without affecting the amount of control exerted over the polymerization. Based on the basic RAFT mechanism, shown above, its value mainly governs the extent of rate retardation in RAFT polymerizations [278].

Calitz, Tonge, and Sanderson reported the results of a study of RAFT polymerization by means of electron spin resonance spectroscopy [276]. They observed intermediate radical signals that were not consistent with current RAFT theory [276].

Sawamoto and coworkers reported obtaining simultaneous control of molecular weight and steric structure in RAFT polymerization of *N*-isopropylacrylamide by addition of rare earth metal, Y(*O*-tetrafluoromethanesulfonate)$_3$, Lewis acid. The M_w/M_n ratio of the products ranged between 1.4–1.9 and the isotactic content was 80–84% [277].

Goto et al. [279] developed a process that they describe as **reversible living chain transfer radical polymerization** [278], where they us Ge, Sn, P, and N compounds iodides in the iodide mediated polymerizations.^{ref} In this process, a compound such as GeI_4 is a chain transferring agent and the polymer-iodide is catalytically activated via a RFT process. They proposed that the new reversible activation process be referred to as RTCP [279]. The process can be illustrated by them as follows [279]:

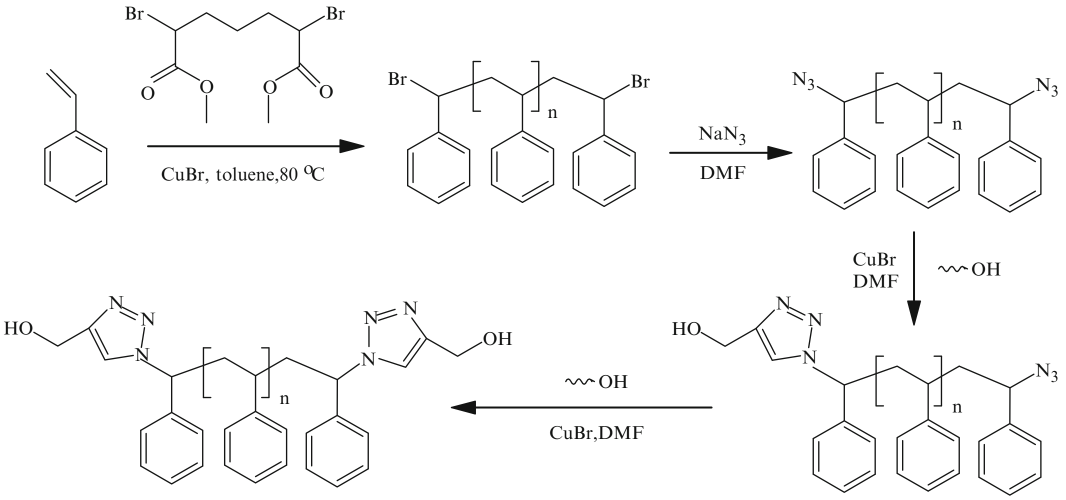


where, I—A is GeI_4; SnI_4; PI_3; NIS; etc.

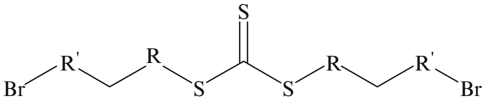
3.14.4.1 Combinations of Click Chemistry and ATP as Well as ATP and RAFT Polymerizations

In the last few years, “click reactions,” as termed by Sharpless et al. [280] received attention due to their high specificity, quantitative yields, and good fidelity in the presence of most functional groups. The “click chemistry” reaction includes a copper-catalyzed Huisgen dipolar cycloaddition reaction between an azide and an alkyne leading to 1,2,3-triazole. Recent publications on this “click reaction” indicate that it is a useful method for preparation of functional polymers [281].

Matyjaszewski and Gao synthesized functional polymers by combining ATRP and the "click reactions." They also prepared telechelic polymers, star polymers and brush polymers [282]. Formation of telechelic polymers was illustrated as follows:



Also, a synthesis of an iniferter that consists of a trithiocarbonate moiety and two bromine chains ends was reported [282]. This iniferter was used to conduct either independently or concurrently both ATRP and reversible addition-fragmentation chain transfer polymerizations. The iniferter was illustrated as follows:

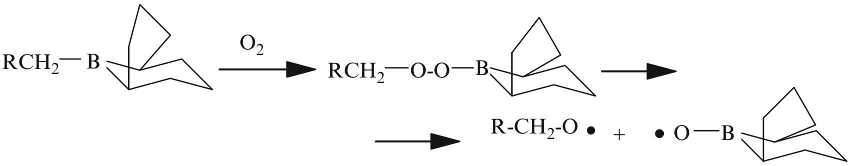


RAFT polymerizations with this iniferter of *N*-butyl acrylate and styrene yielded polymers with M_w/M_n equal to 1.15 and 1.16 respectively. Polymerization of methyl methacrylate, however, yielded a polymer with a broad M_w/M_n ratio. On the other hand, polymerization in the presence of CuBr/TMPA by ATRP exclusively through the bromine chain ends yielded a polymer with narrow M_w/M_n ratio [282].

3.14.5 Special Types of Controlled/"Living" Polymerizations

It was reported that it is possible to employ persistent phosphorus-based radicals in controlled/living free-radical polymerization [283, 284]. Also, in cases of low stability of the hyper coordinated radicals, the ligand exchanges become facile and some organoaluminum, organoboron, and other compounds have been used successfully as transfer agents in polymerization of styrene, acrylics, and vinyl acetate [283, 284].

Chung and coworkers [286] described a "living" radical initiator that is based on oxidation adducts of alkyl-9-borabicyclononanes, such as hexyl-9-borabicyclononane. The "living" radical polymerizations take place at room temperature. The initiators form in situ by reactions with oxygen:



The alkoxy radicals are very reactive and initiate radical polymerizations readily On the other hand, the borinate radicals are stabilized by the empty p-orbitals of boron through back-donating electron density and are too stable to initiate polymerizations. During the polymerization, the borinate radicals may form weak and reversible bonds with the growing chains.

Boroxyl mediated living radical polymerizations were subsequently described by Chung [287] in a review article. The chemistry is centered on the living radical initiator, i.e., alkylperoxydialkylborane (C—O—O—BR) species, similar to the one shown above, that are formed by mono oxidation of an asymmetric trialkylborane with oxygen. In the presence of polar monomers (including acrylates and methacrylates), the C—O—O—BR., undergoes a spontaneous hemolytic cleavage at ambient temperature to form an active alkoxy radical and a stable boroxyl radical The alkoxyl radical is active in initiating the polymerization of vinyl monomers, and the stable boroxyl radical forms a reversible bond with the propagating radical site to prevent undesirable termination reactions. The living polymerizations were characterized by predictable polymer molecular weight, narrow molecular weight distributions, and by formation of telechelic polymers and block copolymers through sequential monomer addition. Furthermore, this living radical initiator system benefits from two unique features of trialkylborane. These are (a) easy incorporation into polymer chains (chain ends or side chains) and (b) in situ auto-transformation to living radical initiators.

Lacroix and coworkers reported a reverse iodine transfer polymerization (RITP), where elemental iodine is used as a control agent in living radical polymerization [288]. Styrene, butyl acrylate, methyl acrylate, and butyl α-fluoroacrylate were homopolymerized, using a radical catalyst and I_2 as a chain transfer agent. Methyl acrylate was also copolymerized with vinylidene chloride using this process.

3.14.6 *Kinetics of Controlled/Living Free-Radical Polymerizations*

Several papers were published to describe the kinetics of controlled free radical polymerization. Goto and Fukuda [289] postulate two activation processes for nitroxy/styrene polymerization systems:

$$\text{process I:}\ \ \text{P—X} \underset{k_c}{\overset{k_d}{\rightleftharpoons}} \text{P}\bullet + \text{X}\bullet$$

$$\text{process II:}\ \ \text{P—X} + \text{P}'\bullet \underset{k_{ex}}{\rightleftharpoons} \text{P}\bullet + \text{P}' - X$$

The equilibrium constant, $K = K_d/K_c$. Stationary-state concentrations of P• and X• are

$$[\text{P}\bullet] = (R_i/k_i)^{1/2}$$

$$[\text{X}\bullet] = k[\text{P} - \text{X}]/[\text{P}\bullet]$$

The stationary concentration of P• and X• are determined by different mechanisms. [P•] is determined by the balance of the initiation rate R_I and the termination rate k_t [P•] [2]. This is the same as in conventional free radical polymerization systems. [X•] is determined, however, from the equilibrium equation shown for process I. It depends, therefore upon the equilibrium constant K and on the concentration of the adduct [P–X] and [P•] [289]. The rate of polymerization during the stationary state is

$$R_p = k_p[\text{P}\bullet][\text{M}] = (k_p/k_t)^{1/2} R_i^{1/2}[\text{M}]$$

The polymer-nitroxyl adduct P–X reversibly dissociates thermally, in process I into the polymer radical P• and the nitroxyl radical X•. The rate constants of dissociation and combination are k_d and k_c, respectively. The, so-called, "degenerative transfer" takes place in process II. The second-order rate constant for active species in either direction is k_{ex}. Here all the rate constants are assumed to be independent of chain length. Since the frequency of cleavage of the P–X bond is proportional to [P–X] in process I and to [P•1[P′–X]] in process II, the overall frequency, f_a per unit time and per unit volume, of the bond-cleaving or activation reactions, may be expressed by [277]:

$$f_a = k_a[\mathrm{P-X}]$$

with $k_a = k_d + k_d[\mathrm{P}\bullet]$
where k_a is the overall activation rate constant, viewed as a first-order reaction. Goto and Fukuda concluded that it may be more convenient to represent the above equation in the form [289]:

$$k_a = k_d + (k_{ex}/k_p)(R_p/[\mathrm{M}])$$

and show the general expression of the time-averaged k_a for a batch system:

$$k_a = k_d + (k_{ex}/k_p T)\ln([\mathrm{M}_0]/[\mathrm{M}])$$

Matyjaszewski et al. wrote the kinetic equation for atom transfer polymreization [290, 291]. It is based on the ATP reaction mechanism that was described above. By assuming fast initiations, insignificant termination reactions and steady concentrations of the propagating radicals, the following relationship was derived [290, 291]:

$$R_p = k_p k_{eq}[\mathrm{M}][\mathrm{RX}]_0 \frac{[\mathrm{Mt^Z L_m}]}{[\mathrm{XMt^{z+1}L_m}]} = k_{app}[\mathrm{M}]$$

3.15 Thermodynamics of the Free-Radical Polymerization Reaction

3.15.1 Effects of Monomer Structure on the Thermodynamics of the Polymerization

There is a close relationship between monomer structure and changes in free energy, in enthalpy and in entropy. Thus, for instance, knowledge of changes in enthalpy will allow appropriate thermal control of the reaction and yield proper rate of propagation and molecular weight distribution. The quantities of ΔF, ΔH, and ΔS relate only to the rate of propagation because initiation and termination are single steps, while propagation consists of multiple steps.

Free radical polymerization is generally exothermic because it involves conversion of π bonds to σ bonds. Thus, the change in enthalpy ΔH is negative. Also, because there is a decrease in randomness in conversion of monomers to polymer, the change in entropy ΔS is also negative. The overall change in free energy of the free radical polymerization process is,

$$\Delta F = \Delta H - T\Delta S$$

The free energy is generally negative for the free-radical polymerization process. Variations in monomer structures have a significant effect on the values of ΔH for the following reasons. These are differences in resonance stabilizations due to differences in conjugation and hyperconjugation. Also, due to steric strains that arise from bond angle deformation and bond stretching, as well as variations in secondary bond forces, such as hydrogen bonding and dipole interactions.

3.15.2 Thermodynamics of the Constrains of the Free-Radical Polymerization Reaction

Free-radical polymerization reactions are equilibrium reactions. The equilibrium between the monomer and the growing polymer is subject to thermodynamic conditions. At equilibrium, therefore, the change in free energy is zero:

$$\Delta F = 0$$

The change in free energy for the reaction can, therefore, be written;

$$\Delta F = \Delta F^0 + RT\ \ln K = \Delta H^0 - T\Delta S^0 + RT\ \ln K = 0$$

In the above equation, ΔF^0, ΔH^0, and ΔS^0 represent statistical variations in the changes in free energy, enthalpy, and entropy, representing the transition that the monomer undergoes by being placed into the polymeric chain.

The equilibrium constant can then be written as:

$$K = [\mathrm{PM}^*_{\mathrm{n+1}}]/\{[\mathrm{PM}^*_{\mathrm{n}}][\mathrm{M}]\}$$

where, $\mathrm{PM}^*_{\mathrm{n+1}}$ and $\mathrm{PM}^*_{\mathrm{n}}$ are concentrations of species. Assuming that they are practically equal, one can write:

$$K = 1/\mathrm{M}$$

it would then mean that:

$$RT \ln \mathrm{M} = \Delta H^0 - T\Delta S^0$$

$$RT\ \ln \mathrm{M} = (\Delta \boldsymbol{H}^{\mathbf{0}}/T) - \Delta \boldsymbol{S}^{\mathbf{0}}$$

The ceiling temperature can then be written as

$$T_{\mathrm{c}} = \ \Delta H^0/\{\ \Delta S^0 + R \ln[\mathrm{M}]_{\mathrm{equ}}\}$$

3.16 Polymer Preparation Techniques

Four general techniques are used for preparation of polymers by free-radical mechanism: polymerization in ***bulk***, in ***solution***, in ***suspension*** and in ***emulsion***. The ***bulk*** or ***mass*** polymerization is probably the simplest of the four methods. Only the monomer and the initiator are present in the reaction mixture. It makes the reaction simple to carry out, though the exotherm of the reaction might be hard to control, particularly if it is done on a large scale. Also there is a chance that local hot spots might develop. Once bulk polymerization of vinyl monomers is initiated, there can be two types of results, depending upon the solubility of the polymer. If it is soluble in the monomer, the reaction may go to completions with the polymer remaining soluble throughout all stages of conversion. As the polymerization progresses, the viscosity of the reaction mixture increases markedly. The propagation proceeds in a medium of associated polymeric chains dissolved in or swollen by the monomer until all the monomer is consumed.

If the polymer is insoluble, it precipitates out without any noticeable increase in solution viscosity. Examples of this type of a reaction can be polymerizations of acrylonitrile or vinylidene chloride. The activation energy is still similar to most of the polymerizations of soluble polymers and the initial rates are proportional to the square root of initiator concentration. Also, the molecular weights of the polymerization products are inversely proportional to the polymerization temperatures and to initiator concentrations. Furthermore, the molecular weights of the resultant polymers far exceed the solubility limits of the polymers in the monomers. The limit of acrylonitrile solubility in the monomer is at a molecular weight of 10,000. Yet, polymers with molecular weights as high as 1,000,000 are obtained by this process. This means that the polymerizations must proceed in the precipitated polymer particles, swollen and surrounded by monomer molecules.

The kinetic picture of free-radical polymerization applies best to bulk polymerizations at low points of conversion. As the conversion progresses, however, the reaction becomes complicated by chain transferring to the polymer and by gel effect. The amount of chain transferring varies, of course, with the reactivity of the polymer radical.

Bulk polymerization is employed when some special properties are required, such as high molecular weight or maximum clarity, or convenience in handling. Industrially, bulk polymerization in special equipment can have economic advantages, as with bulk polymerization of styrene. This is discussed in Chap. 6.

Solution polymerization differs from bulk polymerization because a solvent is present in the reaction mixture. The monomer may be fully or only partially soluble in the solvent. This, the polymer may be (1) completely soluble in the solvent, (2) only partially soluble in the solvent, and (3) insoluble in the solvent.

When the monomer and the polymer are both soluble in the solvent, initiation and propagation occur in a homogeneous environment of the solvent. The rate of the polymerization is lower, however, than in bulk. In addition, the higher the dilution of the reactants the lower is the rate and the lower is the molecular weight of the product. This is due to chain transferring to the solvent. In addition, any solvent that can react to form telomers will also combine with the growing chains.

If the monomer is soluble in the solvent, but the polymer is only partially soluble or insoluble, the initiation still takes place in a homogeneous medium. As the chains grow, there is some increase in viscosity that is followed by precipitation. The polymer precipitates in a swollen state and remains swollen by the diffused and adsorbed monomer. Further propagation takes place in these swollen particles.

Because propagation continues in the precipitated swollen polymer, the precipitation does not exert a strong effect on the molecular weight of the product. This was demonstrated on polymerization of styrene in benzene (where the polymer is soluble) and in ethyl alcohol (where the polymer is insoluble). The average molecular weight obtained in benzene at 100°C was 53,000 while in ethyl alcohol at the same temperature it was 51,000 [280]. When the monomers are only partially soluble and the polymers are insoluble in the solvents the products might still be close in molecular weights to those obtained with soluble monomers and polymers. Polymerization of acrylonitrile in water can serve as an example. The monomer is only soluble to the extent of 5–7% and the polymer is effectively insoluble. When aqueous saturated solutions of acrylonitrile are polymerized with water-soluble initiators, the systems behave initially as typical solution polymerizations. The polymers, however, precipitate out rather quickly as they form. Yet, molecular weights over 50,000 are readily obtainable under these conditions.

There are different techniques for carrying out solution polymerization reactions. Some can be as simple as combining the monomer and the initiator in a solvent and then applying agitation, heat and an inert atmosphere [292]. Others may consist of feeding into a stirred and heated solvent the monomer or the initiator, or both continuously, or at given intervals. It can be done throughout the course of the reaction or through part of it [293]. Such a set up can be applied to laboratory preparations or to large-scale commercial preparations. It allows a somewhat better control of the exotherm during the reaction.

In both techniques the initiator concentration changes only a few percent during the early stages of the reaction, if the reaction temperature is not too high. The polymerization may, therefore, approach a steady state character during these early stages. After the initial stages, however, and at higher temperatures, the square root dependence of rates upon the initiator concentration no longer holds. This is a result of the initiator being depleted rapidly. The second technique, where the initiator, or the monomer and the initiator are added continuously was investigated at various temperatures and rates of addition [294–299]. If the initiator and monomer are replenished at such a rates that their ratios remains constant, steady state conditions might be extended beyond the early stages of the reactions. How long they can be maintained, however, is uncertain.

Suspension polymerization [298] can be considered as a form of mass polymerization. It is carried out in small droplets of liquid monomer dispersed in water or some other media and caused to polymerize to solid spherical particles. The process generally involves dispersing the monomer in a non solvent liquid into small droplets. The agitated stabilized medium usually consists of nonsolvent (often water) containing small amounts of some suspending or dispersing agent. The initiator is dissolved in the monomer if it is a liquid or it is included in the reaction medium, if the monomer is a gas.

To form a dispersion, the monomer must be quite insoluble in the suspension system. To decrease the solubility and to sometimes also increase the particle size of the resultant polymer bead, partially polymerized monomers or prepolymers may be used. Optimum results are obtained with initiators that are soluble in the monomer. Often, no differences in rates are observed between polymerization in bulk and suspension. Kinetic studies of styrene suspension polymerization have shown that all the reaction steps, initiation, propagation, and termination, occur inside the particles [299].

The main difficulty in suspension polymerization is in the forming and in the maintaining uniform suspensions. This is because the monomer droplets are slowly converted from thin immiscible liquids to sticky viscous materials that subsequently become rigid granules. The tendency is for the sticky particles to attach to each other and to form one big mass. The suspending agent’s sole function is to prevent coalescing of the sticky particles. Such agents are used in small quantities (0.01–0.5% by weight of the monomer). There are many different suspending agents, both organic and inorganic. The organic ones include methylcellulose, ethyl cellulose, poly(acrylic acid), poly(methacrylic acid), salts of these acids, poly(vinyl alcohol), gelatins, starches, gums, alginates, and some proteins, such as casein or zein. Among the inorganic suspending agents can be listed talc, magnesium carbonate, calcium carbonate, calcium phosphate, titanium and aluminum oxides, silicates, clays, such as bentonite, and others. The diameter of the resultant beads varies from 0.1 to 5 mm and often depends upon the rate of agitation. It is usually inversely proportional to the particle size. Suspension polymerization is used in many commercial preparations of polymers.

Zhang, Fu, and Jiang, reported a study of factors influencing the size of polystyrene microspheres in dispersion polymerization [300]. The found that that the size of polystyrene microspheres decreased with an increasing amount of stabilizer and also increased with increasing the amount of monomer and initiator. The amount of stabilizer and monomer concentration were the major factors influencing the size distribution of polystyrene microspheres. The size of the microspheres decreased with an increase of the solvency of reaction media. The size distribution, however, hardly changed. The size of polystyrene microspheres increased with an increase in the reaction temperature. but the size distribution hardly changed.

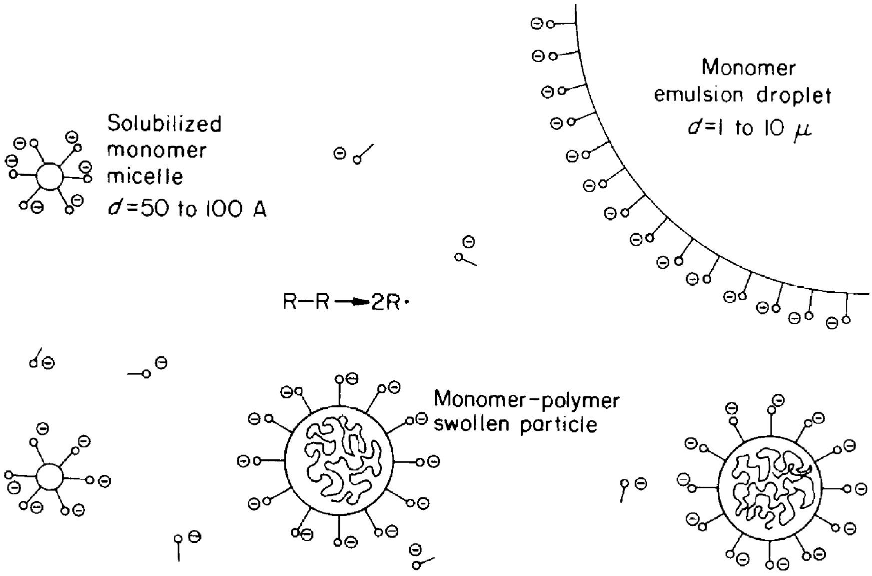


Fig. 3.3 Early stages of emulsion polymerization (from ref. [306])

Emulsion polymerization is used widely in commercial processes [300, 301]. The success of this technique is due in part to the fact that this method yields high-molecular-weight polymers. In addition, the polymerization rates are usually high. Water is the continuous phase and it allows efficient removal of the heat of polymerization. Also, the product from the reaction, the latex, is relatively low in viscosity, in spite of the high molecular weight of the polymer. A disadvantage of the process is that water-soluble emulsifiers are used. These are hard to remove completely from the polymers and may leave some degree of water sensitivity.

The reaction is commonly carried out in water containing the monomer, an emulsifier or a surface-active agent, and a water-soluble initiator. Initiation may be accomplished through thermal decomposition of the initiator or through a redox reaction. The polymer forms as a colloidal dispersion of fine particles and polymer recovery requires breaking up the emulsion.

The full mechanism of emulsion polymerization is still not completely worked out. It is still not clear why a simultaneous increase in the polymerization rate and in the molecular weight of the product is often observed. Also, in emulsion polymerization, at the outset of the reaction the monomer is in a form of finely dispersed droplets. These droplets are about 1 μ in diameter. Yet, during the process of a typical polymerization, they are converted into polymer particles that are submicroscopic, e.g., 1,000 Å in diameter.

At the start of the reaction the emulsifier exists simultaneously in three loci: (a) as a solute in water; (b) as micelles; (c) and as a stabilizing emulsifier at the interface between the monomer droplets and the water. The bulk of the emulsifier, however, is in the micelles. The monomer is also present in three loci: (a) in the monomer droplets that are emulsified and perhaps 1–10 μ in diameter; (b) it is solubilized in the micelles, perhaps 50–100 Å in diameter; (c) and it is present as individual molecules dissolved in the water. The bulk of the monomer is in the droplets. There are on the average 10^{18}/mL of monomer-swollen micelles in the reaction mixture at the outset of the reaction [302]. At the start of the reaction there are also on the average 10^{12}/mL monomer droplets that act as reservoirs. The monomer is supplied from the droplets to radical-containing micelles when the reaction progresses by a process of diffusion through the aqueous phase (Fig. 3.3).

The first hypothesis of the mechanism of emulsion polymerization was formulated by Harkins [305]. According to this hypothesis, the water-soluble initiator decomposes in the aqueous phase.

This results in formation of primary radicals. The primary radicals in turn react with the monomer molecules dissolved in the water (though their number may be quite small). Additional monomer molecules may add to the growing radicals in the water until the growing and propagating chains of free radicals acquire surface-active properties. At that stage, the growing radicals consist of inorganic and organic portions:

These growing radical-ions tend to diffuse into the monomer-water interfaces. The probability that the diffusion takes place into monomer-swollen micelles rather than into monomer droplets is backed by the considerations of the relative surface areas of the two. There are on the average 10^{18} micelles in each milliliter of water. These are approximately 75 Ā in diameter and each swollen micelle contains on the average 30 molecules of the monomer. At the same time, the diameters of the monomer droplets are approximately 1 μ. and it is estimated that there are only approximately 10^{12} such droplets per milliliter of water. Thus, the micelles offer 60 times more surfaces for penetration than do the droplets. The initiating radicals are almost always generated in the water phase. After formation in the water phase, a number of free radicals may be lost due to recombination. Termination is also possible after reaction of free radicals with some of the monomers dissolved in the water.

Several theories tried to explain the entry process. Thus, a “diffusion control” model [307, 308] supposes that diffusion of aqueous-phase radicals into the particle surface is the rate-controlling step for entry. Another theory suggests that displacement of surfactant from the particle surface is the rate-determining step [309]. A third one assumes that the entry can be thought of as a colloidal interaction between a latex particle and primary phase oligomeric aqueous-phase radical. These are the radicals formed through reactions of initiating radicals and monomer molecules dissolved in water [310]. The most accepted entry model appears to be the “control by aqueous-phase growth” model of Maxwells et al. [311]. This theory postulates that free radicals generated in the aqueous phase propagate until they reach a critical degree of polymerization (let us call it z), at which point they become surface-active and their only fate is irreversible entry into a latex particle; the rate of entry of *z-mers* into a particle is assumed to be so fast as not to be rate-determining. An efficiency of less than 100% arises if there is significant aqueous-phase termination of the propagating radicals.

The entry model of Maxwells et al. was derived from and/or supported by data on the influence of particle surface characteristics (charge, size) on the entry rate coefficient [312]. It was assumed that the aqueous radicals became surface active when the degree of polymerization reached 2–3. This was based on thermodynamic considerations of the entering species.

Further data on the Maxwell et al. entry model was obtained by Gilbert and coworkers [313] who studied the effects of initiator and particle surface charges. They obtained kinetic data for radical entry in the emulsion polymerization of styrene and concluded that their data further supports the Maxwell et al. entry model and refutes the alternative models mentioned above.

Once the radicals penetrate the micelles, polymerization continues by adding monomers that are inside. The equilibrium is disturbed and the propagation process proceeds at a high rate due to the concentration and crowding of the stabilized monomers. This rapidly transforms the monomer-swollen micelles into polymer particles. The changes result in disruptions of the micelles by growths from within. The amount of emulsifier present in such changing micelles is insufficient to stabilize the polymer particles. In trying to restore the equilibrium, some of the micelles, where there is no polymer growth, disintegrate and supply the growing polymer particles with emulsifier. In the process many micelles disappear per each polymer particle that forms. The final latex usually ends up containing about 10^{15} polymer particles per milliliter of water. By the time conversions reach 10–20% there are no more micelles present in the reaction mixtures. All the emulsifier is now adsorbed on the surface of the polymer particles. This means that no new polymer particles are formed. All further reactions are sustained by diffusion of monomer molecules from the monomer droplets into the growing polymer particles. The amount of monomer diffusing into the particles is always in excess of the amount that is consumed by the polymerization reaction due to osmotic forces [297].

This extra monomer supplied is sufficient for equilibrium swelling of the particles [298]. As a result, the rate of polymerization becomes zero order with respect to time.

When conversion reaches about 70%, all the remaining monomer is absorbed in the polymer particles and there are no more monomer droplets left. At this point the reaction rate becomes first order with respect to time.

The qualitative approach of Harkins was put on a quantitative basis by Smith and Ewart [314–316]. Because 10^{13} radicals are produced per second and can enter between 10^{14} and 10^{15} particles, Smith felt that a free radical can enter a particle once every 10–100 s. It can cause the polymerization to occur for 10–100 s before another free radical would enter and terminate chain growth [317]. A period of inactivity would follow that would last 10–100 s and then the process would repeat itself. Such a "stop and go" mechanism implies that a particle contains a free radical approximately half of the time. It can also be said that the average number of radicals per particle is 0.5. This is predicted on conditions that (a) the rate of chain transfer out of the particle is negligible and (b) the rate of termination is very rapid compared with the rate of radical entry into the particle.

The kinetic relationships derived by Smith and Ewart for the system are as follows:

$$\text{The rate of primary radical entering a particle} = r_{\mathrm{i}} = R_{\mathrm{i}}/N$$

$$\text{Rate of polymerization} = R_{\mathrm{P}} = k_{\mathrm{P}}[\mathrm{M}]N/2$$

$$\text{Average degree of polymerization} = \mathrm{DP} = Nk_{\mathrm{P}}[\mathrm{M}]/R_{\mathrm{i}}$$

where, k_{P} is the constant for propagation, [M] is the concentration of monomer, N is the number of particles containing n radicals (~0.5) and the expression for the number of particles formed:

$$N = K(\rho/\mu)^{0.4}(A_{\mathrm{S}}S)^{0.6}$$

where, μ is the volume increase of the particles, A_{S} is the area occupied by one emulsifier molecule. S is the amount of emulsifier present. K is a constant $= 0.37$ (based on the assumption that the micelles and polymer particles compete for free radicals in proportion to their respective total surface areas). K can also be equal to 0.53 (based on the assumption that the primary radicals enter only micelles, as long as there remain micelles in the reaction mixture). ρ is the rate of entry into the particles. The kinetic chain length can be written as:

$$\overline{\upsilon} = k_{\mathrm{p}}N_{\mathrm{p}}[\mathrm{M}]/2\mathrm{d}[\mathrm{RM}^{*}]/\mathrm{d}t$$

The Smith-Ewart mechanism does not take into account any polymerization in the aqueous phase. This may be true for monomers that are quite insoluble in water, such as styrene, but appears unlikely for more hydrophilic ones such as methyl methacrylate or vinyl acetate. In addition, it was calculated by Flory that there is insufficient time for a typical cation-radical (such as a sulfate ion radical) to add to a dissolved molecule of monomer such as styrene before it becomes captured by a micelle [317]. This was argued against, however, on the ground that Flory's calculations fail to consider the potential energy barrier at the micelle surfaces from the electrical double layer. This barrier would reduce the rate of diffusion of the radical-ions into the micelles [316].

Considerably different mechanisms were proposed by several groups [317, 318]. They are based on a concept that most polymerizations must take place at the surface of the particles or in their outer "shell" and not within the particles. It is claimed that the interiors of the particles are too viscous for free radicals to diffuse inside at a sufficiently fast rate. Two different mechanisms were proposed to explain why polymerization takes place preferentially in the shell layer. One of them suggests that the monomer is distributed nonuniformly in the polymer particles. The outer shell is rich in monomer molecules, while the inside is rich in polymer molecules [319]. The other explanation is that the radical ions that form from the water-soluble initiator are too hydrophilic to be able to penetrate the polymer particles [320].

Surfactant-free emulsion polymerization are carried out in the absence of a surfactant [321]. The technique requires the use of initiators that yields initiating species with surface-active properties and imparts them to the polymer particles. Examples of such initiators are persulfates. The lattices that form are stabilized by chemically bound sulfate groups that are derived from persulfate ions. Because the surface-active groups are chemically bound, the lattices are easier to purify and free the product from unreacted monomer and initiator. Generally, the particle number per milliliter from a surfactant-free emulsion polymerization is smaller than the particle number from typical emulsion polymerization.

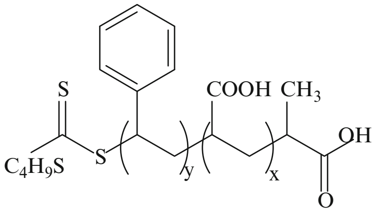
In an ***inverse emulsion polymerization*** an aqueous solution of a hydrophilic monomer is emulsified in an organic solvent and the polymerization is initiated with a solvent soluble initiator. This type of emulsion polymerizations is referred to as ***water in oil*** polymerization. Inverse emulsion polymerization is used in various commercial polymerizations and copolymerization of water-soluble monomers. Often nonionic emulsifiers are utilized. The product emulsions are often less stable than the oil in water emulsions.

A special approach to emulsion polymerization is called ***miniemulsion polymerization*** [322]. These reactions contain both micelles and monomer droplets, but the monomer droplets are smaller than in macrosystems. Usually, a water-soluble surfactant is used for emulsification. An example of such a surfactant can be sodium dodecyl sulfate. In addition, a highly water-insoluble costabilizer is added, such as hexadecanol. Thus, miniemulsions are dispersions of critically stabilized oil droplets with a size between 50 and 500 nm prepared by shearing a system containing oil, water, a surfactant and a hydrophobic material. Polymerizations in such miniemulsions, when carefully prepared, result in latex particles which have about the same size as the initial droplets. An appropriate formulation of a miniemulsion suppresses coalescence of droplets. The polymerization of miniemulsions extends the possibilities of the widely applied emulsion polymerization and provides advantages with respect to copolymerization reactions of monomers with different polarity, incorporation of hydrophobic materials or with respect to the stability of the formed latexes. Although labeled “emulsion,” it appears that some may involve a combination of emulsion and suspension polymerizations. It was reported [323] that by using a difunctional alkoxyamine as an initiator for the homopolymerization of butyl acrylate in miniemulsion, to increase the achievable molar mass and to use the polymer as a difunctional macroinitiator for the synthesis of triblock copolymers in aqueous dispersed systems. Well-defined polymers with one alkoxyamine functionality at each end were obtained, providing that monomer conversion was kept below 70%. Beyond this conversion, extensive broadening of the molar mass distribution was evidenced, as the consequence of termination and transfer to polymer.

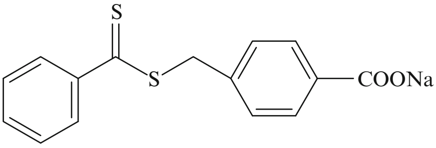
Tsavalas et al. [324] reported that a phenomenon seemingly unique to hybrid miniemulsion polymerization was observed by them, where monomer conversion would either plateau at a limiting value or quickly switch to a dramatically lesser rate. They attributed this phenomenon to a combination of three factors. The first one is the degree to which the monomer and resinous component are compatible. The second is the resultant particle morphology after approximately 80% monomer conversion, which roughly corresponds to the portion of reaction where this morphology is established. The third factor is the degree of interaction between the growing polymer and the resin (a grafting reaction). Of these three, the first two factors were found by them to be much more significant in contributing to the limiting conversion.

RAFT emulsion polymerization is a new development that has attracted considerable attention. It be carried out in a regular emulsion polymerization [325] and in a reverse emulsion polymerization [326].

Also, recently, several reports in the literature have described miniemulsion RAFT polymerizations. In some instances, use is made of water-soluble RAFT agents to control polymer molecular weight [327]. Also, Hawkett and coworkers reported using surface active RAFT agents to emulsify the dispersed phase, stabilize the particles and also control the molecular weight. This yielded polymer latexes that were free from surfactant and costablilizer [328]. One of these special RAFT agents was illustrated as follows:



The other two RAFT agents used by them had similar structures. A surface active iniferter was also reported by Choe and coworkers [330, 331]:



This RAFT agent allowed polymerization of methyl methacrylate initiated by ultraviolet light irradiation in the absence of added surfactant or initiator.

Rieger and coworkers [332] reported a surfactant free RAFT emulsion polymerization of butyl acrylate and styrene using poly(*N*,*N*-dimethylacrylamide) trithiocarbonate macromolecular transfer agent. They observed that the polymerizations were fast and controlled with molar masses that matched well the theoretical values and low polydispersity indexes. Monomer conversions close to 100% were reached and the polymerizations behaved as controlled systems, even at 40% solids contents. The products were poly(*N*,*N*-dimethyl acrylamide)-b-poly(*n*-butyl acrylate) and poly(*N*,*N*-dimethylacrylamide)-b-polystyrene amphiphilic diblock copolymers formed in situ.

Review Questions

Section 3.1

1. What are the three steps in free-radical polymerization? Illustrate each step in free-radical chain polymerization.
2. What is the rate-determining step in free-radical polymerization?
3. Write the kinetic expressions for initiation, propagation, termination, and transfer.
4. What is the steady state assumption? How is it expressed? Why is it necessary?
5. What is the expression for the rate of propagation? Rate of monomer disappearance? The average lifetime of a growing radical under steady state conditions?
6. Why is an initiator efficiency factor needed for the rate equation? What is a kinetic chain length?
7. In polymerization of styrene in benzene at 60°C using 0.1 mol benzoyl peroxide initiator and 1 mol of monomer, k_d is 1.38×10^{-5}, assume steady state and calculate the free-radical concentration during the reaction. If k_p is 176/mol what is the rate of propagation? What is the lifetime of a growing radical if k_t is 7.2×10^{-5}? What is the rate of propagation if the initiator efficiency is 72%?

Section 3.2

1. What sources of initiating free radicals do you know? Illustrate the decomposition reaction of α,α'-azobisisobutyronitrile. Illustrate how free radicals can recombine inside or outside the solvent cage and be lost to the initiation process.
2. Illustrate one or more inorganic and also one or more organic peroxides.
3. How does solvent "cage" affect the initiating free radicals? Explain and illustrate.
4. Explain homolytic and heterolytic cleavage of peroxides.
5. Explain and give chemical equations for *redox* initiations with Fe++, Co++, and Ce++++ ions in the reaction mixture.
6. How are peroxides such as benzoyl peroxide decomposed by aromatic tertiary amines. Show the two postulated mechanisms for the reaction of benzoyl peroxide with dimethyl aniline.

Section 3.3

1. Describe the reaction of the initiating free radical with the monomer. Show this reaction with equations, using a phenyl initiating radical and styrene monomer as an example.
2. Do the same as question 1, but with a redox mechanism, showing a sulfate ion-radical adding to vinyl acetate.

Section 3.4

1. Illustrate the transition state in the propagation reaction.
2. Explain the steric. polar and resonance effects in the propagation reaction.
3. Explain why there is a tendency for a *trans–trans* placement in the propagation reactions when carried out at low temperatures.
4. How does the reaction medium affect the propagation reaction?
5. What is ceiling temperature and what is the kinetic expression for this phenomenon?
6. Explain what is meant by autoacceleration and how does it manifest itself.
7. What is cyclopolymerization? Explain and give several examples.

Section 3.5

1. What are the three termination processes in free-radical polymerization?
2. What is meant by degenerative chain transferring? Illustrate back-biting. The telomerization reaction.
3. What is meant by chain transferring constants?
4. Write the equation for the degree of polymerization including all the chain transferring constants. In a benzoyl peroxide initiated polymerization of 2 moles of styrene in benzene at 85°C ($K_d = 8.94 \times 10^{-5}$ L/mol-s at 85°C). How much benzoyl peroxide will be required in the polymerization solution to attain an average molecular weight of 250,000? Assume that termination occurs only by recombination and no chain-transferring takes place.

5. In the above polymerization, the transferring constant to monomer, $C_M \times 10^{-4} = 3.74$, the transferring constant to solvent, $C_S = 5.6 \times 10^{-4}$ and transferring constant to the initiator, $C_I = 0.75$. Assuming that $f = 0.72$, and k_t is 7.2×10^{-5}, k_p is 176/mol, (k_d is shown above) calculate R_p and the average DP.

Section 3.6

1. Explain what is meant by reactivity ratios and how they are derived.
2. Write the copolymerization equation. In a copolymerization of 1 mol of styrene with 1 mol of butadiene, $r_1 = 0.78$ and $r_2 = 1.39$, what is the expected composition of the copolymer at the early stages of the polymerization?
3. How do substituents on the monomer molecules affect reactivity of the monomers toward attacking radicals?
4. Explain the *Q* and *e* scheme and write the Price–Alfrey equation.
5. How can r_1 and r_2 be derived from the *Q* and *e* values. Show the relationship.
6. From chemical structures alone predict the products from free-radical copolymerizations of pairs of (1) styrene and methyl methacrylate, (2) styrene and vinyl acetate, (3) methyl methacrylate and vinyl chloride. Consult Table 3.8 for reactivity ratios.

Section 3.7

1. How many reactivity ratios are there in a terpolymerization?
2. Write the equation for the terpolymerization reaction.

Section 3.8

1. What is allylic polymerization? If allyl alcohol does not polymerize to a high-molecular-weight polymer by free-radical polymerization, why does triallyl cyanurate form a high-molecular-weight network structure by the same mechanism?

Section 3.9

1. What is inhibition and retardation? Explain.
2. Give an example of a good inhibitor and a good retarder and show by chemical equations the reaction with free radicals.
3. Show the reaction of quinone with free radicals.
4. Write the equation that relates rate data to inhibited polymerizations.
5. Calculate R_p for the polymerization of 1 mol of styrene containing 0.01 mol of hydroquinone inhibitor. with $k_p = 176$/mol and $k_t = 7.2 \times 10^{-5}$.

Section 3.10

1. What is thermal polymerization? Show by chemical equations the postulated mechanism of formation of initiating radicals in styrene thermal polymerization.

Section 3.11

1. Show the proposed charge-transfer mechanism for copolymerization of styrene with maleic anhydride and dioxene with maleic anhydride.
2. What determines the stability of charge-transfer complexes? Explain and give examples.

Section 3.12

1. How do some polar monomers complex with Lewis acids? How does that affect polymerization of these monomers? Copolymerization?

Section 3.13

1. How can canal complexes be used for steric control in free-radical polymerization? Give examples.

Section 3.14

1. How do controlled/"living" polymerizations differ from typical living polymerizations?
2. List the different types of controlled/"living" free-radical polymerizations that you can think of. What are the three classes of homogeneous controlled/"living" polymerizations as described by Matyjaszewski? Illustrate.
3. Describe cobalt mediated polymerizations. Illustrate.
4. Describe and illustrate atom transfer polymerizations controlled by copper/bipyridine complex and by carbon tetrachloride, dichloro(triphenyl-phosphine)-ruthenium(II), and methylaluminum bis(2,6-di-*tert*-butyl-phenoxide). Explain what (*ARGENT*)*ATRP* and (SET-*LRP*) mean. Illustrate the proposed Percec mechanism and the Matyjaszewski mechanisms.
5. Describe nitroxyl radical mediated polymerizations. Illustrate TEMPO controlled polymerization of styrene. What is meant by in situ NMP?
6. Explain and illustrate a reversible addition-fragmentation chain transfer polymerization (RAFT).
7. Write the Matyjaszewski proposed kinetic equation of ATP polymerization.

Section 3.15

1. What is meant by bulk or mass polymerization? Explain and discuss.
2. What are some of the techniques for carrying out solution polymerizations?
3. Give a qualitative picture of emulsion polymerization as described by Harkins.
4. How did Smith and Ewart put the Harkins picture of emulsion polymerization on a quantitative basis? What is the equation for the rate of emulsion polymerization?
5. Describe a surfactant-free emulsion polymerization, and inverse emulsion polymerization and a miniemulsion polymerization.

Section 3.16

1. Discuss the effect of monomer structure on the thermodynamics of the free-radical polymerization process.

Recommended Reading

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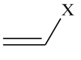
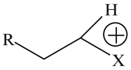
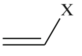
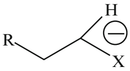
Chapter 4
Ionic Chain-Growth Polymerization

4.1 The Chemistry of Ionic Chain-Growth Polymerization

Ionic polymerization can be either cationic or anionic. This difference stems from the nature of the carrier ions on the growing polymeric chains. If in the process of growth, the chains carry positive centers, or carbon cations, the mechanism of chain growth is designated as ***cationic***. On the other hand, if the growing chains carry negative ions, or carbanions, then the polymerization is designated as ***anionic***.

The two different modes of polymerization can be compared further by examining the two types of initiation. The cationic ones occur by electrophilic attacks of the initiators on the monomers. Conversely, the anionic-ones take place by nucleophilic attacks. The two reactions can be shown as follows:

Type of Reaction	Reagent	Monomer	Transition State
Electrophilic addition	$R^{\oplus}$ +		→ 
Nucleophilic addition	$R^{\ominus}$ +		→ 

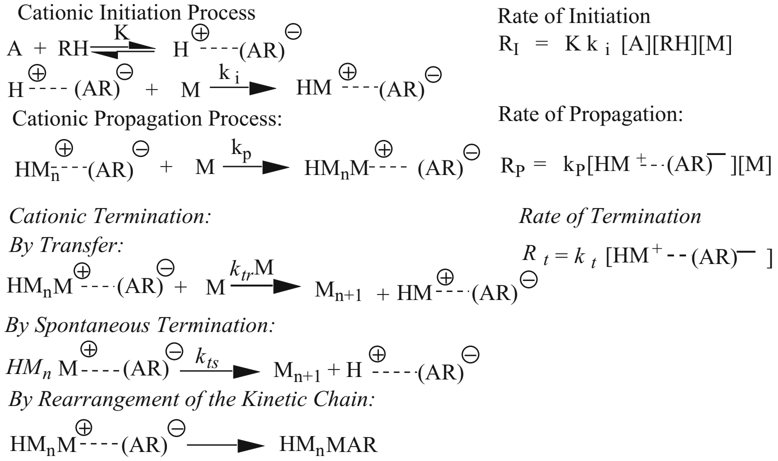
Generally, the ionic polymerizations depend upon initial formations of positive and negative ions in an organic environment. Propagations in these chain reactions take place through successive additions of monomeric units to the charged or “reactive” terminal groups of the propagating chains [1].

The transition states for the steps of propagation are formed repeatedly in liquid medium systems, containing monomer, initiator, the formed polymer, and frequently a solvent. There are many different types of initiating reactions. These polymerization, however, never terminate by combination or by disproportionation as they do in free-radical chain-growth polymerizations. Instead, terminations of chain growths are results of unimolecular reactions, or transfers to other molecules, like monomers or solvents, or impurities, like moisture. They can also result from quenching by deliberate additions of reactive terminating species.

A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_4,

4.2 Kinetics of Ionic Chain-Growth Polymerization

The kinetic picture of ***cationic chain polymerization*** varies considerably. Much depends upon the mode of termination in any particular system. A general scheme for initiation, propagation, and termination is presented below [1, 2]. By representing the coinitiator as A, the initiator as RH, and the monomer as M, we can write:



In the above expressions, $[\mathrm{HM}^{+}\text{——}(\mathrm{AR})^{-}]$ represents the total concentration of all the propagating ion-pairs; and K is the equilibrium constant for the formation of initiating cations. When a steady state exists, the rates of initiation and termination are equal to each other:

$$[\mathrm{HM}^{+}\ldots\ldots(\mathrm{AR})^{-}] = Kk_{\mathrm{i}}[\mathrm{A}][\mathrm{RH}][\mathrm{M}]^{2}/k_{\mathrm{t}}$$

The rate of propagation can be written as:

$$R_{\mathrm{P}} = Kk_{\mathrm{i}}k_{\mathrm{t}}[\mathrm{A}][\mathrm{RH}][\mathrm{M}]^{2}/k_{\mathrm{t}}$$

The number average degree of polymerization is equal to:

$$\overline{\mathrm{DP}} = \frac{R_{\mathrm{p}}}{R_{\mathrm{t}}} = \frac{k_{\mathrm{P}}[\mathrm{M}]}{k_{\mathrm{t}}}$$

During the reaction terminations can occur by transferring to a monomer or to a chain transferring agent S. Termination can also occur by spontaneous termination or by combination with the counterion. If S is relatively small the number of propagating chains will remain unchanged. The degree of polymerization will then be decreased by the chain-breaking reactions. The number average degree of polymerization becomes:

$$\overline{\mathrm{DP}} = \frac{R_{\mathrm{p}}}{R_{\mathrm{t}} + R_{\mathrm{ts}} + R_{\mathrm{tr,M}} + R_{\mathrm{tr,S}}}$$

The rates of the two transfer reactions, to a monomer or to a transferring agent (S), as well as spontaneous terminations can be written as:

$$R_{\mathrm{tr,M}} = k_{\mathrm{tr,M}}[\mathrm{HM}^{+} \text{ - - - - - } (\mathrm{AR})^{-}][\mathrm{M}]$$
$$R_{\mathrm{tr,S}} = k_{\mathrm{tr,S}}[\mathrm{HM}^{+} \text{ - - - - - } (\mathrm{AR})^{-}][\mathrm{S}]$$
$$R_{\mathrm{ts}} = k_{\mathrm{ts}}[\mathrm{HM}^{+} \text{ - - - - - } (\mathrm{AR})^{-}]$$

The number average degree of polymerization is then:

$$\overline{\mathrm{DP}} = k_{\mathrm{p}}[\mathrm{M}]/(k_{\mathrm{t}} + k_{\mathrm{tr,M}} + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{ts}})$$

The above can be rearranged to be written as follows:

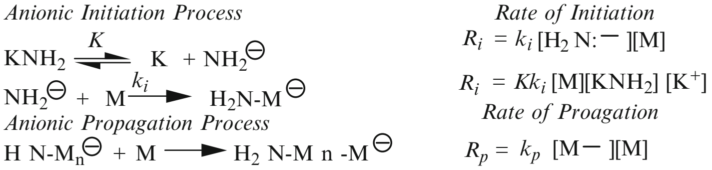
$$1/\overline{\mathrm{DP}} = k_{\mathrm{t}}/k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{ts}}/k_{\mathrm{p}}[\mathrm{M}] + \mathrm{C_M} + \mathrm{C_S}[\mathrm{S}]/[\mathrm{M}]$$

where $\mathrm{C_M}$ and $\mathrm{C_S}$ are the chain transferring constants for the monomer, and S is the chain transferring agent. Here $\mathrm{C_M} = k_{\mathrm{tr,M}}/K_{\mathrm{p}}$ and $\mathrm{C_S} = k_{\mathrm{tr,S}}/k_{\mathrm{p}}$. When a chain transferring agent is present and chain growth is terminated,

$$R_{\mathrm{p}} = Kk_{\mathrm{i}}Kk_{\mathrm{p}}[\mathrm{A}][\mathrm{RH}][\mathrm{M}]^2/(k_{\mathrm{t}} + k_{\mathrm{tr,S}}[\mathrm{S}])$$

The validity of the steady-state assumption in many cationic polymerizations may be questioned, because many reactions occur at such high rates that a steady state is not achieved. Nevertheless, the above equations were shown to be generally followed [3, 4].

The kinetic picture of *anionic chain polymerization* also depends mostly upon the specific reaction. For those that are initiated by metal amides in liquid ammonia the rate of initiation can be shown to be as follows:



where $[\mathrm{M}^-]$ represents the total concentration of propagating anions. If there is a termination reaction and it takes place by transfer to a solvent, the rate of transfer can be written:

$$R_{\mathrm{tr}} = K_{\mathrm{tr,S}}[\mathrm{M}^-][\mathrm{NH_3}]$$

When steady state conditions exist,

$$R_{\mathrm{P}} = \frac{Kk_{\mathrm{i}}k_{\mathrm{p}}[\mathrm{M}]^2[\mathrm{KNH_2}]}{k_{\mathrm{tr,S}}[\mathrm{K}^+][\mathrm{NH_3}]}$$

If the quantities of potassium and amide ions are equal, which is the normal situation, then a somewhat different expression can be written:

$$R_{\mathrm{i}} = k_{\mathrm{i}}K^{1/2}[\mathrm{M}][\mathrm{KNH_2}]^{1/2}$$

$$R_{\mathrm{p}} = \frac{k_{\mathrm{i}}K^{1/2}k_{\mathrm{p}}[\mathrm{M}]^2[\mathrm{KNH_2}]^{1/2}}{k_{\mathrm{tr,S}}[\mathrm{NH_3}]}$$

In non-terminating or “living” polymerizations, the rate of propagation can be written as:

$$R_{\mathrm{P}} = k_{\mathrm{p}}[\mathrm{M}^-][\mathrm{M}]$$

and the rate of living polymerization is

$$-\,\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{P_n}^*][\mathrm{M}]$$

When the effect of the medium is such that the propagation takes place both, with ion pairs and with free-propagating ions, the rate of propagation is written as follows [4, 5]:

$$R_\mathrm{p} = k_\mathrm{p}{}^{-}\ldots\mathrm{C}^{+}[\mathrm{P}^{-}\ldots.\mathrm{C}^{+}][\mathrm{M}] + k_\mathrm{p}[\mathrm{P}^{-}][\mathrm{M}]$$

where, $k_\mathrm{p}{}^{-}\ldots\mathrm{C}^{+}$ and $k_\mathrm{p}{}^{-}$ are rate constants for the propagation of the ion pairs and the free-ions, respectively. C^{+} is the positive counterion, $\mathrm{P}^{-}\ldots.\mathrm{C}^{+}$ and P^{-} are the concentrations of the two propagating species, and [M] is the monomer concentration.

The number average degree of polymerization of a living polymer is shown as follows:

$$\text{Ave. DP} = [\mathrm{M}]/[\mathrm{M}^{-}]$$

It is simply a ratio of the concentration of the monomer to the number of living ends.

A model was developed for a unified treatment of the kinetics of both cationic and anionic polymerizations [6]. It is based on a system of kinetic models that cover various initiation and propagation mechanisms and on a pseudosteady-state assumption. The treatment is beyond the scope of this book.

The principal kinetics of propylene polymerization with a magnesium chloride supported Ziegler–Natta catalyst was also developed [7]. The polymerization rate is described by a Langmuir—Hinshelwood equation showing the dependence of the rate on the concentration of the aluminum alkyl:

$$R_\mathrm{P} = Kk_\mathrm{A}[\mathrm{A}]/(1 + k_\mathrm{A}[\mathrm{A}])^2$$

where $[\mathrm{A}] = [\mathrm{AlR_3}]$.

Because the polymerization rate is first order with respect to the concentration of the monomer, the rate equation can be written as follows [7]:

$$R_\mathrm{P} = k_\mathrm{p}[\mathrm{M}]k_\mathrm{A}[\mathrm{A}]/(1 + k_\mathrm{A}[\mathrm{A}])^2$$

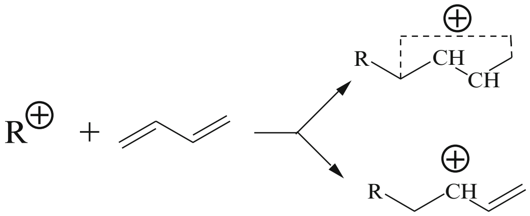
4.3 Cationic Polymerization

As mentioned, in cationic polymerizations the reactive portions of the chain ends carry positive charges during the process of chain growth. These active centers can be either unpaired cations or they can be cations that are paired and associated closely with anions (counterions).

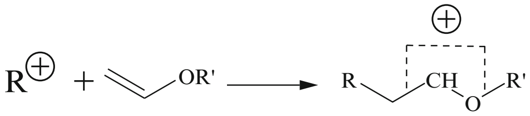
The initiations result from transpositions of electrons, either as pair or as single one. A two-electron transposition takes place when the initiating species are either protons, or carbon cations. Ion generations take place through heterolytic bond cleavages or through dissociations of cationic precursors. Such initiating systems include Lewis acid/Bronsted acid combinations, Bronsted acids by themselves, stable cationic salts, some organometallic compounds, and some cation forming substances.

When, however, initiations take place by one electron transposition, they occur as a direct result of oxidation of free radicals. They can also take place through electron transfer interactions involving electron donor monomers. The carbon cations can form from olefins in a variety of ways. One way is through direct additions of cations, like protons, or other positively charged species to the olefins. The products are secondary or tertiary carbon cations:

When the cations add to conjugated dienes, the charges can be distributed over several centers in the products



The charge may also be distributed in polar monomers like, for instance, in vinyl ethers:



Chemical considerations indicate that the more diffuse the charges the more stable are the ions.

Cationic polymerizations are not affected by common inhibitors of free-radical polymerizations. They can, however be greatly influenced by impurities that can act as ion scavengers. These can be water, ammonia, amines, or any other compounds that can be basic in character, affecting rates and molecular weights of the products. Typical cationic polymerizations proceed at high rates even at low temperatures, as low as −100°C [8]. In the literature one can find many reports of cationic polymerizations of many different monomers with many different initiators. Often, however, such initiators are quite specific for individual monomers and their activities are strongly influenced by the solvents.

The initiation processes can be summarized as follows:

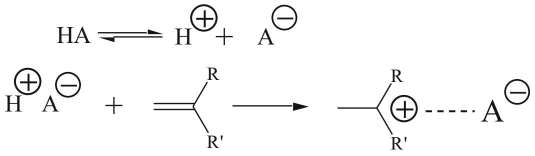
I. Initiation by chemical methods
  A. Two electron transposition (heterolytic) initiation by reactions with:
    1. Protonic acids
    2. Lewis acids
    3. Stable carbon cations
    4. Certain metal alkyls
    5. Cation forming substances
  B. One electron transposition (homolytic) initiations by reactions of:
    1. Direct oxidation of radicals
    2. Cation-radicals formed through charge-transfers
II. Initiation by physical methods
  A. Photochemically generated cations
  B. High-energy irradiation
  C. Electro initiation

4.3.1 Two Electron Transposition Initiation Reactions

The step of cationic initiation can be subdivided into two separate reactions [9]. The first one consists of formation of ionic species and the second one of reactions of these ionic species with the olefins, a cationization process. This reaction, termed “priming” by Kennedy and Marechal [9] is a process of ion formation in a non-nucleophilic media through: (1) dissociation of protonic acids to form protons and counterions, (2) through reactions of Lewis acids with Bronsted acids, (3) through dissociation of dimeric Lewis acids, (4) through complexation of Lewis acids with water or with alkyl halides or with ethers, and so on. These reactions may take place through a series of complicated steps. The second reaction, the cationization of the olefins may also include several intermediate steps that will eventually lead to propagating species.

4.3.1.1 Initiation by Protonic Acids

The ability of a proton from a protonic acid to initiate a polymerization depends upon the nucleophilicity of the conjugate base, A^- [10, 11]. If it is low, protonation or cationization of the olefin is a step of initiation [12]:

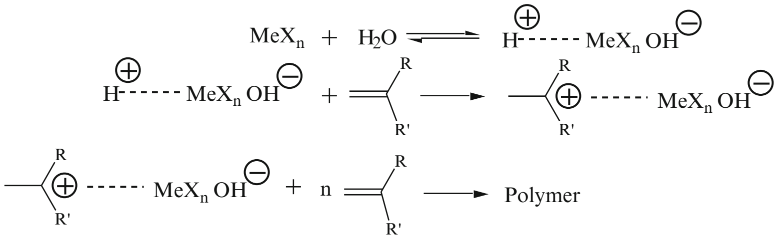


In protonic acids, where the complex anion assists ion generation, the acid may be considered as providing its own counterion, A^-. When such counterions are highly nucleophilic, then complexing agents such as metal salts, or metal oxides have to be used to immobilize the anions. Such complexing agents are in effect coinitiators.

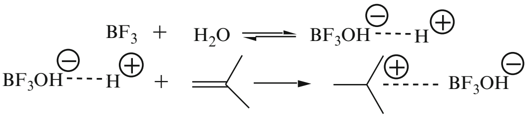
Thus, the differences in activities of protonic acids are due to the quality of the corresponding anion or to its tendency to form chemical bonds with the carbon cation. If the anion is unable to form such bonds without extensive regrouping or decomposition, the addition of the proton is followed by polymerization. Should the reactivity of the anion be suppressed by solvation, the tendency to polymerize is enhanced. Consequently, the efficiencies of protonic acids depend very much upon the polarities of the media and upon the reaction conditions [12, 13]. Also, the stronger the protonic acid the higher the reaction rate and the resultant degree of polymerization [14]. Generally, hydrogen halide acids do not initiate polymerizations of alkyl-substituted olefins. They may, however, initiate polymerizations of aryl-substituted olefins and vinyl ethers in polar solvents. The same is true of sulfuric acid [15].

4.3.1.2 Lewis Acids in Cationic Initiations

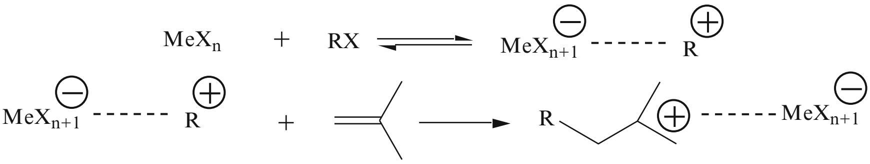
Complexation of Lewis acids with water is another case of formation of electrophiles that can initiate chain growth. MeX_n represents a Lewis acid



The above can be shown on boron trifluoride initiation of the polymerization of isobutylene:



In the same manner, a reaction of a Lewis acid with an alkyl halide and subsequent initiation can be illustrated as follows:

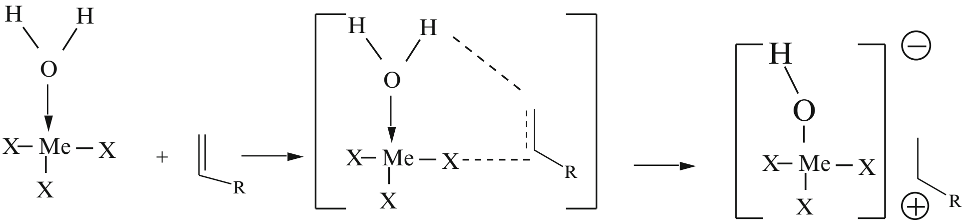


In the above shown examples the Lewis acid is actually the ***co-initiator*** and the water or the alkyl halide are the ***initiators***.

Numerous studies confirm the need by many Lewis acids for other molecules like, water or alkyl halides to form initiating ions. For instance, pure $TiCl_4$ will not initiate the polymerization of isobutylene [16, 17]. This led many to believe that none of the Lewis acids are capable of initiating cationic polymerizations of olefins by themselves [18]. Subsequent investigations, however, demonstrated [28, 30] that some strong Lewis acids, are capable of initiating such polymerizations.

Whether a Lewis acid is capable of initiating these polymerizations by itself was tested with the aid of an early discovery. It has been known for some time that hindered bases like crowded pyridine derivatives exhibit specificity toward reactions with protons [19]. Such bases might be used to discriminate between two types of initiating mechanisms encountered with Lewis acids [20]. The base will not interfere with direct electrophilic additions of the Lewis acids to the monomer. On the other hand, it should prevent an initiation process by protons from taking place. If both pathways are operative, then the pyridine derivatives can only quench the protonic initiation and will offer a means of assessing the relative importance of each process.

Kemedy et al. investigated polymerizations initiated by Lewis acids–water in the presence of one such "proton trap," 2,6-di-*t*-butylpyridine [21]. The presence of this base markedly decreased conversion from almost 100%, in some cases, to only a few percent. At the same time, there was a marked increase in the molecular weight and a narrowing of the molecular weight distribution of the products. This shows that the protonic reaction is by far the most important mode of initiation. It also suggested to Kemedy et al., that not all the protonic initiations occur exclusively by free protons. They might also proceed through concerted protonations. These would not be blocked by the "proton traps" [21]:



where, MeX_3 represents a Lewis acid. The di-*t*-butyl pyridine does not block the above reaction due to steric compression. It also suggested that protonic initiations by water in the presence of Lewis acids are probably unlikely when sufficient quantities of materials that act as "proton traps" are present.

This was felt to be true even in polar media [21]. Sigwalt and coworkers, however, disputed that [28]. They based their opinions on cationic dimerizations of 1,1-diphenylethylene with $\mathrm{AlCl_3{-}H_2O}$ in the presence of 2,6-di-*t*-butyl-4-methylpyridine. The results suggested to them that sterically hindered amines do not inhibit co catalytic initiation by $\mathrm{AlCl_3}^{-}\mathrm{H_2O}$. Also, that the free hindered amine is a powerful terminating agent and that the sterically hindered pyridine forms a strong complex with $AlCl_3$. When engaged in a complex with $AlCl_3$ the reactivity of the hindered amine in termination is much reduced [28].

Alkyl halide solvents in the polymerization reaction mixture may cause an initiation to result from a transfer of $AlX_2{}^{\oplus}$ or $(RX)AlX_2{}^{\oplus}$ to the more basic monomer [23]:

$$2AX_3 + 2RX \rightleftharpoons AlX_2\bullet(RX)_2{}^{\oplus} + A1X_4{}^{\ominus}$$

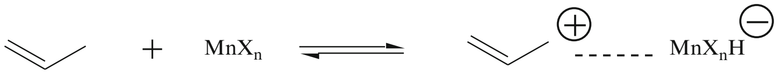
$$\underset{\text{(monomer)}}{(RX)_2A1X_2{}^{\oplus}} + M \longrightarrow RX\bullet X_2A1M^{\oplus} + RX$$

where X = halogen; R = alkyl.

In summarizing the initiation mechanism by complexed Lewis acids [24], the catalysts must be present in the reaction mixture in three forms: (1) as ionized molecules, (2) as ion pairs, and (3) as free ions. All three forms are in equilibrium. When the monomer is introduced, it complexes with some of the ionized molecules and a new equilibrium is established. Additional ion pairs form by a slow process. This depends upon a change in the monomer concentration [25].

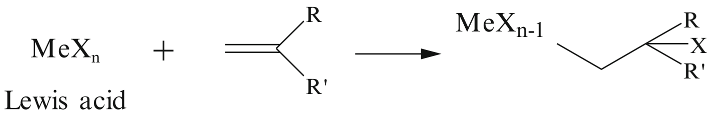
Some strong Lewis acids are actually capable of initiating carbon cationic polymerizations without a co-catalyst. As a result, many mechanisms were offered to explain the reaction paths of initiations by Lewis, like aluminum halides and some others, without the aid of any co-reactant. Following are some more prominent ones.

One mechanism [26] was based on an observation that olefins with allylic hydrogens like isoprene, methyl styrene, indene, and cyclopentadiene can be polymerized by super dry, pure Lewis acids, alone. This led to a suggestion that the process may involve an allylic self-initiation [26]:

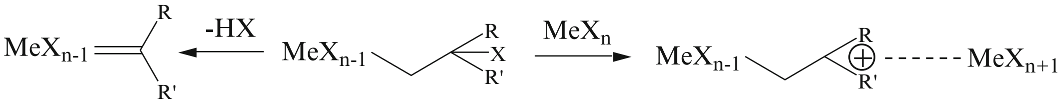


The above suggested mechanism can only apply to polymerizations of monomers with allylic hydrogens. Also, it is contradicted by the ability of 1,1-diphenylethylene to dimerize in a super dry system in the presence of aluminum halides. Yet, this compound lacks allylic hydrogens [27].

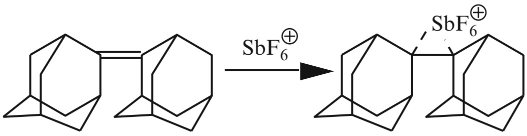
Two other very similar mechanisms [28] are based on a concept that initiation takes place by a process of halometalation:



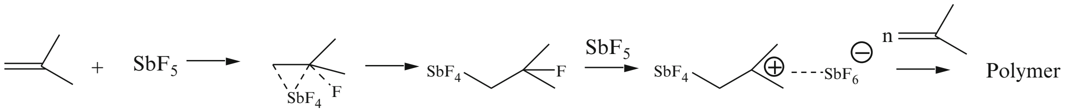
Depending upon the substituents on the olefins, the metal organic compound may ionize in the presence of a second molecule of a Lewis acid, or it may eliminate HX:



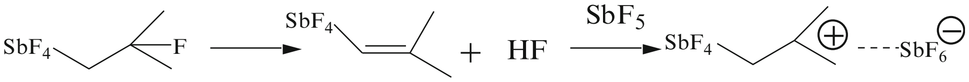
The above mechanism [29] is based on an observation that strong Lewis acids can form stable molecularly bound complexes with hindered alkenes, as for instance with adamantyladamantane:



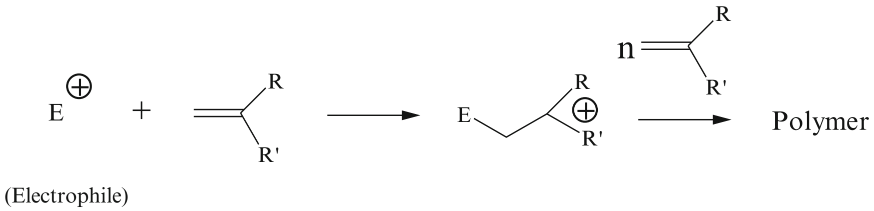
The carbon cation, which forms, from the above shown complex, actually cannot initiate a cationic polymerization of excess alkene molecules that are present in the reaction mixture, due to steric hindrance [29, 31]. The less hindered alkenes, however, like isobutylene polymerize rapidly under the same conditions with antimony pentafluoride. It was, therefore, suggested [29, 31] that initiation involves an opening of a previously formed π complex of SbF_5 with the double bond, through halide participation. The α,β-haloalkylantimony tetrafluoride ionizes with excess Lewis acid to form a related carbon cation and is capable of initiating cationic chain growth:



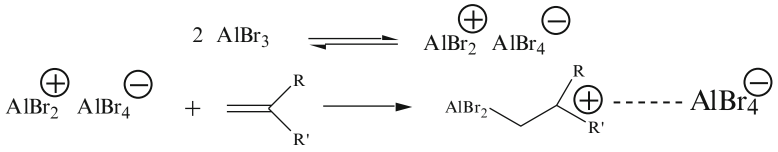
Alternately, the intermediate could be shown as splitting of HF that can then react with another molecule of Lewis acid, because the metalated alkene is a tertiary halide and can eliminate hydrogen halide:



The initiation mechanism of olefins by AlB_3 was explained similarly [29]. The intermediate compound of aluminum bromide and the olefin is expected to lose HBr. Although initially the reaction mixture is free from protonic acid, it could form under conditions where initiation takes place by a conjugate acid catalyzed system. In addition, all cationic polymerizations of olefins should be considered as typical examples of general carbocationic reactivity in electrophilic reactions [29]. The separate mechanisms are to be looked upon as various examples that differ only in the nature of the initial electrophile. They always lead to the related trivalent alkyl cation when polymeric chain growth is initiated [29]:



Much of the evidence gathered to date, however, supports the concept of initiation due to auto ionization of Lewis acids. This was originally proposed in 1948 [30]. Lewis acids can aggregate, generally into dimers, and then auto ionize. The electrophilic portion adds to the olefin:



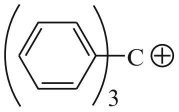
Afterwards, in 1965, a separate investigation [32] also led to the conclusion that the evidence does support the above mechanism. The additional data [33] shows that isobutylene can be polymerized by super dry, pure $AlBr_3$. At the same time, however, BF_3 and $TiCl_4$ require addition of water to initiate polymerizations of this monomer. Furthermore, the rate of $AlBr_3$ initiated polymerization of isobutylene is enhanced considerably by addition of other Lewis acids, like $SnCl_4$, $SbCl_5$, $TiCl_4$, and VCl_4 [34, 35]. Significantly, these Lewis acids by themselves are incapable of initiating polymerizations of isobutylene [16, 17]. It is believed, therefore, that mixed Lewis acids interact and generate ions that lead to rapid polymerizations.

There were many investigations of isobutylene [36] polymerization. The earlier ones yielded additional supporting evidence. In this study, aluminum chloride and bromide catalysts were used in alkyl halide solutions. The reaction was monitored by conductivity measurements and tritium radiotracer techniques. Conductivity changes during and after polymerization and unexchanged tritium in the polymer support the theory that initiation does take place by addition of $AlX_2^{\oplus}$ to the double bonds of the monomers. This results in formation of the carbon cations [36]. It was also observed [36] that: (1) Only a very small fraction of the aluminum halide is ionized. (2) "Active species" are formed from reactions of $AlX_2^{\oplus}$ with the double bonds and covalent bonds are formed between aluminum and carbon atoms. The cations that form start the polymerizations. Other cations may form from some impurities and may also act as initiators. The polymerizations that follow are terminated fairly rapidly because the concentration of the initiating cations is much smaller than the amount of aluminum halide. This explains the low efficiency of these particular initiators. Only a little polymer forms per mole of aluminum halide used. (3) Most of the unionized aluminum halide complexes with unreacted monomer molecules. These complexes do not act as initiators. The result is that the concentration of aluminum halide and the formation of $AlX_2^{\oplus}$ becomes very small and there is no further initiation. Such conclusions explain why yields are low when the reactions are started by additions of the initiator solutions to the monomers, but are high, however, when the monomers are added to the initiator solutions [36]. Faust et al. carried out a detailed kinetic investigation to compare polymerization rates of isobutylene with Et_2AlCl, $EtAlCl_2$, and $TiCI_4$. They demonstrated that $EtAlCl_2$ induced faster polymerizations than did $TiCI_4$ in hexanes/CH_3Cl at −80°C. Polymerization with $EtAlCl_2$ was also examined in dichloromethane or chloroform at low temperatures. The feasibility of living cationic polymerization with aluminum-based Lewis acids was examined in hexanes/CH_3Cl also at −80°C. $MeAlCl_2$ induced rapid and less controlled reactions were completed within 30 s. On the other hand, slow and well-controlled polymerizations took place with Me_2AlCl. Despite rapid reactions, product polymers had narrow molecular weight distributions [36].

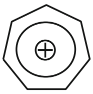
It is not clear why other Lewis acids like BCl_3 require water or other compounds and must be added to the monomer to obtain high conversions [37]. Boron trifluoride can initiate polymerizations of styrene, presumably by itself, in a methylene chloride solvent [38]. One explanation that was offered for the different behaviors of various Lewis acids is based on differences in the electronic configurations around the metal atoms [12].

4.3.1.3 Initiation by Stable Cations

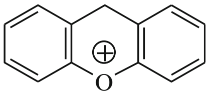
These initiations were originally reported by Bawn et al. [39]. The cations must be used in low concentrations to insure complete dissociation from their respective counterions. Stable organic cations can be formed from olefins, aromatic structures, or compounds with heteroatoms possessing unshared electrons, like oxygen, nitrogen, or sulfur. Some examples of stable cations that can initiate cationic polymerizations are [40]:



Triphenylmethyl ion



Cyclopentatrienyl
(tropylium) ion

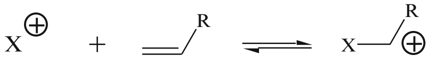


Xanthylium ion

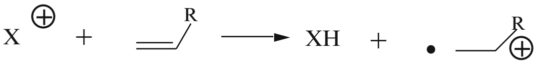
The above shown cations form crystalline salts with anions. These anions are ClO_4^-, $SbCl_6^-$, BF_4^-, PF_6^-, SbF_6^-, $FeCl_4^-$, and AsF_6^- [40].

The initiation reactions by stable cations, designated as ($X^{\oplus}$), may proceed by several possible mechanisms [41]:

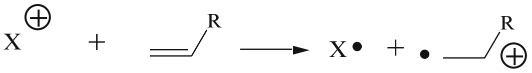
(A) By direct additions to unsaturated systems:



(B) By hydride abstractions:

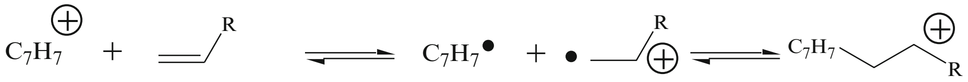


(C) By formations of cation-radicals through electron transfer or through some other mechanisms:

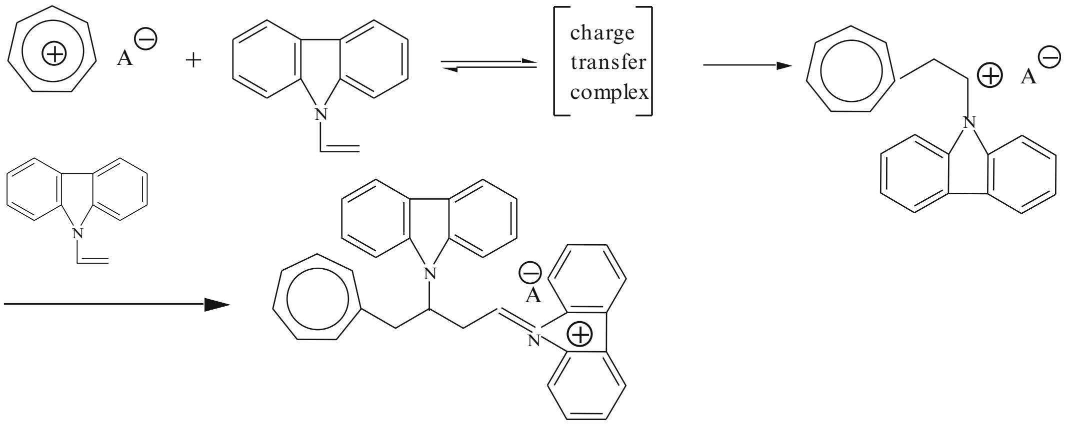


In (A) the reaction will predominate on the left-hand side. Exceptions appear to be olefins with strong electron releasing substituents that confer thermodynamic stability to the newly formed cation, ~CH_2–$CHR^{\oplus}$ [40]. This either results from a suitable charge delocalization over the π-electron system or from a presence of a heteroatom. Accordingly, only those olefins that possess relatively strong nucleophilic characteristics can be polymerized by stable carbon cations. Such olefins are alkyl vinyl ethers, *N*-vinyl carbazole, *p*-methoxystyrene, indene, and vinylnaphthalenes. Styrene and α-methyl styrene, however, will not polymerize, because they are less reactive.

The initiation mechanism, as suggested by Ledwith [40], follows the path of reaction (A) and is a result of a direct addition of the cation to the olefin. This is based on observations of the reaction of the xanthylium cation with 1,1-diphenylethylene. It is also based on the reaction of the tropilium cation with *N*-vinyl carbazole. The last may, perhaps, be influenced by steric factors. The high initiating efficiency of the tropilium ion, which has a stable six π-electrons system, may be a result of formation of a charge transfer complex [39]:



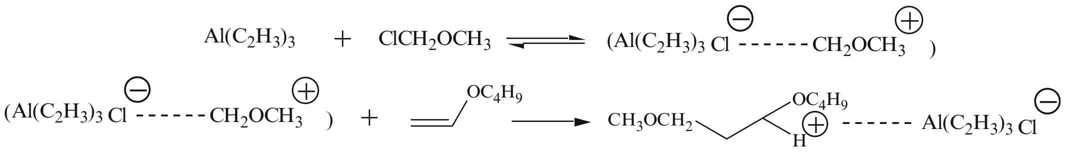
Based on the above, polymerization of *N*-vinylcarbazole can be shown as follows [40]:



4.3.1.4 Metal Alkyls in Initiations of Cationic Polymerizations

Initiations of polymerizations of vinyl and other monomers by metal alkyls generally take place by anionic mechanisms. This is discussed further in this chapter. There are, however, reports in the literature [41] of cationic polymerizations that are initiated by some metal alkyls. These are polymerizations of monomers like vinyl ethers, *o*- and *p*-methoxystyrene [42], and isobutylene [43, 44] that are initiated by compounds like dialkyl aluminum chloride.

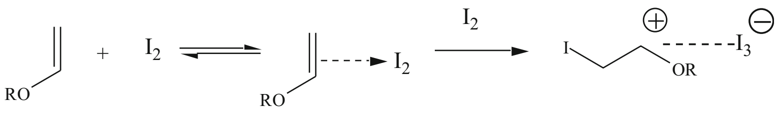
One explanation is as follows [45]. These metals are strong electron acceptors. Their valence shells and their unfilled orbitals can accommodate electrons from donor molecules. As a result, the organometallic compounds behave like Lewis acids. This was observed in a polymerization of isobutyl vinyl ether [46]. While triethylaluminum is not by itself an initiator for the polymerizations, the reactions will take place in the presence of typical electron acceptors [45]:



The catalyst components must be combined in the presence of the monomer. This is due [45] to high instability of the carbon cation complexes $[Al(C_2H_5)_3Cl]^-$ $[CH_3OCH_2]^+$. It is interesting that the polymerizations by $C_2H_5AlCl_2{}^{-}H_2O$ also show rate decreases as the reaction progresses [47]. When, however, additional water is added, rapid polymerizations start again [47].

It is possible to modify the catalytic activity of metal alkyls by controlled additions of ***modifiers***. These are water, alcohol [45], oxygen [48], carbon dioxide [49], aldehydes [50], organic peroxides [45], and metal oxides, like V_2O_5, NiO, and HgO [45]. The exact action of these modifiers is not clear and it is not certain if they should be considered to be co-initiators or initiators. Their addition, however, can affect catalytic activity, yield, stereospecificity, and molecular weight of the products. Oxygen, for instance, can act as a modifier for the Grignard reagent, which by itself does not initiate cationic polymerizations of vinyl ethers. Yet, introduction of oxygen to a vinyl ether-Grignard reagent system will initiate the polymerization and will yield high molecular weight products [50]. It was suggested [45] that oxygen may cause transformation of the alkyl magnesium groups into N alkoxy magnesium groups. This results in greater concentrations of magnesium dihalides that can induce the polymerizations.

Substances that generate cations can vary widely. They can be molecules that dissociate into ions or react with other compounds like solvent or monomer to form cations. Iodine is an example of such a substance. In a system of *n*-butyl vinyl ether-iodine-diethyl ether, the iodine apparently first forms an inactive π-complex with the solvent. It subsequently dissociates and rearranges into an isomeric active ion [12]:

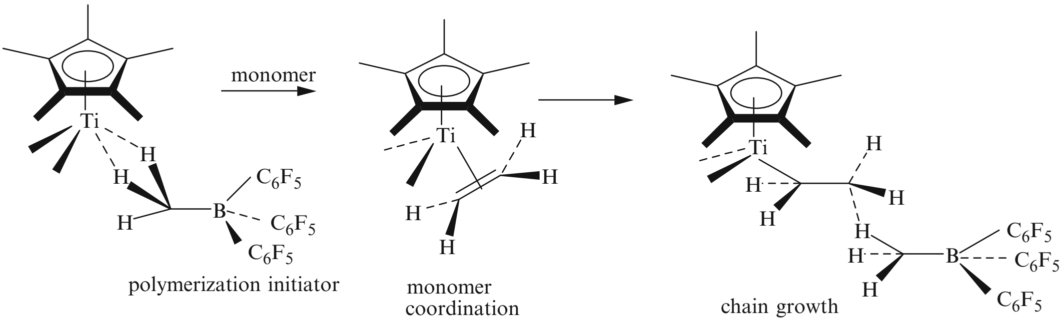


Another group of compounds that were recently reported as capable of initiating cationic polymerizations are metallocene/borate complexes. Such material can, for instance, be generated from zirconocene dimethyl compounds (Cp_2ZrMe_2) and anilinium borate. Thus, $[HNMe_2Ph]$ + $[B(C_6H_5)_4]$ will polymerize amine-functionalized α-olefins [51] as well as isobutylene homo and copolymerizations [52]. Also, when compounds, like Cp^*MMe_3 (M = Ti, Zr, and Hf; where

$Cp^* = \eta^5$-pentamethylcyclopentadienyl) are reacted with $B(C_6F_5)_3$, a methyl cation is abstracted and a complex forms, as shown below:

$$Cp^*TiMe_3 + B(C_6F_5)_3 \rightarrow [Cp^*TiMe_2{}^+][MeB(C_6F_5)_3{}^-]$$

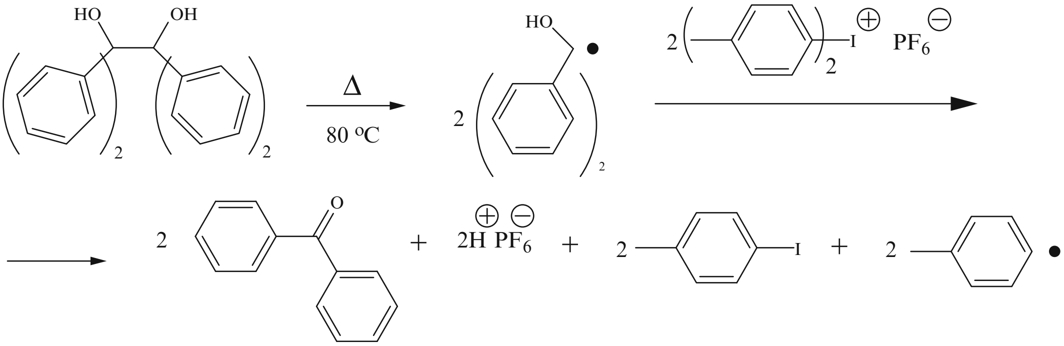
Evidence has now been presented that indicates that the above compound behaves as a carbocationic polymerization initiator for styrene, *N*-vinylcarbazole, vinyl ethers, and isobutylene. The mechanism of initiation and polymerization of these monomers by such metallocene complexes is still being investigated. It was suggested by Wang et al. [53], that the mechanism of carbocationic polymerization of such olefins by the above complex would involve coordination of the olefins, as shown below, in a nonclassical η^1-fashion, with the metal-olefin. This interaction is stabilized by a complementary borate–olefin interaction. The next step in the polymerization process by this mechanism, then involves attack on the carbocationic centers of the metal ions-activated olefin molecules by secondary olefin monomers, followed by chain growth [53]:



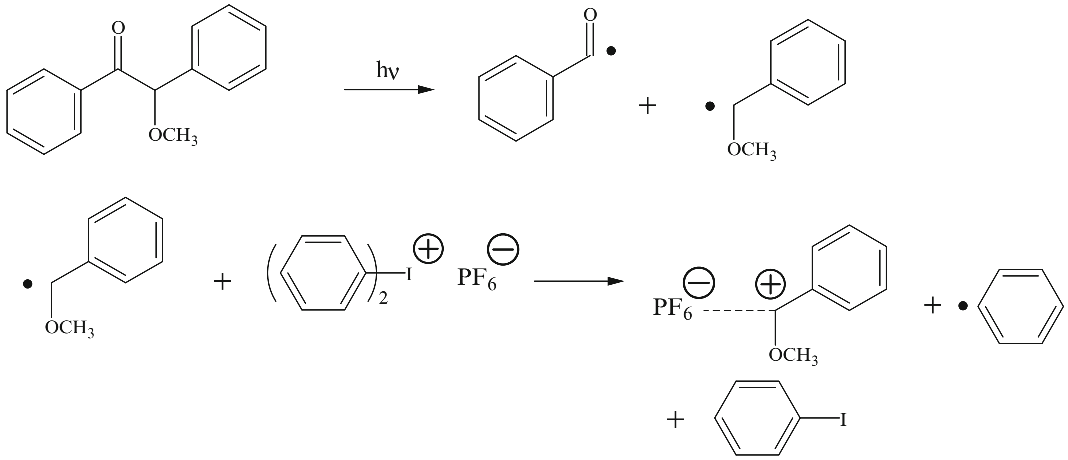
4.3.2 One Electron Transposition Initiation Reactions

Some ***radical sources***, will, in the presence of oxidizing agents, or light, or heat energy, initiate cationic polymerizations of monomers, like *n*-butyl vinyl ether. Those that are most readily oxidized are carbon atom centered radicals that have substituents like benzyl, allyl, alkoxy, or structures with nitrogen or sulfur. Also, radicals that are formed by addition of other radicals to alkyl vinyl ethers are particularly reactive.

Oxidants that can be used in these reactions are salts, like $(C_6H_5)_2I^+PF_6{}^-$. Such salts oxidize the radical and also supply the counter-ions, as shown below [54]:



What happens to the final radical is uncertain. High conversions were reported in polymerizations of *n*-butyl vinyl ether in the presence of azobisisobutyronitrile (as a source of radicals) with $(p\text{ - tolyl})_2\text{–}I^{\oplus}PF_6^{\ominus}$ at 50°C [55]. The above is an illustration of a thermal process [12]. Free radicals can also be generated with the aid of UV light. This, for instance, was done with a UV light decomposition of benzoin methyl ether in the presence of an oxidizing salt [56]:



4.3.2.1 Charge Transfer Complexes in Ionic Initiations

Formations of copolymers by charge transfer mechanisms in free-radical polymerizations are discussed in Chap. 3. Reactions between donor and acceptor molecules, however, can also result in some charge transfers that yield ion-radicals and subsequent polymerization by ionic mechanism:

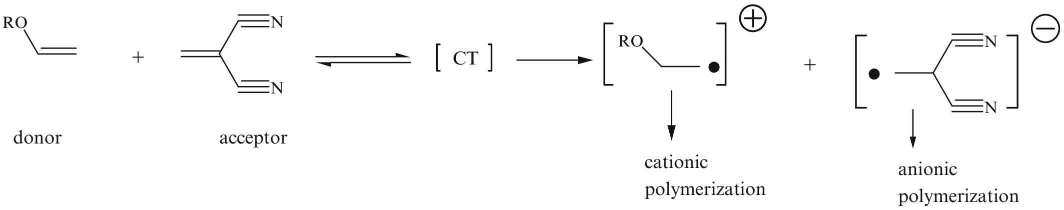
$$D + A \rightleftharpoons \underset{\text{ground state}}{[DA \longleftrightarrow \overset{\oplus}{D}{\bullet}\ \overset{\ominus}{A}{\bullet}\,]} \rightleftharpoons \underset{\text{excited state}}{[\overset{\oplus}{D}{\bullet}\ \overset{\ominus}{A}{\bullet} \longleftrightarrow DA]}$$

The nonbonding form predominates in the ground state while the charge transfer predominates in the excited state. The energy separation between the ground state and the first excited state is small. If the ionization potential of the donor molecule is low and the acceptor molecule has a strong electron affinity, transfer of an electron can occur to a significant extent even in the ground state. Mutual oxidation–reduction takes place:

$$D + A \rightleftharpoons \text{complex} \rightleftharpoons [D^{\bullet\oplus} + A^{\bullet\ominus}]$$

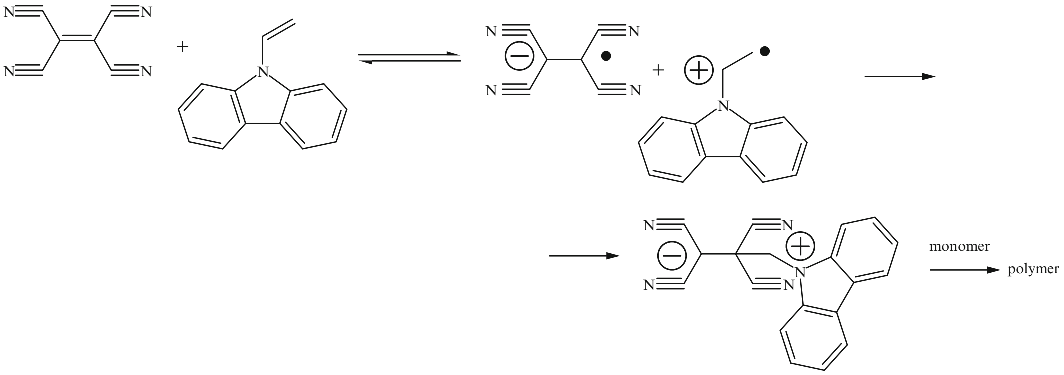
Some vinyl compounds, i.e., vinyl ethers, can function as donor molecules because they possess a low ionization potential. The acceptors can be neutral molecules like, quinones, anhydrides, nitrile compounds, etc. They can also be ionic intermediates, such as metal ions, ionized acids, and carbon cations. An interaction of an acceptor with a donor is followed by a subsequent collapse of the charge transfer complex. This can results in formation of cation-radicals that are capable of initiating cationic polymerizations [57]. The exact mechanism of the reaction of cation-radicals with olefins is still not completely determined.

One example is a combination of an alkyl vinyl ether (donor) with vinylidene cyanide (acceptor) that results in ionic polymerizations [58]. The reaction actually contains the ingredients of both cationic and anionic type polymerizations [59]:

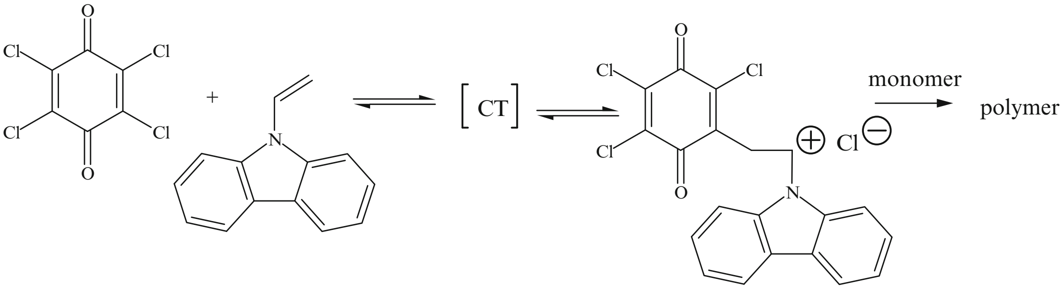


where [CT] represents a charge transfer complex.

Solvation of the charged species accelerates the transfer of electrons and the ionizations are enhanced by polar solvents [57]. Charge transfer reactions studies with tetracyanoethylene, an acceptor, and *N*-vinylcarbazole, a donor, in benzene solution demonstrated that both cation-radicals and anion-radicals form. This can be used in a subsequent cationic polymerizations [60]:



A similar reaction takes place between chloranil and *N*-vinyl carbazole [61]:



Alkyl vinyl ethers also polymerize in the presence of strong acceptors like tetracyanobenzoquinone, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, and tetracyanoethylene [60]. A similar reaction mechanism was proposed [60].

Solutions of maleic anhydride in ether will initiate cationic polymerizations of isobutyl vinyl ether or *N*-vinyl carbazole, if subjected to attacks be free radicals. The same is true if the solutions are irradiated with ultraviolet light or gamma rays [62, 63]. Also, active species are generated from reactions of aldehydes or ketones with maleic anhydride when attacked by free radicals or irradiated by UV-light, or gamma rays from ^{60}Co [63]. These active species are presumed to be formed through charge-transfer reactions that occur between the electron acceptors, π-acids, or electron donors, π-bases, which form cations [64].

Some Lewis acids can form charge transfer complexes with monomers that yield cation radicals when irradiated with ultraviolet light [65, 66]. This was shown with such Lewis acids as VCl_4, $TiCl_4$, and $TiBr_4$ in polymerizations of isobutylene. The charge transfer complexes collapse after irradiation [66]:

$$VCl_4 + [M]\ \text{monomer} \rightleftharpoons [VCl_4M]$$

$$[VCl_4M]h_v[VCl_4M]^{\bullet} \rightarrow VCl_4{}^{\oplus}------M^{\bullet\ominus}$$

$$2M^{\bullet\ominus} \rightarrow {}^{\oplus}M\text{--}M^{\ominus} \xrightarrow{\text{monomer}} \text{polymer}$$

4.3.2.2 Radiation Initiated Polymerizations

Photochemical initiations of cationic polymerizations [67–71] are used commercially. Irradiation by ***ionizing radiation*** of olefins forms several kinds of active, initiating species. Free-radical, cationic and anionic polymerizations can potentially be initiated by these active species. Generally, the characteristics of ionizing radiation induced polymerizations can be such that free-radical and ionic polymerizations coexist [72]. Under dry conditions, polymerizations will proceed predominantly through cationic intermediates with cyclopentadiene [73] and styrene [74, 75]. Also, radiation-induced polymerizations of some monomers in the liquid state are subject to retardation [76] by very low concentrations of ion scavengers such as ammonia and water [72]. The efficiency of such retardation depends upon the proton affinity of the scavengers [72]. In addition, radiation-induced cationic polymerizations of isobutylene under anhydrous conditions occur through propagation by free ions [77].

4.3.2.3 Electro Initiation of Polymerization

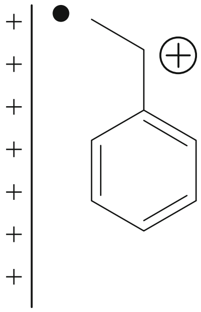
These polymerizations, sometime also called ***electrolytic polymerizations***, are carried out in an electrical field. The field is applied to initiate chain growth. Passage of an electrical current through solutions of monomers in suitable solvents can produce initiating species. Majority of these species, however, are free-radical in nature [78–80].

Early studies on initiation of cationic polymerizations of styrene, isobutyl vinyl ether, and *N*-vinylcarbazole were carried out by dissolving $AgClO_4$ in pure monomers or in nitrobenzene. Electric current was then passed through them at room temperature [81, 82]. Rubbery polymers formed as well as some copolymers, suggesting a cationic path of the polymerization. A mechanism was suggested based on anodic oxidation of the monomer:

$$ClO_4{}^{\ominus} \xrightarrow{-e} ClO_4\bullet + e$$

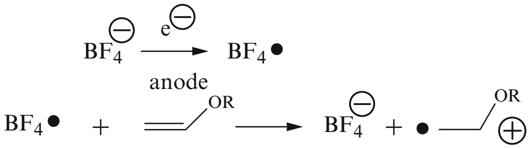
$$ClO_4\bullet + M \longrightarrow ClO_4{}^{\ominus} + M^{\oplus}$$

where, M is monomer. Later, however, it was concluded that the polymerizations are due to formation of cation-radicals as the initiating species [83]. Further studies of the phenomenon led to a proposed mechanism of initiation [84] of styrene polymerization in acetonitrile solution. Controlled potential electrolysis at the anode, with the aid of a salt like tetrabutylammonium fluoroborate, is a result of direct anodic oxidation. Electrons are transferred at the anode. This is accompanied by formations of radical-cations:



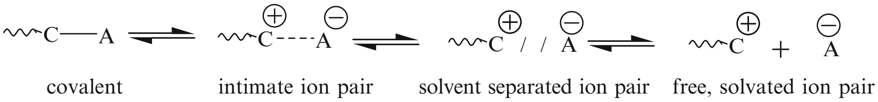
In the above initiation the monomer itself is the initiator and the anode can be regarded as the "co-initiator."

If a supporting electrolyte is first oxidized to a radical, indirect cationic polymerization can result. The radical in a subsequent step oxidizes the monomer to a first initiating entity, the cation-radical [85]. Such an indirect initiation was also suggested for electropolymerization of isobutyl vinyl ether in the presence of BF_4 supporting electrolyte [85]:



4.3.3 *Propagation in Cationic Polymerization*

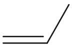
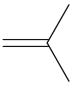
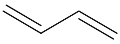
In the propagation step the polarity of the medium affects strongly the reaction because the intimacy of the ion pair depends upon solvent polarity. The bond between the two ions can vary from a high degree of covalence to that of a pair of free, solvated ions [86]:



The chemical structures of the monomers also determine their reactivity toward cationic polymerizations. Electron donating groups enhance the electron densities of the double bonds. Because, the monomers must act as nucleophiles or as electron donors in the course of propagation, increased electron densities at the double bonds increase the reaction rates. It follows, therefore, that electron withdrawing substituents on olefins will hinder cationic polymerizations. They will, instead, enhance the ability for anionic polymerization. The polarity of the substituents, however, is not the only determining factor in monomer reactivity. Steric effects can also exert considerable controls over the rates of propagation and the modes of addition to the active centers. Investigation of polymerizations of alkyl vinyl ethers, for instance, with $BF_3{\cdot}O(C_2H_5)_2$ in toluene or in methylene chloride at −79°C, showed that the rate of monomer consumption falls in the following order [87]:

$$\text{Alkyl group} = t\text{ - butyl} > i\text{ - propyl} > \text{ethyl} > n\text{ - butyl} > \text{methyl}$$

Table 4.1 Relative rates of reactions of alkenes in 1,2-dichloroethane at 24°C with $PhCH_2^{\oplus}$ and $(Ph)_2C^{\oplus}$ cation[a]

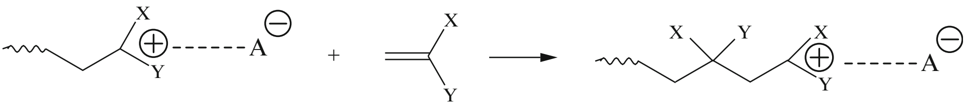
Olefin	$PhCH_2^{\oplus}$	$(Ph)_2CH^{\oplus}$
	1.9×10^6	$<10^5$
	1.9×10^7	9.5×10^6
	2.7×10^7	1.5×10^7
	8.7×10^7	$<10^5$

[a] From Wang and Dorfmann [88], by permission of the American Chemical Society

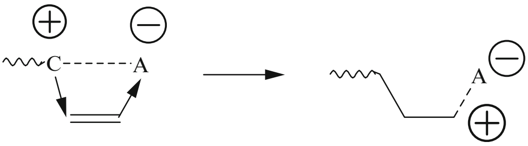
Another example is a study of the differences in the rates of reactions of various alkenes with two cations, $PhCH_2^{\oplus}$ and $(Ph)_2CH^{\oplus}$, generated by electron pulses [88]. Carbon cations, free from complexities, such as ion pairing and cation aggregation that my be encountered in typical polymerizations, were used. Table 4.1 shows some of the data that was reported [88].

Recently, Kolishetti and Faust [89] reported investigations of the polymerizations of *p*-methylstyrene in the presence of isobutylene, styrene, *p*-chlorostyrene, and 1,3 butadiene at −40°C. The polymerizations were carried out in a 50/50 mixture of CH_2Cl_2 with methyl cyclohexane as the solvent and a weak Lewis acid, $SnBr_2Cl_2$. The reactions were conducted by mono additions of each monomer that was followed by instantaneous terminations. The results showed that *p*-methylstyrene is roughly 3.8 times more reactive than isobutylene, 4.8 times more reactive than styrene, 7.2 times more reactive than *p*-chlorostyrene, and 100 times more reactive than butadiene.

Chain growth reactions with fairly tight ion pairs that occur in medium of low polarity require that the monomers be inserted repeatedly between the two ions. These consist of carbon cations on the terminal units paired with the counterions. The ion pairs are first loosened, or "relaxed," complexations with monomers follow, and insertions complete the process. All insertions, of course, results in formations of new carbon cations. They, upon formation, pair off immediately with the counterions, and the process continues:



The mechanisms of such insertions consist of repeated push-pull attacks by the ion pairs on the double bonds of the incoming monomers [90]:



The degree of association of the ion pairs depends also upon the nature of the counterion and on the temperature of the reaction medium. Completely dissociated ion pairs allow chain growth to take place free from the influence of counterions. The carbon cations simply add directly to the double bonds of the incoming monomers. Propagation rates for such reactions are greater than for those with tight ion pairs [91]. The efficiency of the counterion is related to its acid strength.

In isobutylene polymerization at −78°C the following Lewis acids were rated in the order of their efficiencies [92]:

$$BF_3 > AlBr_3 > TiBr_4 > BBr_3 > SnCl_4$$

The polymerization reactions can be complicated, sometimes, by two different types of propagation paths. Some chains may grow without a terminal counter-ion as free propagating species. Other polymeric chains, however, may be paired off with counterions. It should be noted that when references are made to free propagating ions, the ions are free from electrostatic influences of the anions. They are, however, still associated with, and interact with polar or polarizable solvent molecules or monomers.

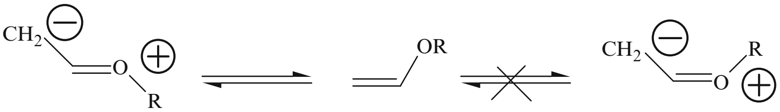
4.3.3.1 Steric Control in Cationic Polymerization

Ionic polymerizations yield highly stereoregular polymer when control is exercised over monomer placement. Much of the steric control in cationic polymerization occurs at low temperatures. The earliest stereospecific vinyl polymerizations were observed in preparation of poly(isobutyl vinyl ether) with a BF_3-ether complex catalyst at −70°C. An isotactic polymer formed in this reaction [93]. The same catalyst was employed later to yield other stereospecific poly(vinyl ether)s [93–96]. The amount of steric placement increases with a decrease in the reaction temperature and, conversely, decreases with an increase in the temperature [96, 97].

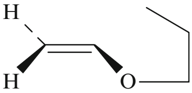
Various mechanisms were proposed to explain steric placement in cationic polymerization. Most of them pertain to vinyl ethers. There is no general agreement. Some of the suggested mechanisms are discussed in this section. Most were offered for homogeneous conditions with soluble initiators like $BF_3–O(C_2H_5)_2$. There are, however, also some explanations of steric control with insoluble catalysts, like $Al(SO_4)_2 \bullet H_2SO_4$.

Control in Homogeneous Polymerizations

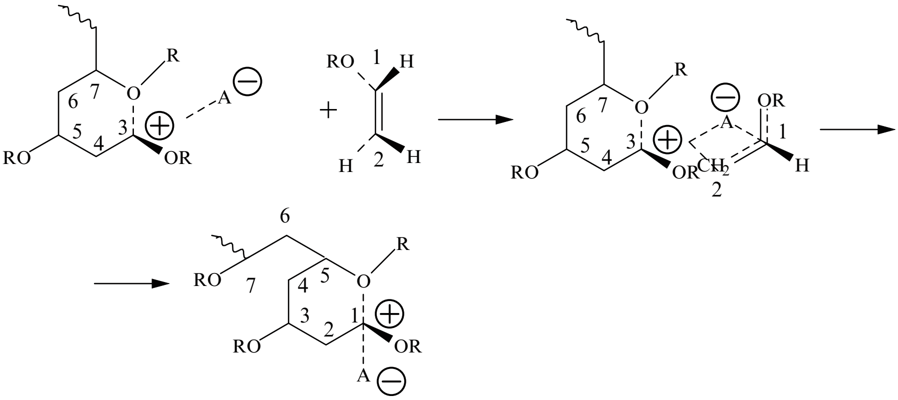
Not all explanations of steric control under homogeneous conditions give equal weight to the influence of the counterion. A Bawn and Ledwith mechanism [99] for the polymerization of vinyl ethers is based on data that suggests that only one mesomeric form of the ethers exists, presumably *trans* [98]



An alkyl substituent composed of a three-carbon chain causes steric blocking of one side of the bond:

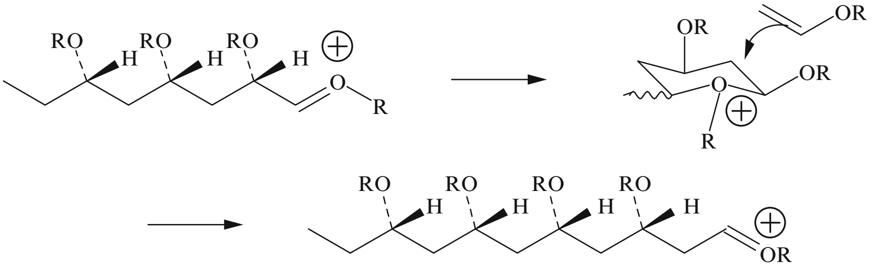


A five-carbon substituent should exhibit the highest degree of steric hindrance, which, on the other hand, should decrease with a decrease in the size of the group. There should be no blocking with an ethyl group or with an isopropyl one [98]. This was, demonstrated experimentally [99]. It was suggested, therefore, that in homogeneous polymerizations of vinyl ethers, the growing cations are stabilized by a form of neighboring group interaction. This interaction (or intramolecular solvation) would be with oxygen atoms from the penultimate monomer units [98]. These are forms of “backside” stabilization of the growing chains that force reactions to occur at the opposite sides from the locations of the counterions. The mechanisms are forms of $\mathrm{S_{N^2}}$ attacks with retention of the configurations. These configuration are formed between existing and newly formed carbon cations in the transition states:



Solvations of the new cations might even occur before they are completely formed, maintaining the steric arrangement throughout, provided that the monomers enter as shown above [98]. One weakness of the above mechanism is that it fails to consider the nature of the counterions.

Another mechanism, proposed by Cram and Kopecky [100], places emphasis on formation of six-membered rings. The growing polymeric chains in vinyl ethers occupy equatorial arrangements with the –OR groups attached to the growing ends by virtue of their size, because they are larger. In reactions between the monomers and the six-membered ring oxonium ions the relative configurations of the two asymmetric centers that form determine total chain configurations. If the configurations are similar, the chains become isotactic, but if they are different they become syndiotactic. Molecular models suggest that isotactic placement should be more likely [100].



The Cram and Kopecky mechanism [43] fails to explain the influence of the various R groups upon the stereospecificity of the final product.

In a mechanism proposed by Kunitake and Aso [101] two factors were given primary importance. These are: (1) steric repulsions determine the conformations of the propagating chains with a special arrangement of the counterions and those of the incoming monomers. (2) The directions of the monomer attacks are determined by the tightness of the growing ion pairs. It is assumed that the growing carbon cations are essentially sp^2 hybridized and that the conformations with the least steric repulsion will, therefore, be [101] as shown in Fig. 4.1.

The position of the counterion is assumed to be at the side of the carbon cation and away from the penultimate unit. The stability of such conformations should be very dependent on the temperature of the polymerization and on the size of the substituents. Experimental evidence confirms this. Thus, it is known that the stereoregular polymers, whether isotactic or syndiotactic, form only at low

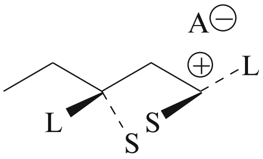


Fig. 4.1 Steric arrangement. *L* large substituent; *S* small substituent

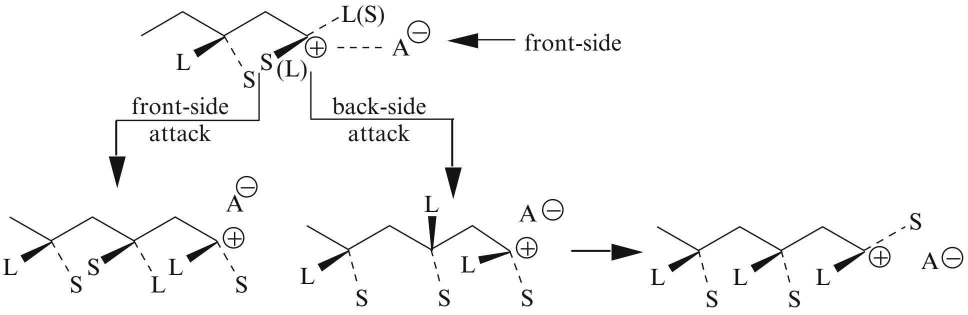


Fig. 4.2 Propagation mechanism

temperatures in homogeneous polymerizations (as stated earlier). This suggests that the fixation of the conformations of the growing chain ends is very important in enhancing polymer stereoregularity.

In polar solvents the counterions interact only weakly with the growing cations. The steric effects become major factors in deciding the courses of propagation. In such situations the carbon cations [101] attack the least hindered side (frontal side attacks). These give rise to syndiotactic structures. The terminal carbon cations probably can rotate freely, so the vinyl monomers should be capable of approaching from any direction. In non-polar solvents, on the other hand, if the ion pairs are tight enough, the incoming monomers may approach the cations from the back sides only, giving rise to isotactic placements. This is illustrated in Fig. 4.2.

If there is steric hindrance to backside approaches due to the large sizes of the penultimate substituents, front-side attacks take place. This occurs even in non-polar medium [101]. The incoming monomers can, therefore, attack the cation either from the frontside or from the backside. All depends upon the tightness or the Coulombic interaction of the ion pair and on the difference in the steric hindrance between the two modes of attack.

In the above reaction mechanism, the possible interactions of the counterions and the monomers are ignored. This was justified by weak interactions of electron-rich monomers, like α-methyl styrene and vinyl ethers with weak anions [101]. The nature of the counterions as such, however, is not ignored in this mechanism, because the tightness of the ion pairs is considered.

Later work by Hirokawa et al. [102], suggested that the sizes of the R groups of alkenyl ethers play an important role in determining the steric structures of the resultant polymers. For instance, allyl vinyl ethers can be polymerized to highly isotactic polymers with the aid of $SbCl_5$. ^1H and ^{13}C NMR data shows no evidence, however, of steric control, though, it does show a relationship between active chain ends and incoming monomers. In addition, the amounts of isotactic placement do not differ significantly at $-10°C$ or at $-75°C$ [103]. This suggests that isotactic selection is generated by orienting the substituents in the monomer and in the chain *away* from each other. A Coulombic attraction is visualized between the counterion and the positively polarized oxygen of the monomer.

Also, in studies with optically active vinyl ethers it was observed [104] that trimethyl vinyl silane, which is bulky and non-chiral forms highly syndiotactic polymers. Equally bulky, but chiral (−)-menthyl vinyl ether, however, produces isotactic polymers in polar solvents. This suggests that isotactic propagation is preferred in a polar medium because of helical conformation of the polymer chain and is forced by a bulky chiral substituent. Kunitake and Takarabe [105], therefore, modified the original Kunitake and Aso mechanism. The growing chain ends are crowded by bulky substituents. This may result in steric interference between a bulky side group and the counterions. The interactions of the propagating ion pairs decrease when the sizes of the counterions increase. A frontal attack and syndiotactic placement of the monomers results. When, however, the monomer side groups are less bulky, steric repulsion becomes insignificant. Larger counterion becomes responsible for retarding the frontside attack and gives more isotactic placement.

Studies of model reactions for cationic polymerization of alkyl propenyl ethers showed that the mode of double bond opening is independent of the geometric structure of the ether. Mainly a *threo* opening takes place, but the mode of monomer addition is dependent on the geometric structure of the monomer or on the bulkiness of the substituent [106].

Finally, in still another investigation of model systems, UV and visible spectroscopy were used together with conductivity measurements. Results showed that charge-transfer complexes do form between the counterions and π-acceptors, which can be Lewis acids or acceptor solvents [196]. This led Heublein to suggest that interactions with monomers lead to alterations of the solvation spheres of the ionpairs in the direction of the counterions. The temporary dissymmetry of the sphere of solvation affects stereoregularities of the structures of the polymers that form. As a result, the propagation reactions are seen by Hueblein as competing interaction between the chain carriers and the monomers, the counterions, and the solvents [106].

Control in Heterogeneous Polymerizations

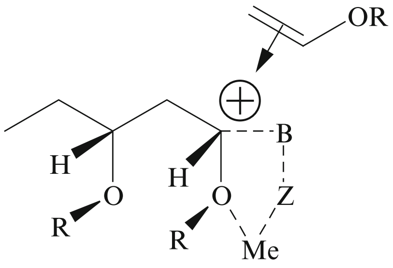
Several reaction mechanisms were also proposed to explain stereospecific placement with insoluble catalysts. Furukawa [46] suggested that here the mechanism for cationic polymerization of vinyl ethers depends upon multicentered coordinations. He felt that coordinations of the polymeric chains and monomers with the catalysts are possible if the complexed counteranions have electrically positive centers. This can take place in the case of aluminum alkyl and boron fluoride:

$$R_3Al + BF_3 \rightarrow [R_2Al]^{\oplus} + [BF_3R]^{\ominus}$$

Further coordination of aluminum alkyl to the anions is possible if the coordination number of the central atom is sufficiently large [46]:

$$[BF_3R]^{\ominus} + AR_3 \rightarrow [R_3Al \rightarrow BF_3R]^{\ominus}$$

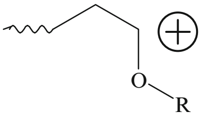
The products are complex counterions that enable multicentered coordination polymerization. Thus, the mechanism of vinyl ether polymerization proposed by Furukawa [46] is as follows. Two neighboring ether oxygens that are linked to the polymer chain close to the terminal cation become coordinated to the metal center of the complexed counterion. The molecules of the monomer can then approach the growing chain only from the opposite side and isotactic placement results:



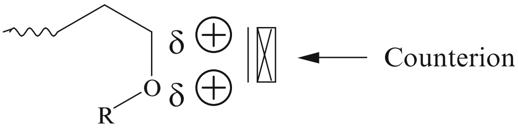
where B represents boron and Me aluminum.

A different mechanism, however, was offered by Nakano and coworkers [47]. They felt that there must be a relationship between the crystal structures of the heterogeneous catalysts and the resultant stereoregularity of the polymers. If the crystal structures of the catalysts are tetrahedral and the crystals have active edges, stereoregular polymers should form even at room temperature. In addition, shorter active edges make the catalysts more suitable for stereospecific polymerization. The following mechanism was, therefore, proposed [47].

If the terminal end of the growing chain ends:

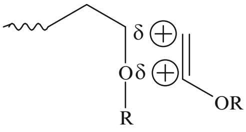


have sp^2 type configurations, vacant orbitals on the terminal carbon atoms of the growing polymeric chains are in a state of resonance with the lone pair of electrons on the adjacent oxygen atoms. This means that the positive charges are distributed to the adjacent oxygens and are not localized on the carbons:

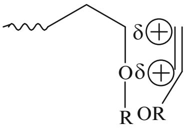


The monomer can potentially add in four different ways:

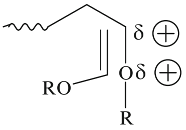
1.



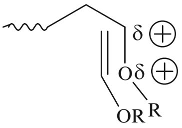
2.



3.



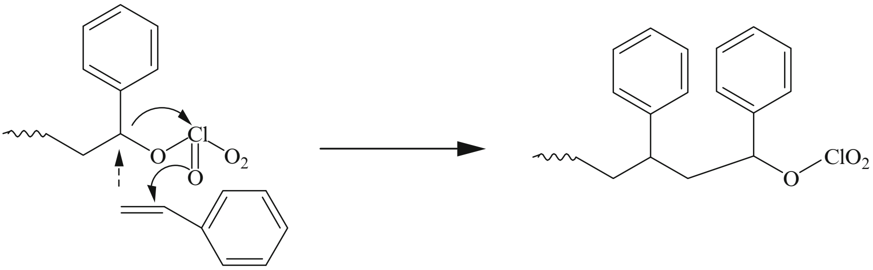
4.



Reaction 3 yields isotactic polymers and should be the mode of addition [47] when isotactic polymer forms.

4.3.3.2 Pseudo-Cationic Polymerization

Most cationic polymerizations of olefins proceed through carbon cation carriers. There are, however, instances of cationic polymerizations where the evidence was interpreted as suggesting that the propagating species are not carbon cations. Instead, the reactions were said to proceed through covalently propagating species. Such reactions were termed ***pseudo cationic*** [109, 110]. In these polymerizations the propagating species may be combinations of ionic (free ions and ion pairs) and covalently bonded species. Reaction conditions were claimed to determine the relative amounts of each. Examples of such polymerizations are cationic polymerizations of styrene or acenaphthene with protonic acids like $HClO_4$ or iodine as the initiators. The propagations were suggested [110] to take place in three successive stages when the reactions are carried out in methylene chloride at −20°C. In the first one, rapid, short-lived ionic reactions take place. In the second stage, the ions can no longer be detected by spectroscopy or conductivity measurements. In the third one, rapid increase in the presence of ionic species was shown (detected by conductivity measurements and spectroscopy). At temperatures between −20 and 30°C there is effectively no stage one and stage three is shorter. On the other hand, at temperatures as low as −80°C there is only stage one. In stages one and three, propagation takes places through combinations of free ions and ion pairs. These combinations of ions were claimed to result in formations of covalent perchlorate esters that are solvated and stabilized by monomer. The propagation in stage two, therefore, is pseudo cationic and covalent because it consists of monomer insertion into the C–O bond of a perchlorate ester [109, 110]:



When there are insufficient amounts of monomer present to stabilize the covalent esters, such as at high conversions, ionizations take place. This leads to rapid ionic, stage three polymerizations. The propagation by free ions and ion pairs in stage three is between 10^4 and 10^5 L/mole s at low temperatures, between −60 and −80°C. By comparison, polymerizations in stage two are much slower, somewhere between 0.1 and 20 L/mole s. The rates depend, of course, upon the solvent and upon the temperature. While ion–ion pair type propagations yield polymers with molecular weights equal to 10^4, the covalent propagations only yield oligomers. Differences in molecular weights and molecular weight distributions of the products from the three stages of polymerization can be detected by size exclusion chromatography. The chromatogram shows bimodal distributions. This was taken as supporting evidence for two modes of propagation, ionic and covalent [110].

Similar results were reported in polymerizations of styrene with CH_3COClO_4, CF_3SO_3H, CF_3COOH, $ClSO_3H$, FSO_3H [109]. Pseudo-cationic mechanism was also claimed in polymerizations of some styrene derivatives, like *p*-methyl styrene, *p*-methoxystyrene, and *p*-chlorostyrene with these protonic acids [109].

Although the concept of pseudo-cationic mechanism may be accepted by some, it is not accepted by many. An alternative mechanisms based on ion pairs were offered instead in the past [111–113]. A publication by Scwarc claims that all detailed re-examinations of the evidence for pseudo-cationic polymerizations shows that all the features of styrene polymerization initiated by acids are accounted for satisfactorily and convincingly by the orthodox ionic mechanism. To support his claim, he reported that optical absorption and electric conductance of the styrene solutions undergoing polymerization induced by perchloric acid in stopped-flow studies demonstrated protonations of the monomer by the acid and formation of ionic species [114].

Further proof against pseudo-cationic polymerization mechanism came from an earlier work by Matyjaszewski who successfully synthesized the styryl perchlorate and demonstrated that it hydrolyzes rapidly in reaction with water [115]:

$$2CH_3CHPh - OClO_3 \xrightarrow{H_2O} (CH_2CHPh)_2O + 2HClO_4$$

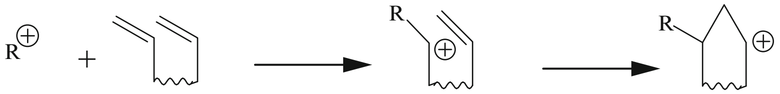
This contradicts the basic claim of pseudo-cationic polymerization mechanism, as originally proposed by Gandini and Plesch, that the hydrolysis of the ester should be negligible [109].

4.3.3.3 Isomerization Polymerization

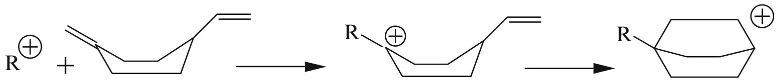
In some cationic polymerizations the monomers may rearrange in the process of placements into the polymeric chains. They isomerize into energetically preferred configurations. The result is that the units in the final polymers are structurally different from the original monomers. Such rearrangements are not limited to cationic polymerizations. In this section, however, are only discussed the isomerizations in cationic polymerizations.

The isomerization polymerizations were classified by Kennedy according to the type of rearrangement that accompanies the propagation and by the particular processes [116]:

1. Propagation reactions accompanied by bond or electron rearrangement:
   A. Intra-intermolecular polymerization
   B. Transanular polymerization
   C. Polymerization by strain relief
2. Propagation reactions accompanied by migration of one or more atoms.
   Examples of ***intra intermolecular polymerizations*** are cyclic polymerizations of nonconjugated dienes. This can resemble cyclopolymerization by free-radical mechanism:

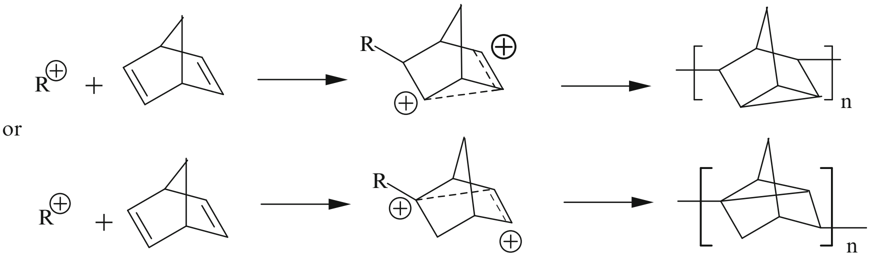


In this group of monomers, aliphatic dienes of various types can also be found . The propagation proceeds through an internal attack by the electrophile on another part of the molecule yielding a new carbon cation. The following is an example of such a reaction [58, 59]:



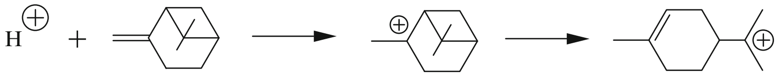
Polynortricyclene [116–118] forms by cationic polymerization of norbornadiene by a ***transanular polymerization***.

The reaction is best carried out below $-100°C$ to prevent crosslinking. Two propagation paths are possible

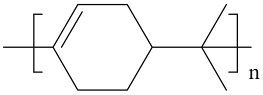


NMR and IR spectra demonstrated that both propagations shown above take place during the polymerization and the resultant polymer is in effect a copolymer of both structures [119]. Similarly, cationic polymerization of 2-methylene, 5-norbornene involves a transanular addition of the initially formed carbon cation to the strained endocyclic double bond. The product is a polymeric nortricyclane [119].

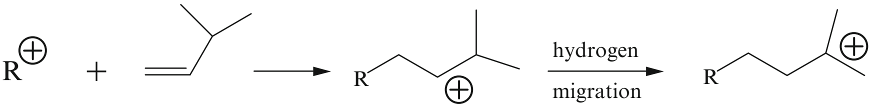
Polymerization by strain relief occurs by opening of strained rings or by rearrangements of internal double bonds during propagation. An example is the polymerization of α-pinene. The propagation is accompanied by rearrangement of the initially formed carbon cation to a tertiary cation that relieves the ring strain [119]:



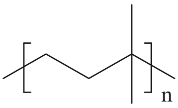
As a result, the formed polymer has the following structure:



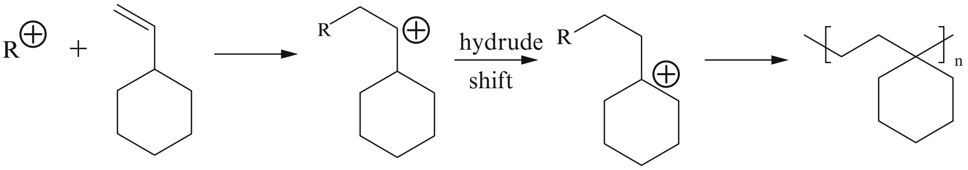
Isomerization polymerizations by material transport include propagation reactions that are accompanied by hydride shifts. One example of this is a 1,2-hydride shift in the polymerization of 3-methylbutene-1 [116]:



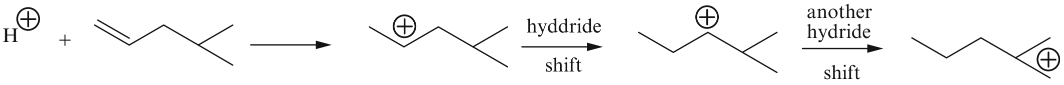
During propagation, a tertiary hydrogen atom migrates as a hydride ion to the second carbon. It results in an energetically favored tertiary carbon cation. The final product is a 1,3-polymer [116]:



Another example of a hydride shift during propagation is a polymerization of vinyl cyclohexane with the aid of $AlCl_3$ at temperatures ranging from −144 to 70°C [120, 121]

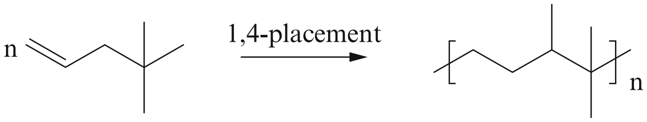


Successive hydride shifts are possible in propagation reactions where the structures of the monomers favor them [121]:

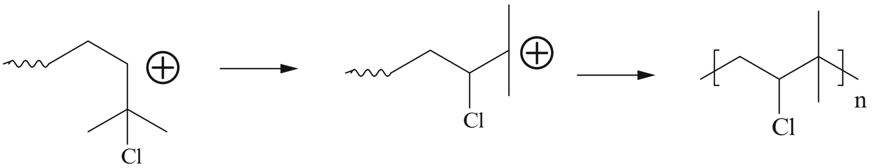


The temperature of polymerization can have some effect. This was observed in the polymerization of 3-methylbutene-1 [122]. At lower temperatures the amount of 1,3 vs., 1,2 placement apparently increases rapidly. At −130°C an essentially pure crystalline 1,3 poly(methylbutene-1) forms. The nature of the counterion also has an effect on the slope of the product composition curve. The polarity of the solvent, however, apparently does not, nor does the monomer concentration [122].

Simultaneous migrations of hydrogen atoms and methyl groups take place in cationic polymerization of 4,4-dimethyl-1-pentene (neopentylethylene) [123]. In the presence of $AlCl_3$ between −78 and −130°C the polymerization proceeds mainly as follows:



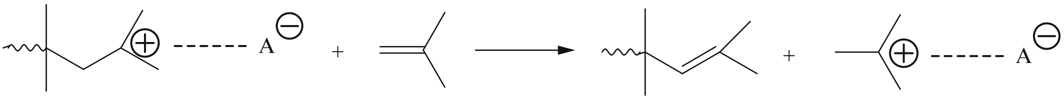
The propagation can also involve an intramolecular halide migration. The polymerization of 3-chloro-3-methylbutene-1 proceeds at low temperatures by a chloride shift (about 50%) [124]:



Recently, Faust and coworkers [125] reported a study of the mechanism of isomerization and polymerization of isobutylene in cationic polymerization. They concluded that β-proton elimination from the tertiary polyisobutylene cation results in exo- and endo-olefins. Tetra-substituted olefins form after initial cationic rearrangements leading to tertiary cations at the second and third positions, followed by deprotonation. All three olefins possess regular carbon numbers. The formation of tri-substituted olefins follows a different mechanism. First, a hydride shift between distant carbons (backbiting) leads to a secondary cation, which undergoes a methyde shift to minimize the energy. The resulting hindered tertiary cation undergoes chain scission, yielding the *n*-substituted polyisobutylene olefin with irregular carbon number. This also results in an oligomeric byproduct, which is known as “light polymer.”

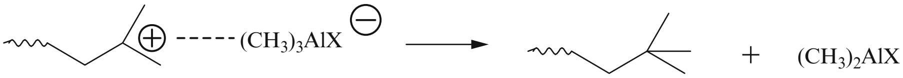
4.3.4 Termination Reactions in Cationic Polymerizations

The termination reaction can occur by a transfer to a monomer at proper reaction conditions:

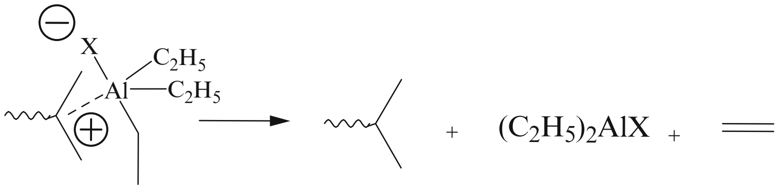


The termination reactions in cationic polymerizations can often lead to low molecular weight products. This can be a result from various effects. Also, the counterions may be involved in the terminations [126]. Thus, with some Lewis acids, the polymer cation may react with the counterion by abstracting a halogen. An example of that is polymerization of isobutylene with BCl_3. In this reaction, termination by chain transferring is absent [126]. Instead, the following mechanism takes place [127]:

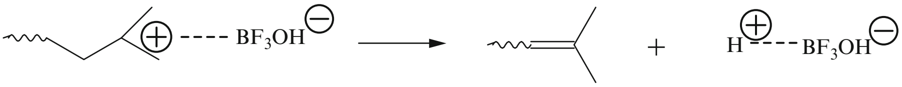
Alkyl aluminum initiated reactions can terminate by a transfer of an alkyl group [127]:



where X is a halogen. When a hydrogen atom is located at β to the aluminum in an alkyl aluminum moiety then termination by hydrogen transfer appears to occur preferentially [125]:



Termination through a rearrangement of the propagating ion-pair is also possible. Such terminations are sometimes called ***spontaneous terminations*** or as chain transfers to counterions. The ion couple is rearranged by an expulsion of hydrogen leaving the terminal unsaturated [120]:



Many substances which act as catalysts (in combination with Lewis acids), like water, are also good chain-transferring agents. A solvent or an impurity can act in the same way.

4.3.5 Living Cationic Polymerizations

In some cationic polymerizations, when conditions are carefully controlled, quasi termination less or termination less systems can be achieved [130–136]. The "living" polymers, or "quasiliving," form as chain transfer to monomer and all other forms of termination are greatly decreased or made reversible throughout reaction. The important aspect of living cationic polymerization is that the propagating centers are sufficiently low in reactivity. Transfer and termination reactions are suppressed. The propagation, however, is maintained. The molecular weights must increase in proportion to the cumulative amount of the monomer added. The lifetimes of the propagating species can be extended in such polymerizations by carrying out continuous slow additions of the monomer. Because chain-transferring reactions are not completely eliminated in all these systems, the term "quasi" is sometimes used.

Living cationic polymerizations have been carried out with a number of monomers, such as isobutylene, styrene, *p*-methyl styrene, *p*-methoxystyrene, *N*-vinylcarbazole, and others [137, 138]. To achieve living conditions, it is necessary to match the propagating carbon cation with the counterion, the solvent polarity, and the reaction temperature. Some examples are offered in Table 4.2.

By stabilizing the inherently unstable carbocationic growing species and preventing chain transfer and termination, living cationic polymerizations are achieved. This can be done by two methods: (1) use of suitable nucleophilic counterions, or (2) external additions of weak Lewis bases [139]. The ion pairs are very tight in these reactions and may border on being covalent. The propagation can be illustrated as follows:

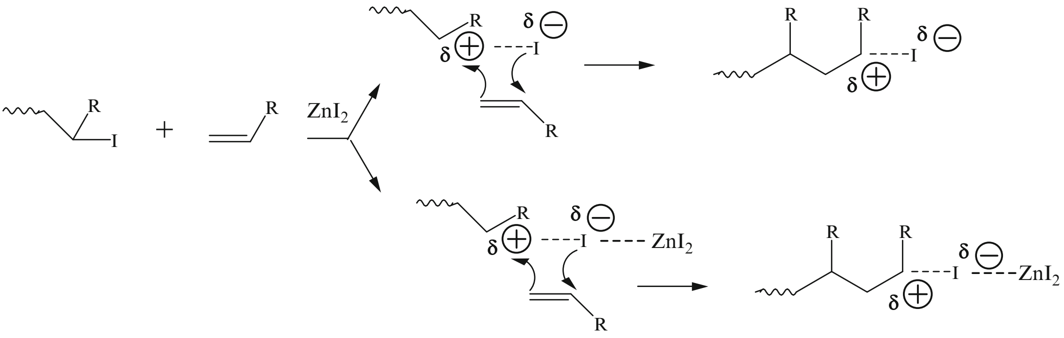


Table 4.2 Conditions for preparations of some living polymers[a,b]

Monomer	Initiating system	Solvent	Temp. (°C)
Vinyl ethers	$HI + ZnI_2$	Toluene	−40 to −25
Isobutyl vinyl ether	Protonic acids[b] + $ZnCl_2$	Toluene	−40 to −0
p-Methyl styrene	CH_3COClO_4	CH_2Cl_2/toluene (1:4)	−78
Isobutylene	BCl_3 + cumyl acetate	CH_2Cl_2	−30
N-vinylcarbazole	HI	Toluene	−40
Styrene	$CH_3CH(C_6H_5)Cl + SnCl_4 + n\text{-}C_4H_9NCl$	CH_2Cl_2	−15
Indene	Cumyl methyl ether + $TiCl_4$	CH_2Cl_2	−40; −75
Indene	2-Chloro-2,4,4-trimethylpentane + $TiCl_4$	$CH_3Cl/CH_3C_6H_{11}$	−80
β-Pinene	$CH_3CH(OCH_2\text{–}CH_2Cl)Cl + TiCl_2(O\text{-}i\text{-}Pr) + n\text{-}Bu_4NCl$	CH_2Cl_2	−78 to 40

[a] From various sources in the literature

[b] Protonic acids used were CH_3SO_3H, $R_2P(O)OH$, and $R'CO_2H$, where $R = OC_6H_5$, C_6H_5, $n\text{-}C_4H_9$; $R' = CF_3$, CCl_3, $CHCl_2$, CH_2Cl

As shown above, the carbon–iodine bond is stretched, with or without the help of a Lewis acid. The Lewis acid assists in further stretching the carbon–iodine bond. Whether it is needed, depends upon the strength of that bond. This strength, in turn, varies with the ability of the solvent, the temperature, and the substituent R to stabilize the δ^+ center. Depending upon conditions, a Lewis acid can convert the counterion, like I^- to a more stable, less nucleophilic species. Lewis bases, like dioxane or ethyl acetate, may function by reacting directly with the propagating centers.

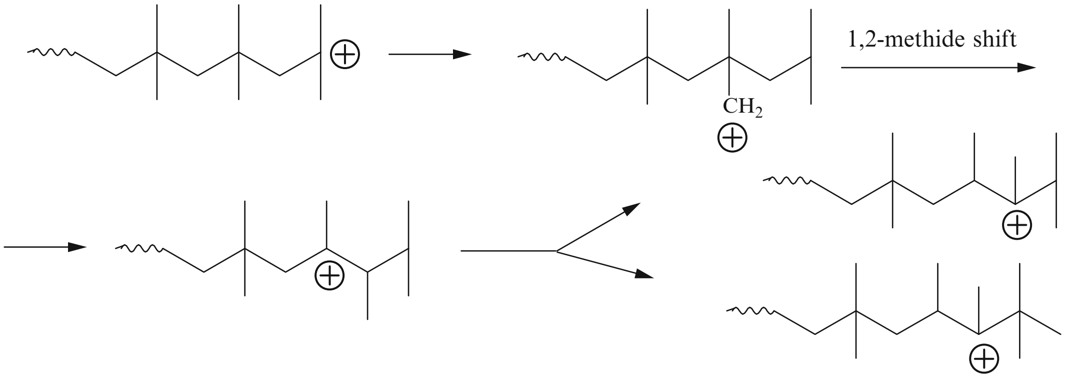
Living cationic polymerizations were also carried out with heterogeneous catalysts. Thus, Aoshima and coworkers [139] reported a heterogeneous living cationic polymerization of isobutyl vinyl ether, using Fe_2O_3 in conjunction with the isobutyl vinyl ether-HCl adduct in toluene. This was done in the presence of an added base at 0°C. Such bases are ethyl acetate and 1,4-dioxane. These bases are effective in homogeneous living cationic polymerization of vinyl ethers in the presence various metal halides. The living cationic polymerization of isobutyl vinyl ether produced polymers with very narrow molecular weight distribution of the product [139]. The number average molecular weight increased in direct proportion to the monomer conversion, and they reported that the molecular weight distributions were very narrow throughout the polymerization [$M_w/M_n = 1.1$]. Stereoselectivity of the products was similar to polymers obtained by soluble catalysts. Controlled polymerization also occurred even at higher temperature (30°C). What is particularly interesting is their report that they separated the catalyst from the mixture by centrifugation, and then used this catalyst to catalyze a second living polymerization under the same conditions, yielding a polymer with narrow molecular weight distribution. The ease of the catalyst separation permitted repeated reuse of the catalyst. Up to the fifth use, the catalyst maintained its activity to give well-defined polymers with very narrow MWD [139].

Heterogeneous conditions, due to poor solubility of heteropoly acid, in polymerization of isobutyl vinyl ether with $H_3PW_{12}O_{40}$ in CH_2Cl_2 were also studied. When bases like 1,4-dioxane or tetrahydrofuran were present the molecular weight distributions were very broad. By contrast, polymerizations in the presence of dimethyl sulfide at −30°C yielded living polymerizations of the ether. Here too, the product had very narrow molecular weight distribution [139]. In summary, some typical features of living cationic polymerizations are:

1. The quasiliving or living/controlled carbocationic polymerizations are characterized by an ionization equilibrium between active and reversibly deactivated chains that are dormant.
2. The number average molecular weight of the polymers that form is proportional to the amount of monomer introduced into the reaction mixture. In most cases, the reactions are rapid, often to a point that it is impossible to stop them before all the monomer is consumed.
3. The concentration of the polymers formed is constant and independent of conversion. This concentration is often equal to the concentration of the initiator.

4. Addition of more monomer to a completed polymerization reaction results in further polymerization and a proportional increase in molecular weight.

Storey et al. [140] point out that in living polymerizations of monomers like isobutylene that are co-initiated by $TiCl_4$ at temperatures as low as −80°C, the livingness is limited not by chain transfer to monomer but rather by a unimolecular termination process. Unimolecular terminations often involve β-proton expulsions to produce polymers with terminal unsaturation. They claim, however, that this does not happen here. Rather the normal *tert*-chloride chain ends of polyisobutylene formed by this type of polymerization gradually become depleted. They propose, therefore, that an isomerization mechanism takes place instead in the presence of an active Lewis acid, under monomer starvation conditions. It can be illustrated as follows [140]:



Storey et al. [140] reported that the rate of depletion of *tert*-chloride end groups follows first-order kinetics with an apparent rate constant of 8×10^{-5} s^{-1}. The ratio of rate constants for propagation and rearrangement, k_p/k_R was found by them to be 3×10^{-4} M^{-1}.

Fedor et al. [141] also studied the living cationic polymerization of isobutylene using 2-chloro-4,4,4-trimethylpentane/$TiCl_4$/2,6-di-*tert*-butyl-pyridine system in hexane/methyl chloride (60/40 and 40/60) solvent mixtures at various temperatures ranging from −25 to −80°C temperatures. Their structural analysis of products obtained at −40°C using ^1H NMR spectroscopy shows the presence olefinic end groups, increasing in content with increased conversion. This led them to conclude that termination in polymerizations carried out at higher temperature does involve terminative chain transfer or β-proton elimination from the living chain ends. They found that the eliminated proton is trapped instantly by a proton trap, 2,6-di-*tert*-butylpyridine [141].

Aoshima and coworkers [142] investigated the living polymerization of isobutyl vinyl ether using pyrrole, metal halides and a weak Lewis base. In conjunction with oxophilic acids such as $ZrC1_4$, long-lived species were produced to yield polymers with narrow molecular weight distributions and number average molecular weight values based on the used amounts of pyrrole. Acid-trapping experiments using silyl ketene acetal, indicated that pyrrole worked not as an initiator but as a transfer agent. The polymerization started from moisture reacting with zirconium chloride, followed by the reactions between the propagating species and the 2- and 5-positions of pyrrole, accompanied by the generation of HCl. In addition to the propagation from the generated HCl, the produced pyrrole-bonded chain-end structures were also activated by the oxophilic chlorides to generate propagating carbocationic via the abstraction of the isobutoxy group. As a result, the number of growing chains increased. Such transfer reactions occur predominantly in the early stage of the polymerization stemming from the highly nucleophilic nature of pyrrole. Thus, the resulting polymers have expected molecular weight values and narrow molecular weight distribution [142].

4.3.6 Thermodynamics of Cationic Polymerization

Sawada [406] described the thermodynamics' of cationic polymerization as follows: The process of protonic acid initiation of cationic polymerization starts with heterolytic bond dissociation of the acid. The energy of this process can be designated by the quantity e_2, the affinity of the proton for the olefin. The potential energy between ion pairs separated at a distance r is

$$e_3 = e^2/rD$$

where e is the unit of electronic charge and D the dielectric constant. The total entropy change of the system is

$$\Delta H = e_1 - e_2 - e_3$$

where, e_1 is the acid strength of the initiator, e_2 is the proton affinity of the monomer, and e_3 is the solvating power of the solvent.

The change in free energy of initiation is,

$$\Delta F_{\mathrm{i}} = \Delta H - T\Delta S$$

By substituting the above values, the free energy change of initiation, can be written as

$$\Delta F_{\mathrm{i}} = e_1 - e_2 - e^2/rD - T\Delta S$$

The entropy change and the enthalpy change are negative for the free energy change to be negative.

In the propagation process, the change in activation entropy is based on two phenomena: (a) the entropy change of immobilization of a free-moving monomer into a polymeric chain and (b) the difference of entropy in the solvation between the reactants and the transition state, which can be written as

$$\Delta S^* = \Delta S^*(\text{immobilization of monomer}) + \Delta S^*(\text{solvation})$$

ΔS^* solvation is a positive term because in the transition state the electric charge is more diffuse and the degree of solvation is lower than that of the more compact dipolar species corresponding to reactants.

The propagation constant, based on Eyring theory,

$$\begin{aligned} k_{\mathrm{p}} &= A_{\mathrm{p}} \exp(-\Delta E_{\mathrm{p}}{}^*/RT) \\ &= (kT/h) \exp(\Delta S^*/R) \exp(-\Delta E_{\mathrm{p}}{}^*/RT) \end{aligned}$$

the activation entropy is $\Delta S_{\mathrm{p}}{}^*$ is the function of f_τ and f_{i}, the partition functions of the transition and initial states of the propagation step, respectively,

$$\Delta S_{\mathrm{p}}{}^* = R \ln(f_\tau/f_{\mathrm{i}}) + RT\,\delta \ln(f_\tau/f_{\mathrm{i}})/\delta T$$

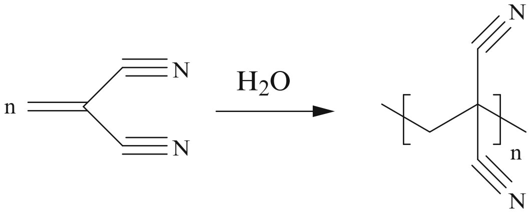
f_τ and f_{i} can be assigned, according to Sawada [406] to be the partition functions of the monomer in the transition sate (f_τ(m)) and that of the monomer in the initial state (f_i(m)), because other parts of the growing chain are common in the transition and initial states of the propagation reaction.

The term: $RT\ \delta \ln(f_\tau/f_i)/\delta T$ are negligible compared with $R \ln(f_\tau/f_i)$. The activation entropy can, therefore be written as:

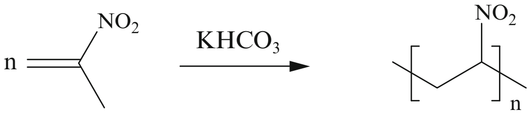
$$\Delta S_p{}^* = R \ln(f_\tau/f_i)$$

4.4 Anionic Polymerization of Olefins

As is stated in the beginning of this chapter, the distinctive features of the anionic chain-growth polymerizations are the negative charges at the active centers. Many different bases initiate such polymerizations, depending on the monomer. The most common ones are organometallic compounds, alkali metals, metal amides, and Grignard reagents. Monomers with carbanion stabilizing substituents, either through resonance or through induction, polymerize most readily. Such substituents, in fact, determine the base strength of the initiators needed to carry out these polymerizations by their electron withdrawing capacity. Thus, for instance, very weak bases, such as water, initiate vinylidene cyanide polymerizations:



Potassium bicarbonate initiates polymerization of 2-nitropropene:



On the other hand, monomers like acrylic or methacrylic esters and conjugated dienes require strong bases, like alkali metals or organometallic compounds.

4.4.1 Initiation in Anionic Chain-Growth Polymerization

Anionic initiations can take different paths. That depends upon the initiator, the monomer, and the solvent [143]. As a rough generalization, however, it is possible to separate the initiation reactions into two types: (1) those that take place through an addition of a negative ion to an olefin, and (2) those that result from an electron transfer.

The polymerization reactions can, furthermore, occur in two ways. One way is in a homogeneous environment, with both monomer and initiator soluble in the solvent. The other way is in a heterogeneous one, where only the monomer is soluble. Organolithium compounds are examples of soluble initiators, while metal dispersions are examples of insoluble ones.

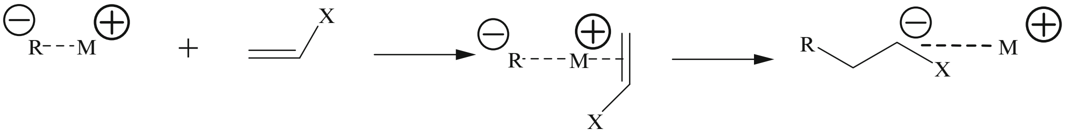
The homogeneous polymerizations can be separated further into those carried out in non-polar solvents and those in polar ones. In non-polar solvents they are confined mostly to organolithium initiators. Other organometallic compounds require polar solvents for solubility.

4.4.1.1 Initiation by Addition of an Anion to an Olefin

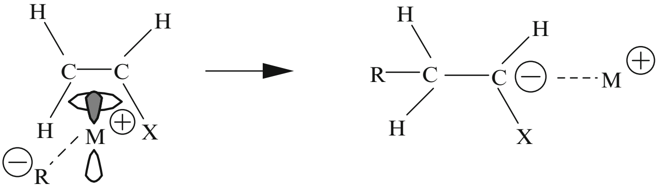
When organolithium compounds are dissolved in non-polar solvents there is a strong tendency of the solute molecules to associate into aggregates. For instance, butyllithium is hexameric in hexane solution. This is true of ethyllithium [144, 145] as well. Addition of Lewis bases to these solutions causes formation of strong complexes between the bases and the organometallic compounds [146, 147]. This causes the clusters to breakup through a succession of equilibrium with tetrameric and dimeric intermediates, all becoming complexes with the Lewis bases [146]. Particularly effective bases are those that allow a close approach of the lithium ion to the heteroatom. Often, the carbon–lithium bond, that normally only ranges between 20 and 40% in ionic character, becomes much more ionic [148, 149].

The breakdown of the aggregates was shown to dramatically enhance the reactivity of the organometallic compounds [150, 151]. For instance, polymerizations of styrene in benzene with butyllithium are slow reactions. When, however, these polymerizations are carried out in tetrahydrofuran they are extremely rapid. Tetrahydrofuran is, of course, a Lewis base. Nevertheless, the breakdown of the aggregates even in such Lewis bases as tetrahydrofuran or diethyl ether are not complete, though the clusters are smaller and more solvated. Differences in reactivity, however, can be observed even in different non-polar solvents [152].

The reaction rates depend to a great extent on the nature of the organometallic compounds, such as polarity of the bonds and the degree of solvation. In polar solvents, where free solvated ion-pairs predominate, the mechanism of initiation may simply consist of a direct addition of the anion to the monomer. If the solvents are non-polar, on the other hand, the initiation is more complex. In these solvents, the metal cation coordinates with the monomer first. This is followed by a rearrangement [153]:



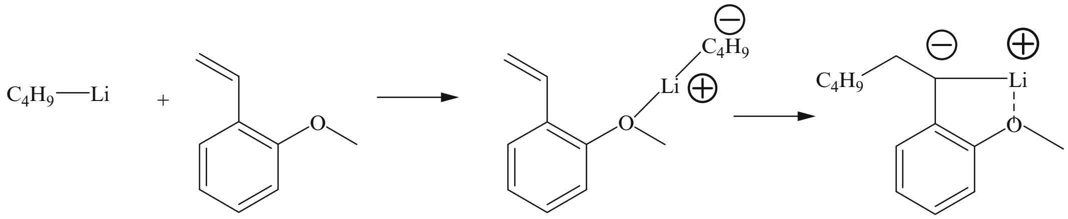
In the initial coordination, the π-electron cloud of the olefin overlaps with the outer bond orbital of the metal cation. This causes stretching and eventual rupture of the R–M (metal) bond. An intramolecular rearrangement follows with the migration of the carbanion ($R^{\ominus}$) to the most electron-deficient carbon atom of the double bond. A new covalent bond and a new carbanion are formed simultaneously:



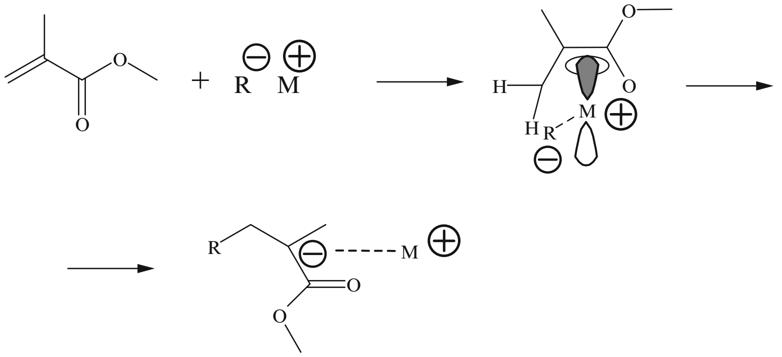
where M represents the metal.

The basicity of the anion portion of the initiating species is also important. For instance, fluorenelithium initiates polymerizations of methyl methacrylate but fails to initiate polymerizations of styrene. A more electronegative butyl anion from butyl lithium, on the other hand, initiates polymerizations of both monomers. Yet, it was also shown that the order of reactivity is often contrary to the inherent basicity.[103–146] This may be due to the size of the aggregates that the particular organometallic compound forms. In addition, higher reactivity may also be due to favorable energy requirements for breaking down the aggregates [146].

Presence of heteroatoms like oxygen or nitrogen in the monomer causes rapid complexation with the organometallic compounds. For instance, when butyllithium initiates polymerization of styrene in hydrocarbon solvents, there is an induction period and the overall reaction is slow and sluggish. When, however, it initiates polymerization of *o*-methoxystyrene under the same conditions, there is no induction period and the reaction is rapid. This is due to the initiator coordinating with the oxygen atom [153–155]:



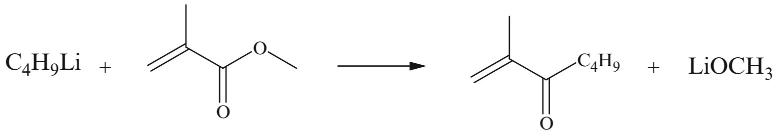
A similar coordination with the heteroatom takes place in polymerizations of acrylic and methacrylic esters [156]. Here, the metal coordinates with the electron cloud of the whole conjugated structure. The overlap stretches and eventually ruptures the metal-alkyl bond. A new carbon to carbon covalent bond forms together with a new metal to carbon linkage:



where M represents the metal.

The product might be a resonance hybrid of the two structures where the metal is associated with the carbanion in one and with the oxygen in the other [157].

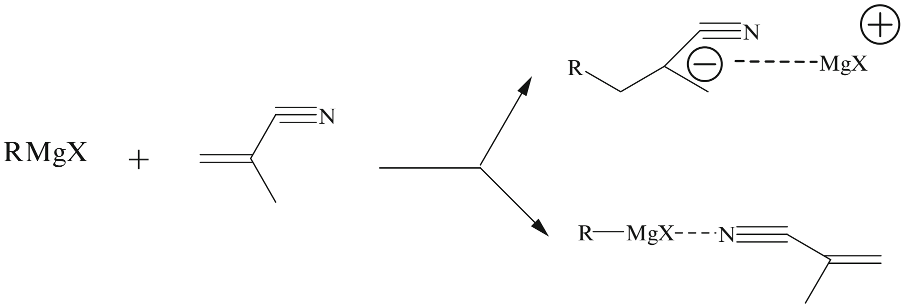
Some abnormalities were reported in the initiations of methyl methacrylate polymerizations in toluene by butyllithium. Their nature is such that they suggest the possibility of more than one reaction taking place simultaneously [158]. One, that must be the major one, is that of the organometallic compound reacting with the carbon to carbon double bond as shown above. The other, minor one, may be with the carbon to oxygen double bond. The major reaction produces methyl methacrylate anions. The minor reaction, however, yields butyl isopropenyl ketone with an accompanying formation of lithium methoxide [158]:



Lithium methoxide does not initiate polymerizations of methyl methacrylate. The methoxide molecules, however, react with carbanions on the growing chain. The resultant anions are less reactive than methyl methacrylate anions and can only add new methyl methacrylate monomers slowly.

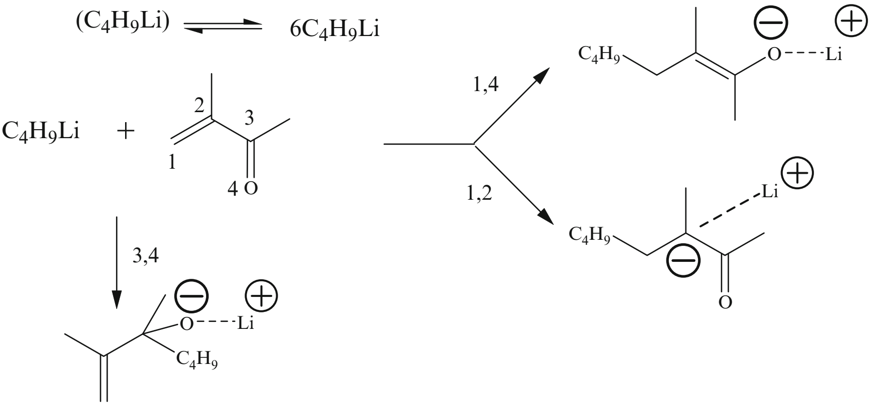
Once added, however, the reaction proceeds at a normal rate [158]. Polymerizations of methyl methacrylate in polar solvents, on the other hand, proceed in what might be described as an ideal manner with formations of only one kind of ion pairs [159–162].

Other monomers can also exhibit abnormal behavior in some anionic polymerizations. Thus, for instance, organomagnesium initiation of methacrylonitrile polymerization results in formation of two types of active centers [163, 164]:

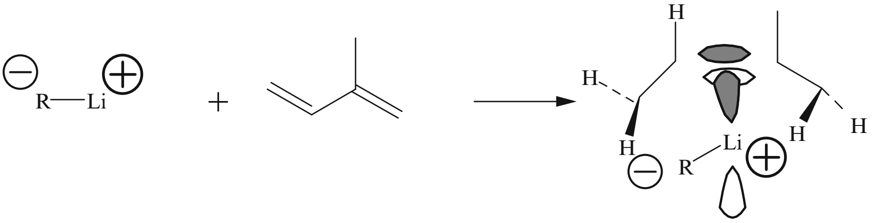


Methyl methacrylate polymerizations, initiated by organomagnesium compounds, also yield abnormal products. Here, the active centers are unusually persistent and stable. In addition, the α-carbon atoms of the monomers were found to assume tetrahedral configurations [165–167]. This suggests that the active centers contain covalent magnesium carbon bonds. Also, gel permeation chromatography curves of the products show that more than one active center operates independently [166, 167]. A "***pseudo anionic***" mechanism was, therefore, postulated for polymerizations of acrylic and methacrylic esters [111, 112] by Grignard reagents.

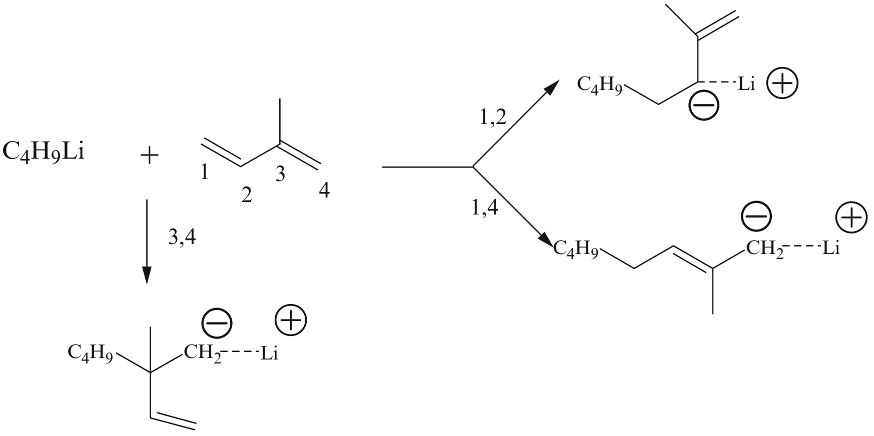
Three different simultaneous reactions appear to be taking place in butyllithium-initiated polymerizations of vinyl ketones in benzene [168]:



The initiations of the polymerizations of the conjugated dienes in inert hydrocarbons are also believed to be preceded by coordination of the organometallic compounds with the π-electron clouds of the monomers:



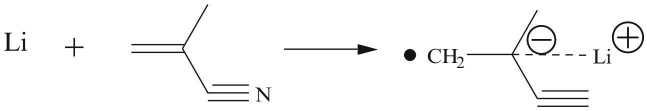
The rearrangement that follows can result in either 1,2; 1,4; or 3,4 additions to the double bond:



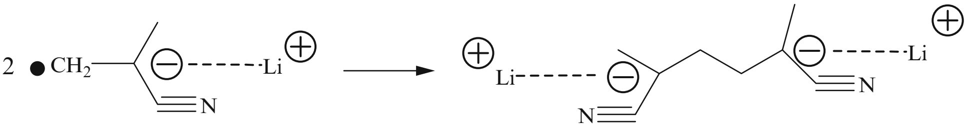
4.4.1.2 One Electron Transfer Initiation

Alkali metals initiate anionic polymerizations of olefins in either homogeneous or heterogeneous conditions. This depends upon the metal and upon the solvent. For instance, potassium is soluble in ethers, like dimethoxyethane or tetrahydrofuran, and the initiation conditions are homogeneous. On the other hand, sodium dispersions are insoluble in hydrocarbons and the initiations are heterogeneous. Liquid ammonia is a solvent for many alkali metals, though for some, like sodium, it can be a reactant and form metal amides, provided that traces of iron are present. Initiation reactions in many metal solutions take place by an electron transfer from the metal to the monomer to form anion radicals. The resultant anion radicals may then undergo propagation reactions. These propagations can proceed anionically, or by a free-radical mechanism, or by both simultaneously. If the radicals are unstable the anion-radicals dimerize and the propagation proceeds by an anionic mechanism at both ends of the chain.

When liquid ammonia is employed as the solvent, as stated earlier, the particular mechanism of initiation will depend upon the metal used. Lithium metal forms solutions in liquid ammonia and initiates polymerization of monomers like methacrylonitrile by an electron transfer [169]:

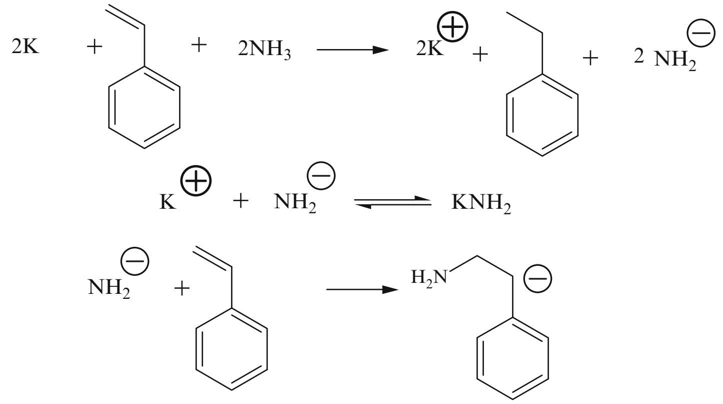


These radical-anions couple and chain growth takes places from both ends of the chains:

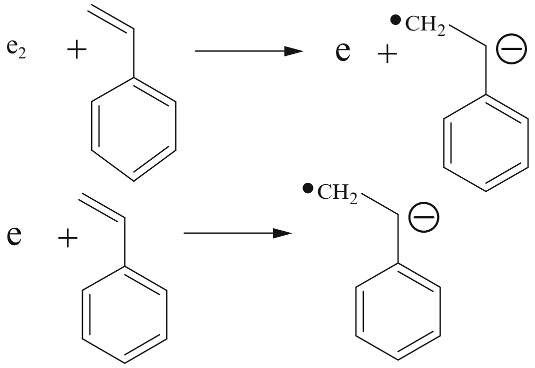


Dimerization of radical-ions depends not only upon the radical’s stability but also upon the π-energy changes that accompany the reaction [170, 171].

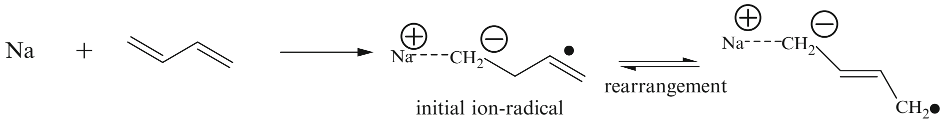
Potassium metal in ammonia, however, initiates polymerizations of monomers like methacrylonitrile or styrene differently. These reactions include additions of amide ions to the olefins and formations of amine groups at the end of the chains [172]:



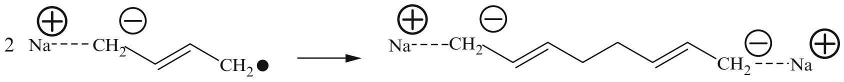
Solutions of potassium metal in ethers, however, form ion radicals through additions of electrons to the monomers. It should be noted, that fresh solutions of potassium metal in various ethers like tetrahydrofuran or dimethoxyethane are blue in color. This blue color is attributed to a presence of spin-coupled electron pairs (e_2). The initiation of styrene polymerization that takes place between 0 and −78°C is, therefore, pictured as both, reactions of the spin-coupled pair with the monomers and also additions of individual electrons [169]:



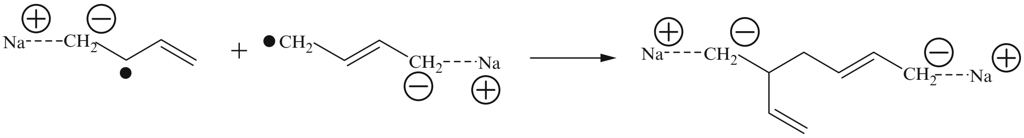
When conditions are heterogeneous and sodium metal dispersions are used in polymerizations of dienes, the initiation mechanism is also by an electron transfer. It is believed [135] that initially a 1,2 anion-radical forms. This is followed by a coupling reaction:



the coupling process:

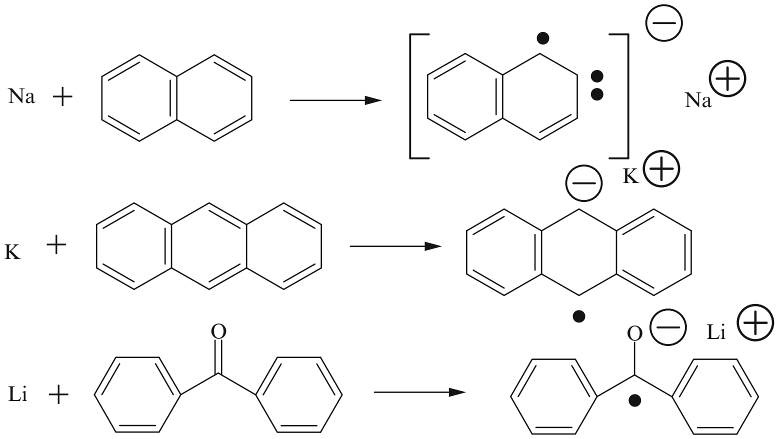


a different kind of coupling is also possible:

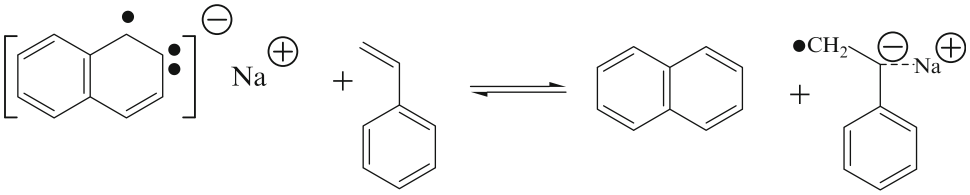


The following initiation mechanism was postulated [173] for heterogeneous conditions. At first, the highly polarized monomers adsorb strongly to the metal surfaces. Electron transfer takes place. The adsorbed molecules are assumed to be still sufficiently mobile to be able to rotate after adsorption. The rotation allows the radical-anions that form to couple. The concentration of the anionic charges that develop on the methine carbons creates strong enough attractive forces to remove the metal cations from the surface. Solvents that strongly solvate the cations, like tetrahydrofuran, enhance the process. To fit the above mechanism [173], the monomers must be capable of adsorbing strongly to the metal surfaces and the solvents must also be strongly solvating. When the reactions are carried out without solvents or in inert solvents like heptane, the free-energy gain due to solvation is largely lost. This increases the probability that in such instances the propagations occur on the surface of the metals until the oligomers grow to a certain length. When sufficient length is reached to create a favorable free-energy change, desorption occurs and the molecules pass into solution [173].

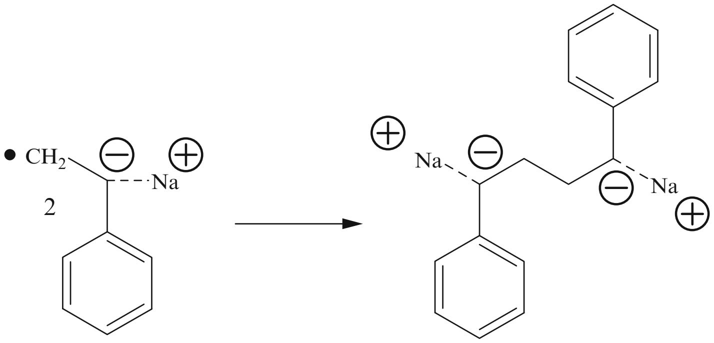
Electron transfer initiations can also result from reactions of alkali metals with aromatic hydrocarbons or with aromatic ketones that result in formations of radical-ions:



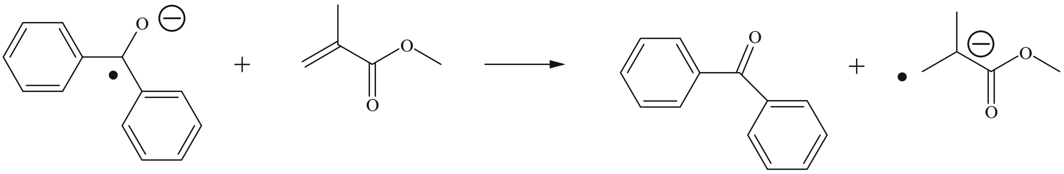
The ion-radicals transfer both the electron and the ion charge to the monomers in the process of initiation, as was shown by Szwarc and coworkers [174–180]:



The styrene monomer-radical-ion is unstable and tends to dimerize:



Metal ketyls form in reactions of alkali metals with aromatic ketones in some polar solvents, like dioxane or tetrahydrofuran. These ketyls exist in equilibrium mixtures of monomeric anion-radicals and dimeric dianions [136]. Originally there was some controversy about the mechanism of initiation of monomers like acrylonitrile or methyl methacrylate by sodium benzophenone. The following mechanism was derived from spectral evidence. The initiation is by transfer of the electron and the ion charge [181–183]:



4.4.1.3 Initiations by Alfin Catalysts

These are catalysts that are formed by combining an alkyl sodium with sodium alkoxide and with an alkali metal halide [184–189]. A typical, effective catalyst for polymerization of dienes consists of allyl sodium, sodium isopropoxide, and sodium chloride. The preparation of such a catalyst is carried out by combining amyl chloride with sodium and then reacting the product with isopropyl alcohol. After that, propylene is bubbled through the reaction mixture to convert amyl sodium to allyl sodium. The reactions can be summarized as follows

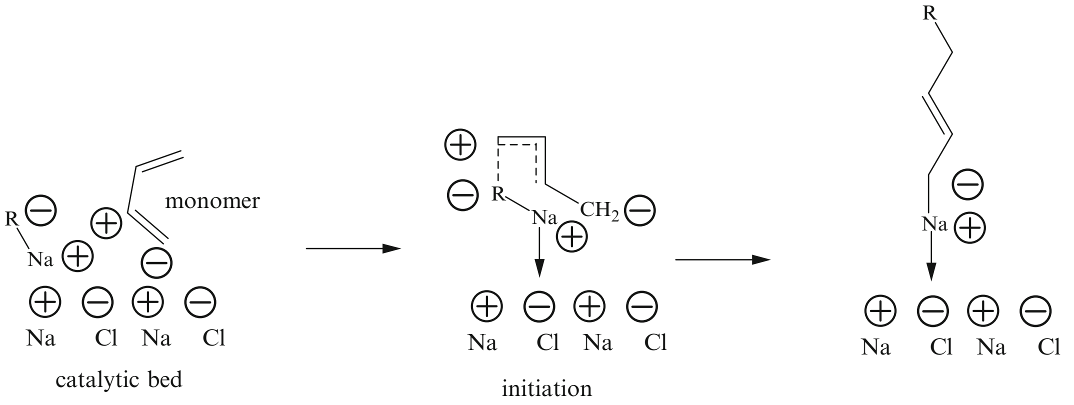
$$1.5C_5H_{11}Cl + 3Na \rightarrow 1.5C_5H_{11}Na + 1.5NaCl$$

$$C_5H_{11}Na + (CH_3)_2CHOH \rightarrow (CH_3)_2CHONa + C_5H_{12}$$

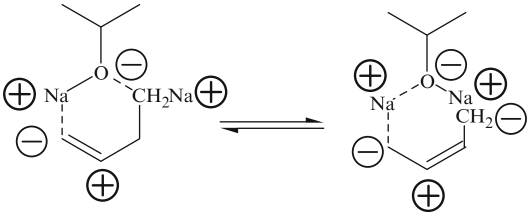
$$C_5H_{11}Na + CH_3 - CH = CH_2 \rightarrow C_5H_{12} + CH_2 = CH - CH_2Na$$

Diisopropyl ether may be used in place of isopropyl alcohol. In that case, the reaction does not require addition of propylene because the olefin forms in situ [189]. These catalysts are particularly effective in polymerizations of some conjugated dienes to very high molecular weight products. Styrene can also be polymerized by these catalysts. Polymers of the dienes that form are high in *trans*-1,4 repeat units. Butadiene is polymerized by these catalysts much more rapidly than is isoprene. On the other hand, 2,3-dimethylbutadiene fails to polymerize.

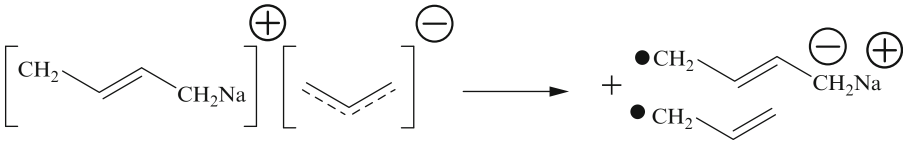
There is no general agreement about the mechanism of these polymerizations. Both anionic and free-radical mechanisms were proposed [184–189] as the most probable reaction paths. The role of sodium chloride is not clear in this mixture, though it was shown that it is essential [184–189]. It may act, perhaps, as a support for the catalyst and may be a part of some sort of lattice involving both sodium alkoxide and allyl sodium. The anionic mechanism is pictured as follows [184–189]:



The free-radical mechanism was suggested due to high predominance of *trans*-1,4 placement in polymerization of butadiene [189]. According to that mechanism a complex of sodium isopropoxide and allyl sodium forms first:



The monomer adsorbs on the surface and is visualized as displacing the allyl anion from the complex to form an ion pair first and then, through an electron rearrangement, a radical [189]:

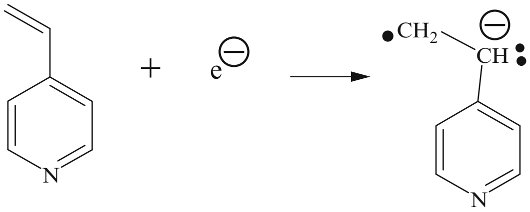


The polymerization is assumed to go on from this point via free-radical mechanism until a combination with an allyl radical takes place. Because the allyl radical is bound to the catalyst surface, combination does not take place readily and high molecular weights are attained.

4.4.1.4 Electroinitiation of Anionic Polymerizations

Electrolytic polymerizations were described in the section dealing with cationic polymerizations. Anionic polymerizations can also be initiated in an electric field. When $LiAlH_4$ or $NaAl(C_2H_5)_4$ are used as electrolytes in tetrahydrofuran solvent "living" polymers can be formed from α-methylstyrene [190]. The deep red color of carbanions develops first at the cathode compartments of divided cells.

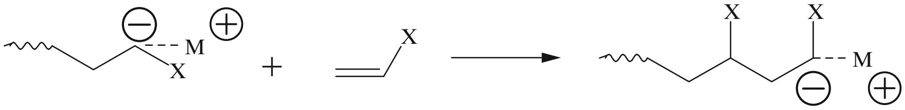
By cooling the solutions to −80°C almost quantitative conversions to high molecular weight polymers take place [190]. Similar conditions yield polystyrene [191]. 4-vinyl pyridine polymerizes in liquid ammonia in the same manner [191]. Initiation results from reduction of the monomer by direct electron transfer at the cathode to form a red–orange vinyl pyridyl radical-anion:



Another example is polymerization of isoprene in an electric field in tetrahydrofuran solution. Here too, a "living" polymer forms [192].

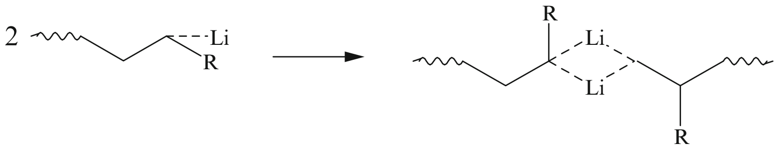
4.4.2 Propagation in Anionic Chain-Growth Polymerization

The propagation reaction consists of successive additions of monomer molecules to the active centers of the growing chains:

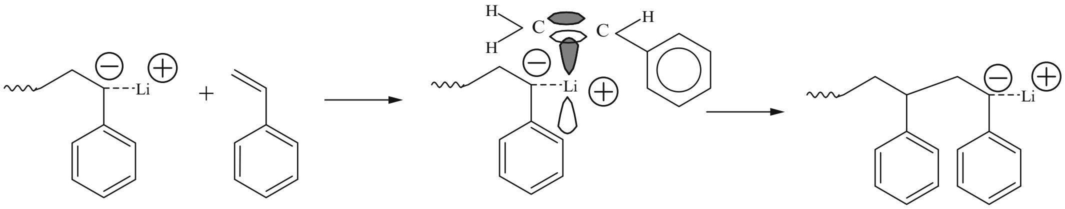


No matter what the mechanism of initiation is, the propagation reaction takes place strictly between the monomer and the growing polymeric chain with or without a counterion.

When the reaction occurs in non-polar solvents the propagation step is not hampered as much by a tendency of ion pairs to cluster into aggregates, as is encountered in initiation. For instance, in butyllithium initiated polymerizations of styrene in benzene, the propagation step is much faster than the initiation [193, 194]. This is probably due to an absence of aggregates. Some association between the growing polymeric chains, however, does occur [193]. It may be shown as follows:



These association equilibriums, however, are mobile in character [193]. The driving force in the propagation reaction is similar to that in the initiation. In non-polar solvents the reaction with the incoming monomers are similar to those in the initiation step. The monomers coordinate with the cations at the end of the chains first. This is followed by intramolecular rearrangements that lead to regenerations of new metal carbon linkages:

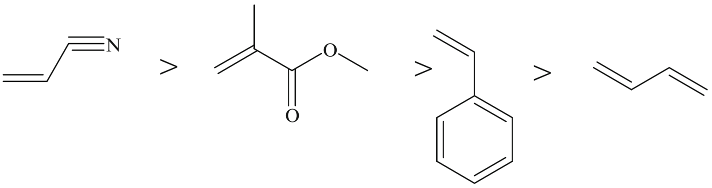


In polar solvents, on the other hand, these reactions can go to the other extreme. The propagation can simply consist of successive additions of the monomers to the growing anions.

In homogeneous anionic polymerizations of simple vinyl monomers steric placement is also temperature dependent, just as it is in cationic polymerizations. Syndiotactic placement is favored in polar solvents at low temperature. In non-polar solvents, however, isotactic placement predominates at the same temperatures. Here too, this results mainly from the degree of association with the counterion [181].

Much of our current knowledge of the propagation reaction is based on studies carried out in highly solvating ether solvents. Less information is available about homogeneous reactions in non-polar medium. Generally, though, the rate of propagation increases with solvent polarity and with the degree of ion pair dissociation [195]. Organolithium compounds undergo the greatest degree of solvation when changed from hydrocarbons to polar ether solvents. Cesium compounds, on the other hand, are least affected by changes in solvent polarity. In addition, NMR studies of polystyryl carbanion structures associated with lithium, potassium, and cesium counter cations were studied in different solvents and at different temperatures [196]. The results show an interaction between the larger radius cations and the phenyl rings of the ultimate monomer units in the chains. The structures with potassium and cesium counterions, judging from model compounds, were found to be planar with sp^2-hybridized α-carbon. It suggests that in the presence of the larger counterions, rotation of the terminal phenyl ring in styrene polymerization is strongly hindered.

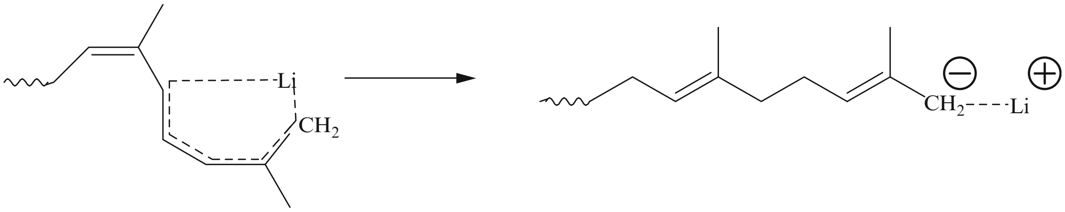
Propagation rates also depend upon the structures of the monomers. For polymerizations initiated by alkali amides the following order of reactivity was observed [197]:



Also, methyl substitution on the α-carbon tends to decrease the reaction rate due to the electron releasing effect of the alkyl group. This tends to destabilize the carbanion and also to cause steric interference with solvation of the chain end and with the addition of the monomer [197].

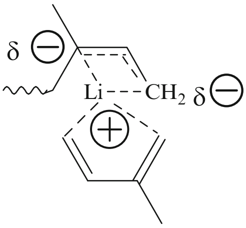
4.4.2.1 Steric Control in Anionic Polymerization

Use of hydrocarbon solvents has an advantage in polymerizations of conjugated dienes because they yield some steric control over monomer placement. This is true of both tacticity and geometric isomerism. As stated earlier, the insertions can be 1,2 or 3,4 or 1,4. Furthermore, the 1,4-placements can be *cis* or *trans*. Lithium and organolithium initiators in hydrocarbon solvents can yield polyisoprene, for instance, which is 90% *cis*-1,4 in structure [99]. The same reaction in polar solvents, however, yields polymers that are mostly 1,2 and 3,4, or *trans*-1,4 in structure. There is still no mechanism that fully explains steric control in polymerization of dienes. High *cis*-1,4 polyisoprene forms with lithium or alkyl lithium initiators in non-polar solvents because, propagation takes place through essentially covalent or intimate ion-pair lithium to carbon bonds [99]. An intermediate pseudo-six-membered ring is believed to form in the process of addition of the diene [99]:



Formation of such intermediates is favorable for lithium because it has a small ionic radius and is high in the proportion of *p*-character. Organometallic compounds of the other alkali metals (sodium, potassium, rubidium, and cesium) are more polar and more dissociated. They react essentially as solvated ions even in a hydrocarbon medium, yielding high 3,4 placement.

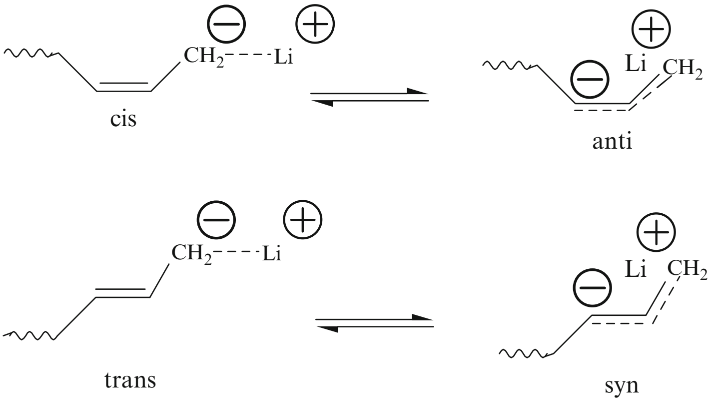
O'Driscoll et al. [198] proposed a mechanism for steric control. In isoprene polymerization the terminal charges are complexed with the metal cations. These cations are close to the active centers through the occupied π-orbitals of the chain ends and the unoccupied p-orbitals of the lithium ions. In the transition state the monomers are complexed with the cations in the same way [198]. The lithium cations are assumed to be in hybridized tetrahedral sp^3 configurations with four vacant orbitals. The chain ends are presumed to be allylic and the diene monomers are bidentate [198]. During the propagation steps both the monomers and the chain ends complex with the same counterions:



In hydrocarbon solvents, the complexes are tight and the rotations of the C_2–C_3 bonds are sterically hindered by the methyl groups. This constrains the 1,4-additions to *cis*-configurations. In polar solvents, however, like tetrahydrofuran, the complexes are loose and thermodynamically favored *trans* additions take place [198].

It was observed, however, that the polymerizations of 2,3-dimethylbutadiene with organolithium initiators in non-polar solvents result in high *trans*-1,4 structures [199]. This appears to contradict the above-proposed mechanism.

Proton NMR spectra show that solvation shifts the structures of the carbanionic chain ends from localized 1,4-species to delocalized "π-allylic" type structures [200]:



The σ-bonded lithium chain can be expected to predominate. In highly solvating solvents, such as ethers, the π-allyl structure is dominant leading to high 1,2 placements. Because the 2,3-bond is maintained, the above shown equilibrium should not be expected to lead to *cis–trans* isomerization [200]. In fact, such isomerizations do not take place for butadiene or for isoprene when they are polymerized in hydrocarbon solvents. They do occur, however, in polar solvents at high temperatures. This suggests that additional equilibrium exist between the π-allylic structures and the covalent 1,2 chain ends [200]. Table 4.3 shows the manner in which different polymerization initiators and solvents affect the microstructures of polyisoprene.

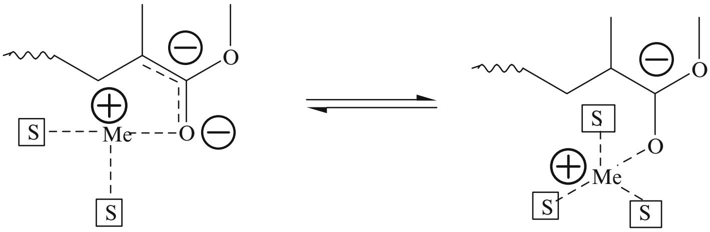
Table 4.3 Effect of counterion and solvent on the microstructure of polyisoprene[a] approximate% of adduct

Initiator	Solvent[a]	*Cis*-1,4	*Trans*-1,4	1,2	3,4
Lithium dispersion	Alkane	93	1	–	5–6
Ethyllithium	Alkane	94	–	–	6
Butyllithium	Alkane	93	–	–	7
Sodium dispersion	Alkane	–	43	6	51
Ethylsodium	Alkane	6	42	7	45
Butylsodium	Alkane	4	35	7	54
Potassium dispersion	Alkane	–	52	8	40
Ethylpotassium	Alkane	24	39	6	31
Butylpotassium	Alkane	20	41	6	33
Rubidium dispersion	Alkene	5	47	9	39
Cesium dispersion	Ether	4	51	8	37
Ethyllithium	Ether	6	30	5	59
Ethylsodium	Ether	–	14	10	76
Lithium dispersion		3	27	6	64

[a]From various sources in the literature. The alkane is a low boiling aliphatic hydrocarbon

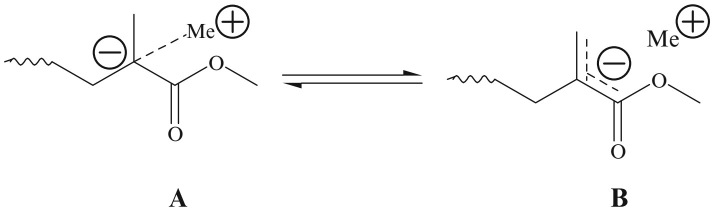
Polymerizations of polar monomers, like acrylic and methacrylic esters with alkyllithium initiators yield the greatest amount of steric control [151]. An almost all isotactic poly(methyl methacrylate) forms at low temperatures. Addition of Lewis bases such as ethers or amines reduces the degree of isotactic placement. Depending upon the temperature, atactic or syndiotactic polymers form [151]. Also, butyllithium in heptane yields an isotactic poly(*N*,*N*′-dibutylacrylamide) at room temperature [201].

The propagation rates for methyl methacrylate polymerization in polar solvents like tetrahydrofuran or dimethylformamide are lower than the rates of initiation [203]. There is no evidence, however, that more than one kind of ion pairs exist [204–206]. The ion pairs that form are apparently contact-ion pairs [203]. Furthermore, based on the evidence, the counterions are more coordinated with the enolate oxygen atoms of the carbonyl groups than with the α-carbons. As a result, they exert less influence on the reactivity of the carbanions [203]. The amount of solvation by the solvents affects the reaction rates. In addition, "intramolecular solvation" from neighboring ester groups on the polymer chains also affects the rates. In solvents like dimethylformamide, tetrahydrofuran, or similar ones [203], the propagating chain ends–ion pairs are pictured as hybrid intermediates between two extreme structures. This depends upon the counterion, the solvent, and the temperature [203]:

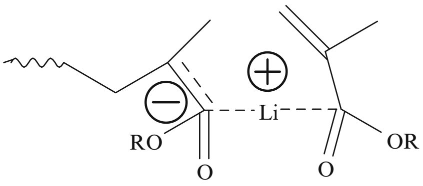


where S means a solvent molecule; Me represents a metal.

Several mechanisms were offered to explain steric control in polymerizations of polar monomers. Furukawa and coworkers [157] based their mechanism on infra-red spectroscopy data of interactions between the cations and the growing polymeric chains in polymerizations of methyl methacrylate and methacrylonitrile. They observed a correlation between the tacticities of the growing molecules and the carbonyl stretching frequencies. The higher the frequency, the higher is the amount of isotactic placement in the resultant chains. The adducts, just as in the initiation reactions, are resonance hybrids of two structures, A and B:

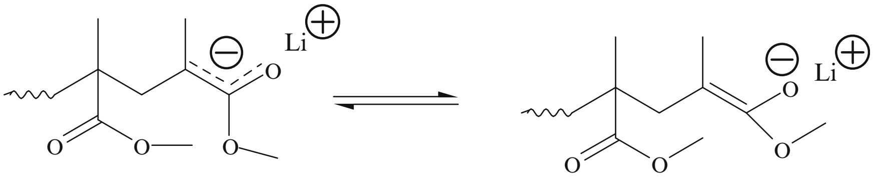


where Me represents a metal. Furukawa and coworkers concluded that due to the extremely low tendency of the adducts to dissociate [157], the carbonyl absorption can only be ascribed to undissociated ion pairs. The magnitude of the carbonyl absorption and the shifts to higher frequencies show the degree of contribution of structure B, shown above. The absorption and the shifts were also explained by the configurations of the electrons in the anti-bonding orbitals of the carbonyl groups. The higher the stretching frequencies, the nearer are the positions of the counterions to the carbonyl groups of the terminal units [207]. This is accompanied by higher tacticity [157]. The carbanions on the terminal units in the transition states are located near the β-carbons of the incoming monomers. At the same time, rotations around the axis through these two carbons may be quite restricted when the cations are in the vicinity of the carbonyl groups of the terminal unit and near the incoming monomers. In this manner, isotactic placement is enhanced [157]:

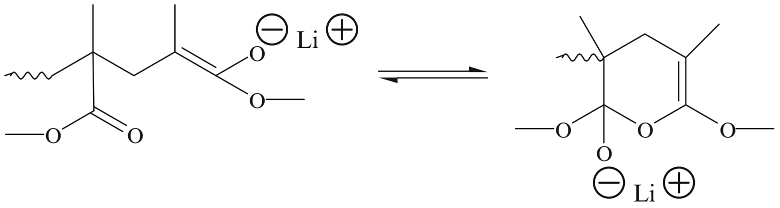


The same mechanism was proposed for the polymerization of methacrylonitrile [157].

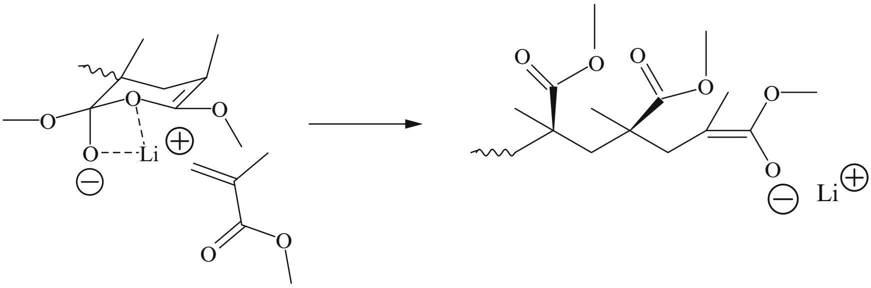
Cram and Kopecky [219] offered a different mechanism of steric control. According to their mechanism, during a methyl methacrylate polymerization the growing ether enolate possesses a complete alkoxide character:



Attacks by the alkoxide ion on the carbonyl groups of the penultimate units lead to formations of six-membered rings:

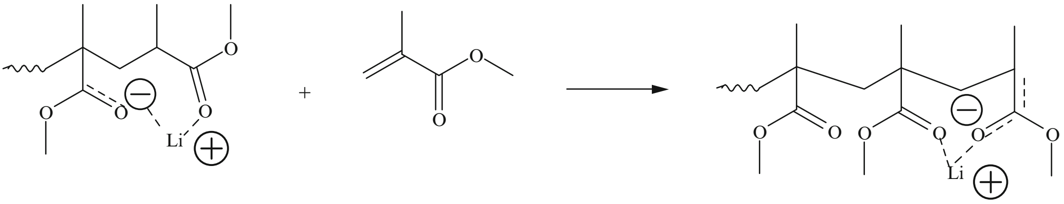


The six-membered ring is destroyed in the process of propagation:



The transition state formed by a 1,4-dipolar addition to a polarized double bond. Coordination of the lithium atom to two oxygen atoms determines stereoregulation. Each new incoming monomer must approach from below the plane because the other side is blocked by an axial methyl group. This favors isotactic placement. There is doubt, however, whether it is correct to assume a rigid six-membered cyclic alkoxide structure for a propagating lithium enolate [209].

A slightly similar model was suggested by Bawn and Ledwith [209]. It is based on the probability that a growing polymeric alkyl lithium should have some enolic character, with the lithium coordinating to the carbonyl oxygen of the penultimate unit:

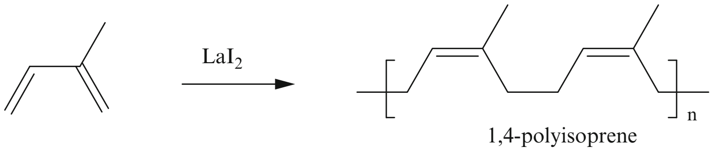


The cyclic intermediate forms due to intramolecular solvation of the lithium and due to intramolecular shielding of one side of the lithium ion. The nucleophilic attack by the monomer, therefore, has to occur from the opposite side. The transition state is similar to an S_{N^2} reaction. When the bond between the lithium and the incoming monomer forms, the oxygen lithium bond ruptures. Simultaneously, the charge migrates to the methylene group of the newly added monomer. The resultant new molecule is stabilized immediately by intramolecular solvation as before. In this manner, the retention of configuration is assured, if the incoming monomer always assumes the same configuration toward the lithium ion.

NMR spectra of poly (*N*,*N*-dimethylacrylamide) formed with *sec*-butyllithium in both polar and non-polar solvents show that the penultimate unit does affect monomer placement [210]. Also, a coordination was observed with both heteroatoms [152, 153], the one on the ultimate and the one on the penultimate unit.

Many refinements were introduced into the various proposed explanations of steric control in anionic polymerizations [211] over the last 30 or more years. Two important features of these mechanisms are: (1) coordinations of the chain ends with the counterions and (2) counterion solvation.

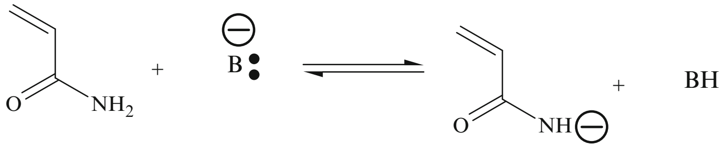
Use of complex lanthanide catalysts allows a very high *cis*-1,4 placement of isoprene monomer and preparation of polymers that are very close to natural rubber [212]. Thus, complex neodymium catalysts can yield polymers that are greater than 98% *cis*-1,4 polyisoprenes. The preparation of such catalyst, however is difficult. Evans et al. reported, however, that simple TmI_2, NdI_2, and DyI_2 will initiate polymerization of isoprene without any additives and can also yield high *cis*-1,4 placement [213]:



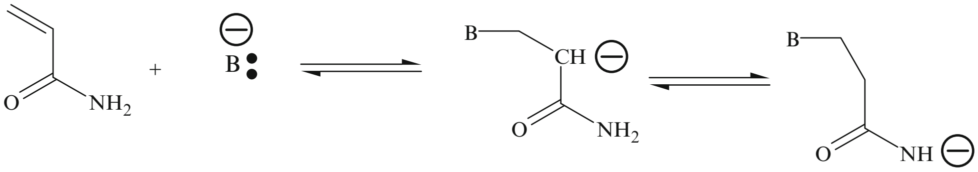
4.4.2.2 Hydrogen Transfer Polymerization

Anionic polymerization of unsubstituted acrylamide, catalyzed by strong bases, does not yield typical vinyl polymers. Instead, the product is a 1,3-adduct, poly(β-alanine) [214]. Two alternate reaction paths were originally proposed [214]. These can be shown as follows:

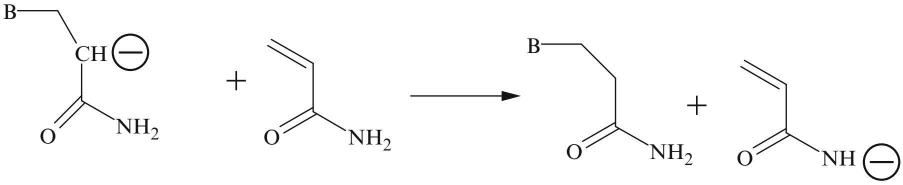
1.



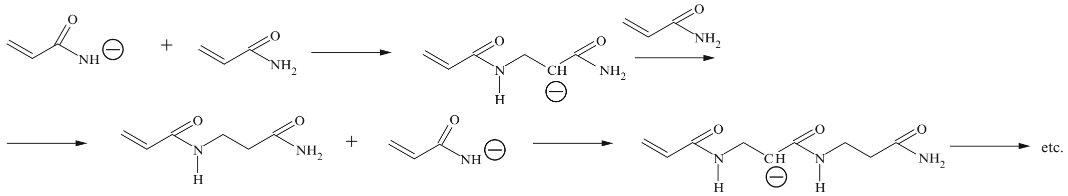
2,



Subsequently, studies of the rate of disappearance of acrylamide in dry sulfolane or pyridine with potassium-*t*-butoxide initiator led to the following proposed mechanism [215]:

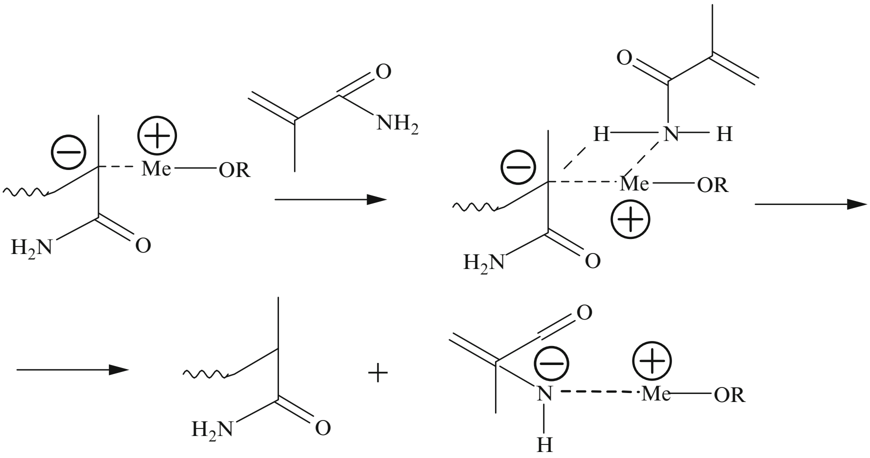


Propagation proceeds in this manner [215]:



The propagating center is neither an ion nor a radical, but a carbon to carbon double bond at the end of the chain. The monomer anion adds to this double bond. This process is a step-growth polymerization and the monomer anion is called an ***activated monomer***. Not all acrylamide polymerizations, initiated by strong bases, however, proceed by a hydrogen transfer process. Depending upon reaction conditions, such as solvent, monomer concentration, and temperature some polymerizations can take place through the carbon to carbon double bonds [216].

Cis and *trans* crotonamides can also polymerize by hydrogen transfer polymerization. Sodium *t*-butoxide in pyridine yields identical polymers from both isomers [217]. Also, hydrogen transfer polymerization of acrylamide with optically active, basic catalysts yields optically active polymers [218]. The reactions can be carried out in toluene, using optically active alcoholates of amyl alcohol. The initiating ability of the metal ions is in the following order, Na > Ba > Ca > Mg > Al [218]. Optically active polymethacrylamide forms with optically active barium and calcium alcoholates, but not with the other cations [218]. In this reaction, however, the asymmetric synthesis takes place through an intermolecular hydrogen transfer rather than through an intramolecular hydrogen migration [218]:



4.4.3 Termination in Anionic Polymerization

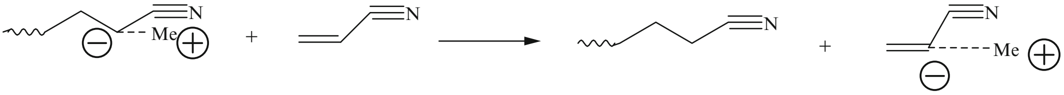
Termination reactions in anionic polymerization, particularly with non-polar monomers and in non-polar solvent are not common. If carbanion quenching impurities are absent, many polymerization reactions may not terminate after a complete disappearance of the monomer. Styryl anion, (one of the most stable ones) for instance, can persist for a long time, such as weeks, after the monomer is consumed. Addition of more monomer results in a continuation of the reaction and a further increase in the molecular weight. The anionic "**living**" polymers retain their activities considerably longer periods of time than do the cationic "living" ones [180].

The termination steps in anionic polymerizations can result from deliberate introductions of carbanion quenchers, such as water or acids, or from impurities. Terminations, however, can take place in some instances through chain transferring a proton from another molecule like a solvent or a monomer or even from a molecule of another polymer. In some solvents, like liquid ammonia, transfer to solvent is extensive, as in styrene polymerization by amide ions [219].

In addition, in some polymerizations termination might occur from the following reactions:

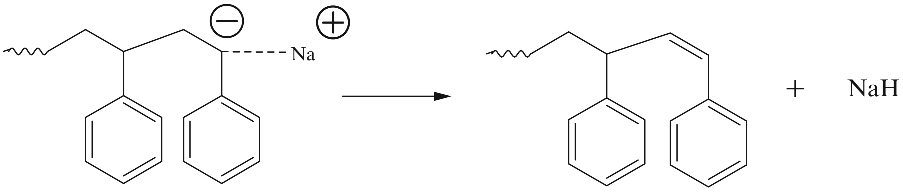
1. Elimination of a hydride-ion to form an unsaturated end.
2. Isomerization to an inactive anion.
3. Some irreversible reaction of the active center with a molecule of a monomer or a solvent.

It was observed, for instance that hydrogen transfer from monomer to the growing chain can be a way of termination in polymerizations of polar monomers, like acrylonitrile [220]:

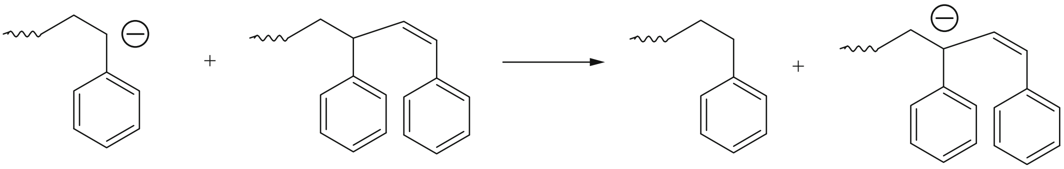


where Me represents the metal cation.

As mentioned above, the polystyryl carbanions are particularly stable and persist for weeks in non-polar solvents. Yet, even in the absence of terminating agents, the concentration of the carbanion active centers decreases with time [159]. The mechanism of decay is not fully understood. Based on spectral evidence, it is believed to consist of a hydride-ion elimination [219]:

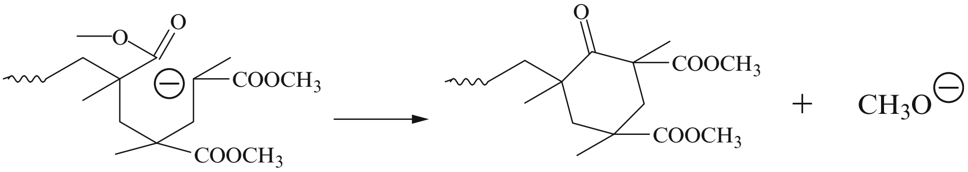


The above reaction can be followed by an abstraction of an allylic hydrogen from the product of elimination by another active center:



Polystyryl carbanions are much less stable in polar solvents. They decay within a few days at room temperature. At lower temperatures, however, the stability is considerably better. The termination in polar solvent occurs by a mechanism of abstracting α-hydrogens and/or by a nucleophilic attack on the carbon–oxygen bonds.

Polar monomers, like methyl methacrylate, acrylonitrile, or methyl vinyl ketone contain substituents that react with nucleophiles. This can lead to terminations and side reactions that compete with both initiation and propagation [219]. An example is a nucleophilic substitution by an intramolecular backbiting attack of a propagating carbanion:



Side reactions like the one shown above can be minimized by using less nucleophilic initiators and low temperatures. This can yield "living" polymerizations of acrylic and methacrylic monomers. In addition, it is possible to add common ions like LiCl to alkyl lithium to tighten the ion pairs of the propagating anion-counterion species. That also increases the tendency to form "living" polymers [221]. This approach, however, offers only limited success.

In addition. it was found that Lewis acid assisted polymerizations of methyl methacrylate with aluminum porphyrin initiators yield "living" polymers [222]. The polymerizations of methacrylate esters with alkylaluminum porphyrin initiators occur through formations of enolate aluminum porphyrin intermediate as the growing species [222]. For the sake of illustration, the methylaluminum porphyrin molecules (see Fig. 4.3) can be designated as:

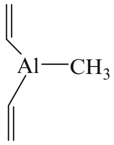
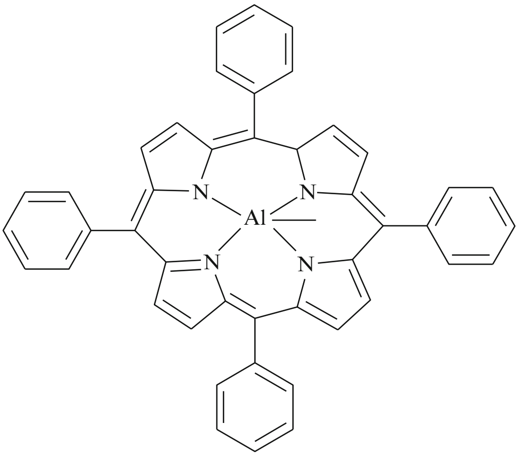
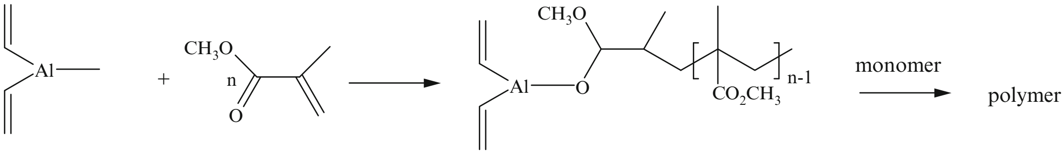


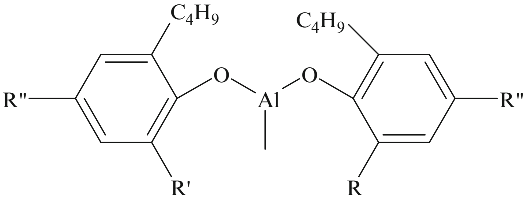
Fig. 4.3 Methylaluminum porphyrin molecule



The reaction can then be illustrated as follows [222]:



The preparatory procedure was improved [222] further by addition of sterically crowded organoaluminum phenolates to the reaction mixture:



where, R′ is H and R″ is butyl, or R′ is butyl and R″ is methyl. This yields "living," very high molecular weight, monodisperse polymers of methyl methacrylate [222]. Monomer insertion might be taking place at the Al–C bond. The mechanism, however, is not yet fully understood [222].

Ishizone and coworkers [223] studied living anionic polymerization of a series of *N*,*N*-dialkyl methacrylamides carried out with diphenyl methyllithium or with triphenylmethylpotassium in the presence of LiCl or diethyl zinc in tetrahydrofuran. Polymers of methacroyl azetidine possessed predicted molecular weights and very narrow molecular weight distributions of 1.1. They were obtained quantitatively with both catalysts at −40 to 0°C within 24 h. The acryloyl counterpart, *N*-acrytoyilazetidine, also underwent the anionic polymerization to afford the well-defined polymer quantitatively. By contrast, no polymer was obtained from the anionic polymerization system of *N*-methacroyl piperidine, nor with *N*,*N*-dimethyl methacrytamide. From the experimental results, it was demonstrated that the polymerizability of a series of *N*,*N*-dialkylmethacrytamides with cyclic substituents decreased drastically with increasing the ring size from 3 to 6.

4.4.4 Thermodynamics of Anionic Polymerization

The change of the equilibrium constant for the dissociation of ion pairs into free ions can be expressed as:

$$\ln K = -\Delta H/RT + \Delta S/R$$

where K increases with decreasing temperatures and ΔH is negative. The rate constant is a composite of the rate constant for ion pairs and the rate constant for solvent separated ion pairs. It can be expressed as:

$$K_{\mathrm{p}}^{\pm} = (K_{\mathrm{C}} + K_{\mathrm{S}}\mathrm{K}_{\mathrm{CS}})/(1 + K_{\mathrm{CS}})$$

where K_{C} is the rate constant for contact ion pair, K_{S} is the constant for solvent separated ion pair, and is the equilibrium constant for the interconversions between unsolvated and solvated ion pairs. The relationship of the three rate constants to temperature can be expressed as follows:

$$\ln K_{\mathrm{C}} = \ln E_{\mathrm{C}} - K_{\mathrm{C}}/RT$$

$$\ln K_{\mathrm{S}} = \ln E_{\mathrm{S}} - K_{\mathrm{S}}/RT$$

$$\ln K_{\mathrm{CS}} = \ln E_{\mathrm{CS}} - K_{\mathrm{CS}}/RT$$

where E_{C}, E_{S}, and E_{CS} are the activation energies. Sawada [406] writes the apparent activation energy, ΔE_{app} as follows:

$$\Delta E_{\mathrm{app}} = \Delta E_{(\pm)\mathrm{S}} + \Delta H_{\mathrm{CS}}^{0}/(1 + K_{\mathrm{CS}})$$

where $\Delta E_{(\pm)\mathrm{S}}$ is the activation energy of propagation for solvent-separated ion pair, and $\Delta H_{\mathrm{CS}}^{0}$ is the enthalpy change of formation of solvent-separated ion pair from contact ion pair.

4.5 Coordination Polymerization of Olefins

The catalysts for these polymerizations can be separated into two groups. To the first one belong the so-called Ziegler–Natta catalysts. To the second one, transition metal oxides on special supports, like carbon black or silica-alumina, etc. Besides the two, there are related catalysts, like transition metal alkyls or metal halides that also catalyze some coordinated anionic polymerization. This group also includes transition metal-π-allylic compounds and transition metal hydrides. The mechanism of polymerization is generally coordinated anionic, based on all the evidence to date.

The Ziegler–Natta catalysts received their initial attention when Ziegler showed that some transition metal halides, upon reaction with aluminum alkyls, can initiate polymerizations of ethylene [224]. Polymers, which form, are linear and high in molecular weight. The reactions require much lower pressures than do free-radical polymerizations of ethylene. Simultaneously, Natta demonstrated [225] that similar catalysts can polymerize various other olefins like propylene, butylene, and higher α-olefins. High molecular weight linear polymers form, as well, and, what is more important, highly stereospecific ones.

The two disclosures stimulated intensive research into the mechanism of catalysis. Much knowledge was gained to date. Some uncertainties about the exact mechanisms of the reactions still persist.

Ziegler–Natta catalysts [226] are products from reactions of metal alkyls or hydrides of Groups I through III of the Periodic Table with metals salts or complexes of Groups IV through VIII. Not all compounds, however, that fit this broad definitions are actually useful catalysts. In fact, they range from very active to useless ones. Also, among them can be found materials that initiate polymerization of some monomers by free-radical, cationic, or anionic mechanisms and not by a coordinated anionic. Nevertheless, the number of active Ziegler–Natta catalysts is still large. The catalysts that are based on metals with large numbers of d-electrons (mostly Group VIII), are effective in polymerizations of conjugated dienes. They don't appear to work too well, however, with α-olefins. On the other hand, metals of Groups IV, V, or VI with fewer d-electrons are useful in polymerizing both, olefins and conjugated dienes. Also, all catalysts [163] that polymerize propylene also polymerize ethylene. Yet, the converse is not always true.

The Ziegler–Natta catalysts can be sub-divided into two groups: (1) heterogeneous insoluble catalysts, and (2) homogeneous, or soluble ones. At times, however, it is difficult to distinguish between the two. For instance, it may be hard to determine whether a particular catalyst is truly in solution or merely in a form of a very fine colloidal suspension (and in fact heterogeneous).

4.5.1 Heterogeneous Ziegler–Natta Catalysts

These catalysts form when a soluble metal alkyl like triethylaluminum or diethyl aluminum chloride is combined with a metal salt, like titanium chloride, in a medium of an inert hydrocarbon diluent. The transition metal is reduced during the formation of the catalyst.

The following chemical scheme illustrates the reactions that are believed to take place between aluminum alkyls and transition metal halides [227, 228]. Titanium chloride is used as an example:

$$\mathrm{TiCl_4 + AlR_3 \rightarrow TiCl_3R + AlR_2Cl}$$

$$\mathrm{TiCl_4 + AlR_2Cl \rightarrow TiCl_3 + AlRCl_2 + R^{\bullet}}$$

$$\mathrm{TiCl_4 + 2AlR_3 \rightarrow TiCl_2R_2 + 2AlR_2Cl}$$

$$\mathrm{TiCl_2R_2 \rightarrow TiCl_2R + R^{\bullet}}$$

$$\mathrm{TiCl_3 + AlR_3 \rightarrow TiCl_2R + AlR_2Cl}$$

$$\mathrm{TiCl_2R \rightarrow TiCl_2 + R^{\bullet}}$$

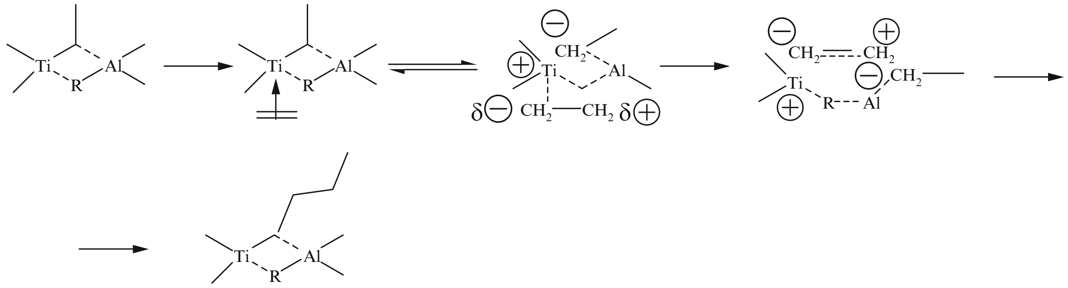
$$\mathrm{TiCl_2R + AlR_3 \rightarrow TiClR_2 + AlR_2Cl}$$

The radicals that form in the above shown reactions probably undergo combinations or other reactions of radicals, or perhaps react with solvents and decay. The reduction of the tetravalent titanium is unlikely to be complete due to the heterogeneous nature of the catalyst. Better catalytic activity results when $\mathrm{TiCl_3}$ is used directly in place of $\mathrm{TiCl_4}$. Many catalysts, however, are prepared with $\mathrm{TiCl_4}$. In addition, $\mathrm{TiCl_3}$ exists in four different crystalline forms, referred to as α, β, γ, and δ. Of these, the β, γ, and δ forms yield highly stereospecific polymers from α-olefins. The α-form, however, yields polymers that are high in atactic material.

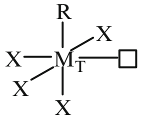
The ratio of the transition metal compounds to those of the compounds from metals in Group I to III can affect polymerization rates. They can also affect the molecular weights, and the steric arrangement of the products. Also, additives, like Lewis bases, amines, or other electron donors help increase the stereoregularity of the product. Thus, for instance, dialkylzinc plus titanium trichloride catalyst yields polypropylene that is 65% stereoregular. Addition of an amine, however, to this catalytic system raises stereoregularity to 93% [229]. Heterogeneous catalysts, typically, form polymers with very wide molecular weight distributions.

Many mechanisms were proposed to explain the action of heterogeneous Ziegler–Natta catalysts. All agree that the polymerizations take place at localized active sites on the catalyst surfaces. Also, it is now generally accepted that the reactions take place by coordinated anionic mechanisms. The organometallic component is generally believed to activate the site on the surface by alkylating the transition metal. Some controversy, however, still exists about the exact mechanism of catalytic action, whether it is ***monometallic*** or ***bimetallic***. Most of the opinion leans to the former. Also, it is well accepted that the monomer insertion into the polymer chain takes place between the transition metal atom and the terminal carbon of the growing polymeric chain [230].

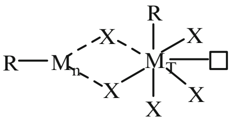
Only one ***bimetallic mechanism*** is presented here, as an example, the one originally proposed by Natta [230]. He felt that chemisorptions of the organometallic compounds to transition metal halides take place during the reactions. Partially reduced forms of the di- and tri-chlorides of strongly electropositive metals with a small ionic radius (aluminum, beryllium, or magnesium) facilitate this. These chemisorptions result in formations of electron-deficient complexes between the two metals. Such complexes contain alkyl bridges similar to those present in dimeric aluminum and beryllium alkyls [231]. The polymeric growth takes place from the aluminum–carbon bond of the bimetallic electron-deficient complexes [232, 234]:



where R represents an ethyl group. The bulk of the evidence, however, indicates that chain growth occurs through repeated four-center insertion reactions of the monomer into the transition metal-carbon σ-bond [230]. It is still not established whether the base metal alkyls serve only to produce the active centers and have no additional function. This would make the mechanism monometallic. If, however, the active centers must be stabilized by coordination with base metals then the mechanism is bimetallic [234]. The two active centers are depicted as follows:

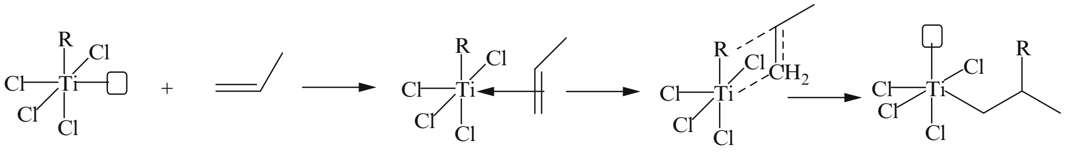


monometallic site



bimetallic site

where M_T represents the transition metal, M_n a base metal, and a vacant site. Both types of active centers might conceivably be present in heterogeneous Ziegler–Natta catalysts [234]. The exact locations of the sites in the solid catalyst crystals are still debated. Some speculations center on whether they are located over the whole crystal surface or only over the edges of the crystals [235]. Most evidence points to location at the edges. An example of the *monometallic* mechanisms is one originally proposed by Cossee and Arlman [236, 237]. This mechanism assumes that the reaction occurs at a transition metal ion on the surface layer of the metal trichloride (or perhaps dichloride) lattice. Here the halide is replaced by an alkyl group (R). The adjacent chloride site is vacant and accommodates the incoming monomer molecule. Using titanium chloride as an illustration:



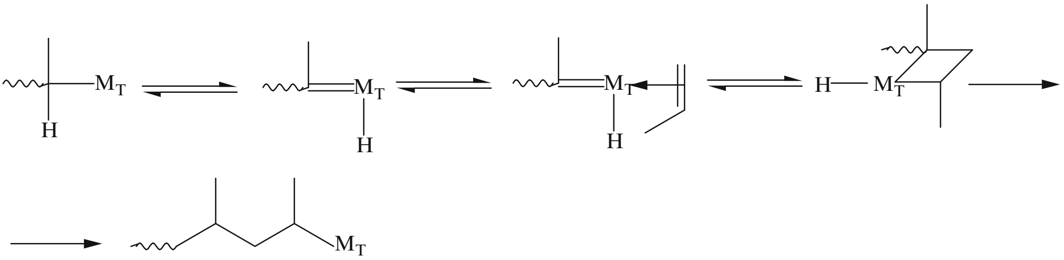
where, —□ represents a vacant site in the d-orbital. The newly formed transition metal–alkyl bond becomes the active center and a new vacant site forms in place of the previous transition metal–alkyl bond.

The driving force for the reactions [236, 237] depends on π-type olefin complexes. In these complexes, the π-electrons of the olefins overlap with the vacant d-orbitals of the transition metals. This results in the π-bonds being transitory. Also, the d-orbitals of the metals can simultaneously overlap with the vacant anti-bonding orbitals of the olefins. This decreases the distances between the highest filled bonding orbitals and the empty (or nearly empty) d-orbitals. In such situations, the carbon–metal bonds of the transition metals weaken and the alkyl groups migrate to one end of the incoming olefin [238]. The insertion process results in a *cis*-opening of the olefinic double bond [237, 239, 240].

The above scheme of propagation might also be pictured for bimetallic active centers. Complexations precede monomer insertions at the vacant octahedral sites and are followed by insertion reactions at the metal–carbon bonds [237]. When the transition metals are immobilized in crystal lattices, the active centers and the ligands are expected to interchange at each propagation step.

The above model for monometallic mechanism, though now widely accepted, is still occasionally questioned. Some evidence, for instance, has been presented over the years to support a bimetallic mechanism [242]. It was shown that elimination of the organometallic portion of the complex catalyst during polymerization of propylene results in deactivation of the catalyst. By contrast, replacement of the initial organometallic compound with another one results in a change in the polymerization rate, but not in deactivation of the catalyst.

In addition, some monometallic mechanisms based on a different mode of monomer insertion were also proposed. An example is a reaction mechanism that was proposed by Ivin et al. [241]. This mechanism is based on an insertion mechanism involving an α-hydrogen reversible shift, carbene, and a metallocyclobutane intermediate:



where, M_T means metal. The stereospecificity is dependent upon the relative configuration of the substituted carbons of the metallocyclobutane ring. Hydrogen transfer from the metal to the more substituted carbon exclude branching [241]. The following evidence supports the above mechanism.

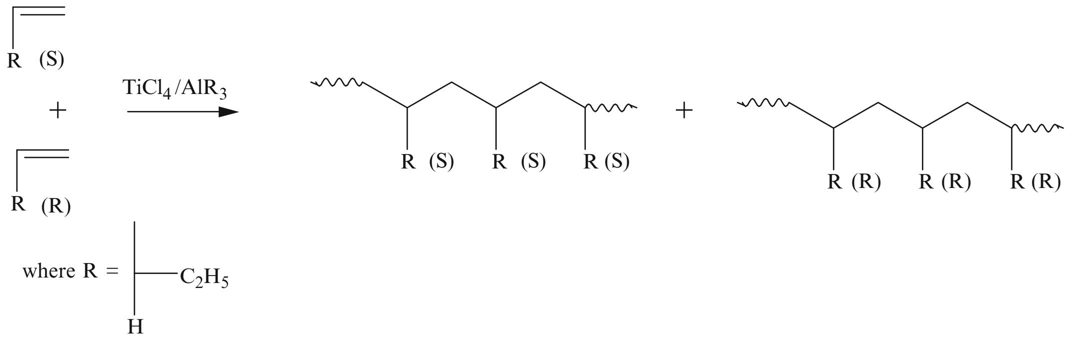
1. There are no unambiguous examples where a characterized metaloalkyl-olefin compound may be induced to react.
2. There is a close identity between the catalysts that cause the Ziegler–Natta type polymerizations and those that cause metathesis type polymerization via a carbene mechanism (see Chap. 5).

This mechanism was argued against, however, as an over simplification, because it ignores the experimentally observed regiospecificity of may propylene polymerizations [243]. On the other hand, it is argued that, correct regiospecificity of the monomer is accounted for by isotactic or syndiotactic propagation. Different energies of steric control can be qualitatively explained by the Ivin mechanism. This can be done through simple considerations of different distances between the substituted carbons of a four-membered ring [243].

In addition, Cavallo et al. [244] reported a study of ethylene polymerization using a model for the heterogeneous Ziegler–Natta catalyst (Mg_2CI_6Ti). Propagation as well as the termination reactions were considered. From this study they concluded that in the absence of a coordinated olefin, the Ti–C (chain) σ-bond does not occupy an octahedral coordination position but is oriented along an axis that is intermediate between the two octahedral coordination positions that are available. The propagation reactions occur in stepwise fashions, and the most favored mechanism requires rearrangements of the growing chains out of the four-center transition-state planes. The insertion reactions are facilitated by α-agostic interactions. The most favored termination reactions are β-hydrogen transfers to the monomers. This type of reaction is favored, relative to the C–H σ-bond activation of a coordinated monomer, as well as to the β-hydrogen transfer to the metal [244].

4.5.1.1 Steric Control with Heterogeneous Catalysts

Different independent approaches were used to investigate the mechanism of polymerization of α-olefins with heterogeneous catalysts. As a result, it was shown that isotactic polymerization of racemic mixtures of α-olefins are stereoselective [245, 246]. Also, optically active polymers form with optically active catalysts [247]. Stereoelectivity and stereoselectivity are due to the intrinsic asymmetry of the catalytic centers [248]. This conclusion comes in part from knowledge that propylene coordinates asymmetrically in platinum complexes [248]. A study of chemical and configurational sequences supports this [249]. In addition, polymerization of a racemic mixture of (*R*)(*S*)-3-methyl-1-pentene with ordinary Ziegler–Natta catalysts (e.g., $Al(C_2H_5)_3 + TiCl_4$ or $Al(C_2H_5)_2Cl + TiCl_3$) yields a racemic mixture of isotactic polymers. The mixture can be separated by column chromatography into pure optically active components. These polymeric chains are exclusively either poly[(*S*)-3-methyl-1-pentene] or poly[(*R*)-3-methyl-1-pentene] [248, 250, 251]. This means that typical Ziegler–Natta catalysts have essentially two types of active sites that differ only in a chiral sense. Such sites polymerize the monomers stereoselectively, i.e., either (*R*) or (*S*) with the exclusion of the other enantiomeric form:



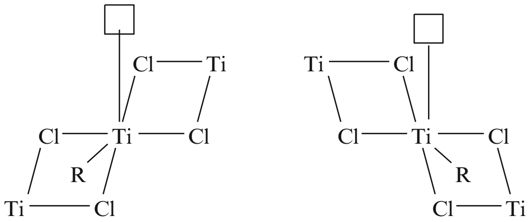
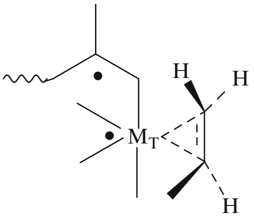


Fig. 4.4 Two enantiomorphs form of the catalyst. R indicates the ligands that was replaced by alkyl groups through alkylation by organometallic compounds from Groups I through III

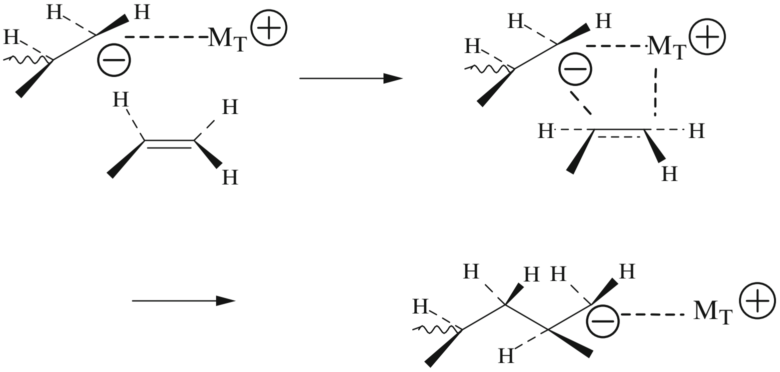
In the heterogeneous catalyst, like α-$TiCl_3$, the crystals are made up of elementary sheets of alternating titanium and chlorine atoms. These atoms are aligned along the principal crystal axis. The chlorines are hexagonally packed and the titanium atoms are at the octahedral interstices of the chlorine lattice. Every third titanium in the lattice is missing. There is a vacancy between pairs of titanium atoms. Many ligand vacancies are present in the crystals in order to accommodate electrical neutrality and the titanium atoms at the surface are bonded to only five chlorines instead of six. Neighboring transition metal atoms that are bridged by chlorines have opposite chiralities [57]. This means that two enantiomorphic forms exist (see Fig. 4.4). The monomers coordinate at either one of the two faces (at the vacant sites). Coordination results in formation of one of two diastereoisomeric intermediate transition states. Both result in isotactic placements, but the products are either ***meso*** or ***racemic*** [240]. In addition, enantioselectivity between the two faces of the crystals requires a minimum amount of steric bulk at the active site. This is enhanced by larger-sized monomers [240]. A schematic representation of a catalytic center, showing chirality by an asterisk, is as follows [252]:



The above means that the active sites act as templates or molds for successive orientations of the monomers. The monomers are forced to approach these site with the same face. This sort of monomer placement is called ***enantiomorphic site control*** or ***catalyst site control***.

So far, the evidence for an initial complex formation between the catalyst and the olefin is not strong. The working hypothesis, commonly accepted today, is as follows. The position in the π-complex of diastereoisomeric and rotameric equilibria and/or activation energy for the insertion reaction cause large regioselectivity. That can also account for the enantioface discrimination necessary for the synthesis of stereoregular poly-α-olefins [252]. ^{13}C NMR analyses of isotactic polypropylenes formed in δ-$TiCl_3$–$Al(^{13}CH_3)_2I$ catalyzed reactions show that the enriched ^{13}C is located only in the isopropyl end group. Also, it is located predominantly at the *threo* position, relative to the methyl group on the penultimate unit [253]. This supports the concept that steric control must come from chirality of the catalytic centers [253].

It might be interesting to note that the proponents of the carbene mechanism (mentioned earlier). point out that this is also consistent with their mechanism [254, 255]. The reaction can consist of (a) an insertion of a metal into an α-CH bond of a metal alkyl to form a metal–carbene hydride complex. This is followed by (b) reaction of the metal-carbene unit with an alkene to form a metal-cyclobutane-hydride intermediate. The final step (c), is a reductive elimination of hydride and alkyl groups to produce a chain-lengthened metal alkyls. This assures that a chiral metal environment is maintained [254]. It is generally believed [258], however, that stereospecific propagation comes from concerted, multicentered reactions, as was shown in the Cossee–Arlman mechanism. The initiator is coordinated with both the propagating chain end and the incoming monomer. Coordination holds the monomer in place during the process of addition to the chain. This coordination is broken simultaneously with formation of a new coordination with the new monomer [258]:



where, M_T means metal.

This capability of the initiator to control the placement of the monomer overrides the common tendency for some syndiotactic placement. While syndiotactic polypropylene has been prepared with heterogeneous catalysts, the yield of syndiotactic placement is low. Soluble Ziegler–Natta catalysts on the other hand can yield high amounts of syndiotactic placement. This is discussed in the next section. When 1,2-disubstituted olefins are polymerized with Ziegler–Natta catalysts, the di tacticity of the products depends on the mode of addition. It also depends on the structure of the monomer, whether it is ***cis*** or ***trans***. A threodiisotactic structure results from a ***syn*** addition of a ***trans*** monomer. A *syn* addition of a *cis* monomer results in the formation of an erythrodiisotactic polymer. For instance, *cis* and *trans*-1-*d*-propylenes give ***erythro*** and ***threo*** diisotactic polymers, respectively [255]. To avoid 1,2-interactions in the fully eclipsed conformation, the carbon bonds in the monomer units rotate after the addition of the monomer to the polymeric chain [240]. Also, a systematic investigation of chain propagation by ethylene insertion into a metal–C_6H_5 bond showed that the backside insertion barriers depend little on the identity of the metal, because backside insertion requires little deformation of the metal–ligand framework [256]. For systems that are sterically unencumbered the insertion reaction proceeds through frontside and backside channels in equal parts. This is due to the fact that both transition states are close in energy. The influence of the ligand upon insertion is such that good π donor ligands lower the front-side insertion barrier, because they favor trigonal planar geometry over trigonal pyramidal coordination. The activity of various metal centers can be strongly influenced, however, by sterically bulky ligands. Insertion barriers are generally lowered by steric bulk, because compression of the active site favors the transition state geometry over the π-complex geometry [256].

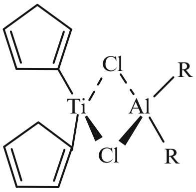
4.5.2 Homogeneous Ziegler–Natta Catalysts

The catalysts that fit into this category are quite diverse chemically. They can be, for instance, reaction products of vanadium tetrachloride with dialkyl aluminum chloride or reaction products of bis-cyclopentadienyl titanium dichloride with aluminum alkyls. Organic titanates also form soluble catalysts upon reactions with certain aluminum alkyls.

The homogeneous catalysts can range in efficiency from very high to very low. Usually, a much narrower molecular weight distribution is obtained in polymers formed with these catalysts than with the heterogeneous ones. In addition, syndiotactic poly(α-olefins) form at low temperatures (−78°C).

The amount of stereospecific placement, however, is usually not as great as is the isotactic placement with heterogeneous catalysts.

Group I–III metal alkyl components are essential to the formation of active centers [239, 240]. Blue complexes of di cyclopentadienyl titanium dichloride with aluminum diethyl chloride or with aluminum ethyl dichloride were some of the early known soluble catalysts [257, 258]:

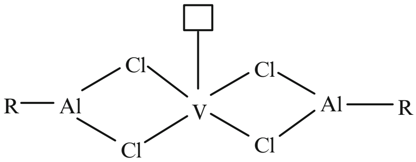


Many other soluble catalysts were developed over the last 30 or more years. Most of these materials must be prepared and used at low temperatures [259]. The polymerization mechanism is also believed to take place by an initial coordination of the monomers with the transition metals. This is followed by a four-center insertion reaction of the monomer into the transition metal–carbon bond.

4.5.2.1 Steric Control with Homogeneous Catalysts

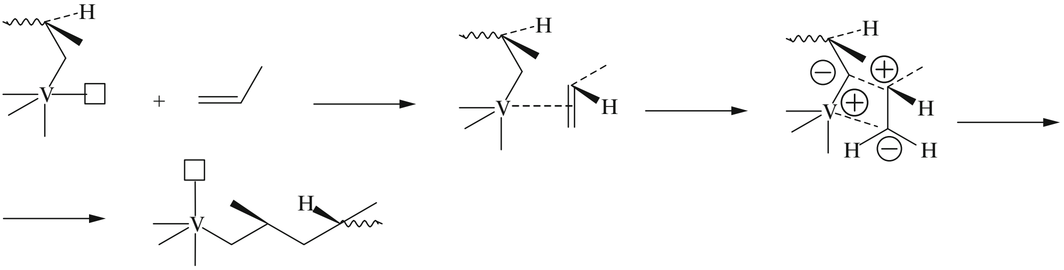
Stereospecific placement appears to result from steric interactions between the substituents on the ultimate units of the growing chains and the incoming monomers [239]. NMR spectral evidence shows that the double bond opening is also *cis*, as with the heterogeneous catalysts [240, 258–262].

The monomer–polymer interaction model, described above, requires sufficient steric hindrance at the active centers to prevent rotation of the penultimate units. Such rotation would cause the substituent to interfere with the incoming monomer. The fact that syndiotactic placement takes place only at low temperatures and atactic placement at elevated ones supports this concept. Following is an illustration of the structure of the catalyst and the active center [258]:



where —□ denotes a vacant site.

A proposed model for syndiotactic placement can be shown as follows [234]:

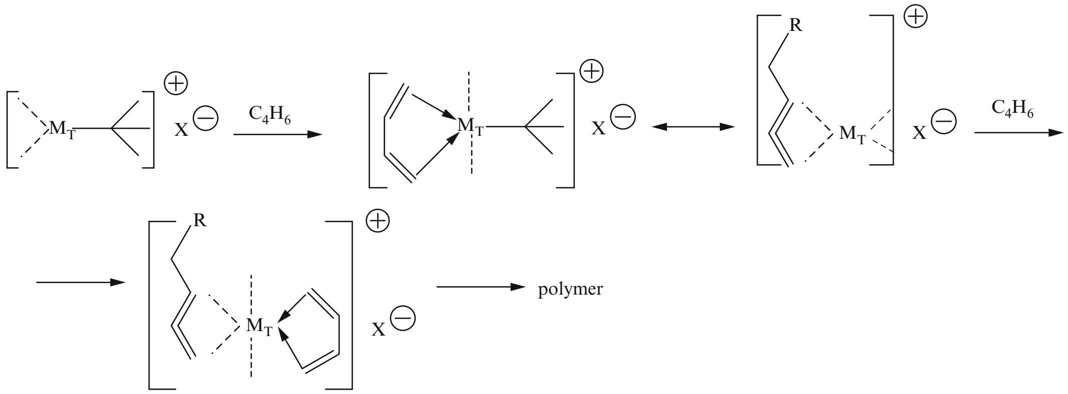


The above model shows the insertion of monomers on σ-metal bonds [239, 240]. NMR spectroscopy supports the hypothesis [243]. Also, the model shows the vanadium to be pentacoordinated, following a Zambelli and Allegra suggestion [243]. Hexacoordinated vanadium has been pictured by others [259, 260]. In the above model, the chain ends control monomer placement. This differs significantly from the mechanism of isotactic placement by catalytic site control with the heterogeneous catalysts. The active sites of homogeneous catalyst do not discriminate between the faces of the incoming monomers in the step of coordination. Instead, steric hindrance between the substituents of the terminal units of the propagating chains and the ligands attached to the transition metals prevent rotations about the metal–carbon bonds. In addition, steric repulsion forces the monomers to coordinate at opposite faces with each successive step of propagation, resulting in syndiotactic placement.

4.5.3 Steric Control in Polymerization of Conjugated Dienes

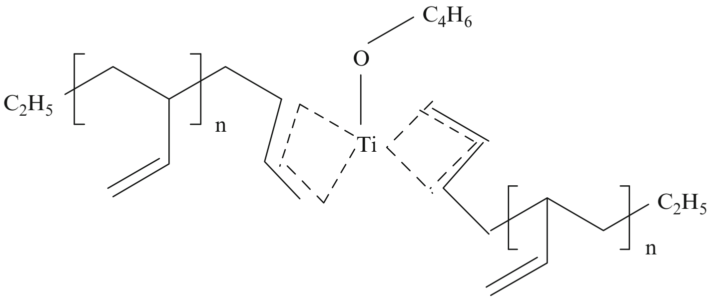
The subject has also received considerable attention. Nevertheless, the mechanism is still not fully understood. It is reasonable to assume that the form and structure of the catalyst and the valence of the transition metals must play a role. The conformation of the monomer (s-*cis* or s-*trans*) is probably also important.

It is known that $CoCl_2/Al(C_2H_5)Cl$ can polymerize *trans*-1,3-pentadiene but not the *cis* isomer [263]. This suggests that a two-point coordination is required. Several reaction schemes that provide for an attack at either C_1 or at C_4 positions were proposed over the years [263]. One mechanism for polymerization of butadiene suggests that complexes of the catalysts in solvents of low dielectric constant will either act as ion pairs or as independent solvated entities. Also, the growing chain may be bound by either a π or a σ linkage, and it is suspected that a continuous $\sigma \rightarrow \pi$ isomerism is possible [264]:



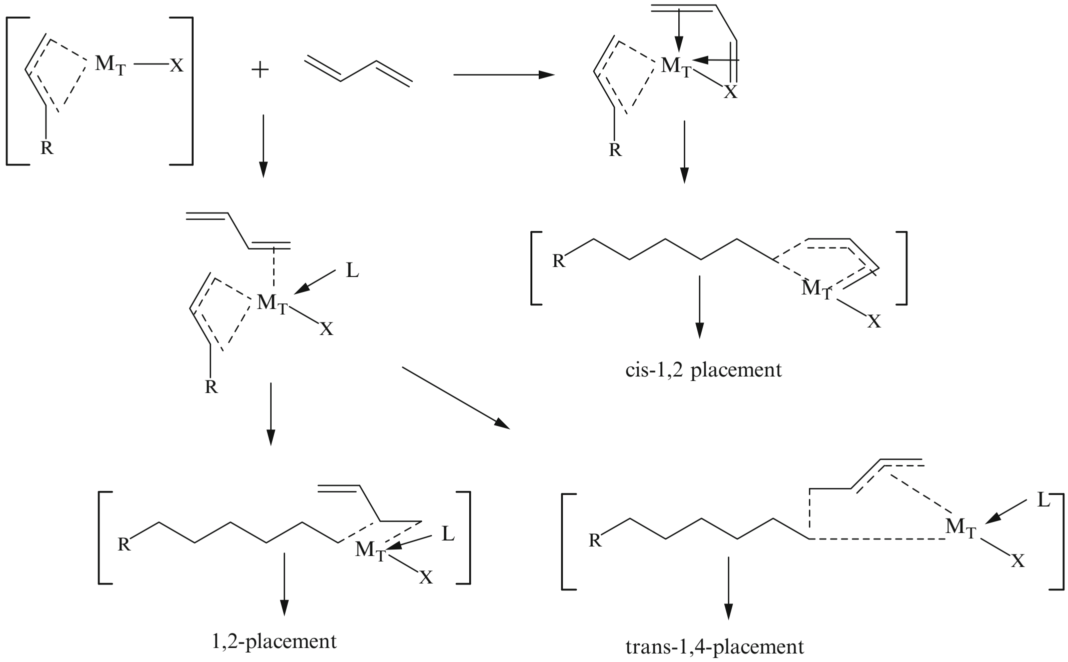
where, M_T means metal.

Soluble catalysts from transition metal acetoneacetonates (from nickel to titanium) combined with triethylaluminum or triethylaluminum chloride yield *cis* polymers of the dienes. The *cis* placement decrease when bases are added [265]. This decrease is proportional to the base strength. The addition is believed to decrease electron densities of the orbitals of the transition metals [266]. This suggests that electrostatic interactions between the nearly non-bonding electrons of transition metals with the dienes or with growing chain ends must play an important role. Such interactions must affect placements of the incoming monomers. Hirai et al. studied ESR signals obtained during polymerizations of butadiene, 1,3-pentadiene, and isoprene [267] with catalyst based on *n*-butyltitanate/triethylaluminum. They concluded that the catalyst must possess two substituted π-allyl groups and one alkoxy group during the chain growing process [267]:



The insertions of the monomers are believed to occur in two steps [268, 269]. In the first one, the incoming monomer coordinates with the transition metal. This results in formation of a short-lived σ-allylic species. In second one, the metal–carbon bond is transferred to the coordinated monomer with formation of a π-butenyl bond. Coordination of the diene can take place through both double bonds, depending upon the transition metal [270] and the structure of the diene. When the monomer coordinates as a monodentate ligand, then a ***syn*** complex forms. If however, it coordinates as a bidentate ligand, then an ***anti*** complex results [271]. In the ***syn*** complex, carbons one and four have the same chirality while in the ***anti*** complex they have opposite chiralities [268]. Due to lower thermodynamic stability the *anti* complex isomerizes to a ***syn*** complex [268]. If the allylic system does not have a substituent at the second carbon, then the isomerization of ***anti*** to *syn* usually occurs spontaneously even at room temperature [268].

Transition metal alkyls probably cannot be classified as typical Ziegler–Natta catalysts. Some of them, however, exhibit strong catalytic activity and were, therefore, investigated [272–275]. This also led to the conclusion that the polymerization mechanisms involve formations of π-allylic complexes as intermediates. It is similar to the mechanism visualized for the Ziegler–Natta catalysis [276–283]. The initial formation of the π-allylic ligands and the solvents used in catalyst preparations strongly influence the catalytic activity and stereospecificity of the product [280]. NMR studies of polymerizations of conjugated dienes with π-crotyl-nickel iodide [281] showed that the monomers are incorporated at the metal-carbon bonds with formations of *syn*-π-crotyl ligands. The *syn*-ligands transform to *trans*-1,4-segments next to the crotyl group and the *trans*-1,4-segments become *trans*-1,4-units in the polymers [282]. In summary, the general mechanisms of ***cis*** and ***trans*** placement by coordinated catalysts were pictured as follows [280]:



where, L means ligand and M_T means transition metal.

It is possible to apply the homogeneous rate equation to some Ziegler–Natta catalysts. This can be expressed as:

$$R_p = k_p[C^*][M]$$

where C* represents the concentration of active sites in moles per liter. Heterogeneous kinetics, however, are needed because the adsorption phenomena are important in most coordinated anionic polymerizations. In addition, because there is likely to be an excess of components of Groups I–III metals in solution, it is assumed that they compete with the monomer for the active sites. The fractions, therefore, of the active sites and the fractions of sites covered by these metal compounds are expressed as follows [283]:

Fraction of the active site coordinated with the monomer:

$$\Theta_1 = K_1[M]/(1 + K_2[M_T] + K_1[M])$$

Fraction of active sites coordinated with components of metal Groups I–III:

$$\Theta_2 = K_2[M_T]/(1 + K_2[M_T] + K_1[M])$$

where M represents the amount of monomer in solution and M_T the concentration of metal components of Group I–III. K_1 and K_2 are the equilibrium constants for the adsorption.

The rate of polymerization that takes place trough the reaction of the adsorbed monomer at the active sites can be expressed as:

$$R_P = k_P[C^*]\Theta_1 = k_P[C^*][K_1[M]/(1 + K_2[M_T] + K_1[M])]$$

If there is no competition with components of metal Group I–III, then

$$R_P = k_P[C^*]\Theta_1 = k_P[C^*][K_1[M]/(1 + K_1[M])]$$

The degree of polymerization can be derived by dividing the propagation rate by the sum of the rates of terminations (by transfer) as follows:

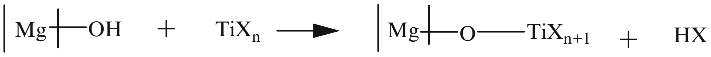
$$1/\overline{\mathrm{DP}_n} = k_{tr,M}/k_p + k_s/k_pK_M[M] + k_{tr,A}K_A[A]/k_pK_M[M] + k_{tr,H}[H]/k_pK_M[M]$$

The above equation is written with the assumption that there is no adsorption of hydrogen at the active sites.

4.5.4 Post Ziegler and Natta Coordination Polymerization of Olefins

In the current industrial practice, coordinated anionic catalysts differ considerably from the original ones, developments by Ziegler, Natta and others. Using the same basic chemistry, new compounds were developed over the years that yield large quantities of polyolefins from small amounts of catalysts. In addition, catalysts can now be designed to yield products that are either wide or narrow in molecular weight distribution, as needed [312]. The multinuclear olefin polymerization catalysts were reviewed recently [313]. The new *catalysts for ethylene polymerization* can be divided into three groups [312]:

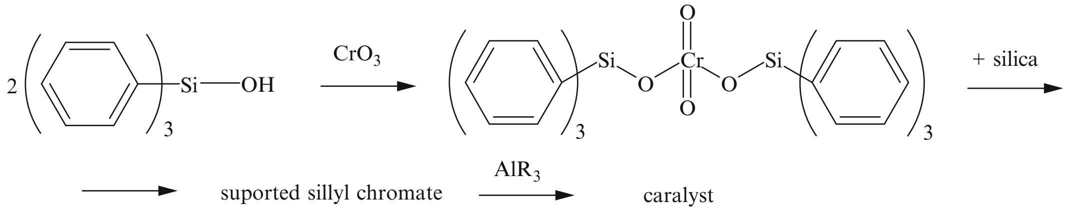
1. Products from reactions of trivalent alkoxy chlorides of transition metals with certain halogen-free organoaluminum compounds, e.g., triisobutylaluminum. Such catalysts are used without any support.
2. Products from reactions of magnesium compounds with titanium compounds. In these catalysts the transition metals are attached chemically to the surfaces of solid magnesium compounds. The reactions take place between the halogen atoms from titanium compounds and the hydroxyl groups at the surfaces of magnesium hydroxide:



Titanium compounds bonded to the surface OH groups of $Mg(OH)_2$ are mainly inactive. The active sites are the ones associated with the coordinated and unsaturated negative oxygen ions [317]. Reactions with aluminum alkyls activate the catalysts [312]. For high efficiency, special carriers must be used together with a correct balance of the reactants, and proper reaction conditions. Some choice combinations are [312]: Mg(OH)Cl with $TiCl_4$; $MgCl_2 \cdot 3Mg(OH)_2$ with $Ti(OR)_xCl_y$; $MgSO_4 \bullet 3Mg(OH)_2$ with $Ti(OR)_xCl_y$; and $Mg(OH)_2$ with $TiCl_4$.

Highly active, unsupported catalysts form from reactions of magnesium alkoxides with tetravalent titanium chlorides. The same is true of reaction products of $MgCl_2$ or $MgCl_2$-electron donor adducts, like $MgCl_2 \cdot 6C_2H_5OH$, with tetravalent titanium compounds.

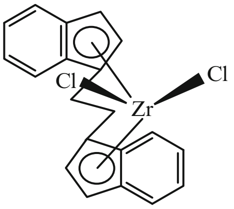
3. Products from reactions of organisilanols with chromium trioxide are also very active catalysts. The silylchromate which forms is deposited on a silica support and activated with alkyl aluminum compounds [312]:

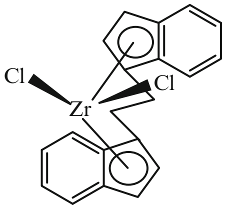


The activity and performance of coordination *catalysts for the polymerization of propylene* has been also very much improved. Titanium compounds are also supported on some carriers and then activated by reactions with aluminum alkyls [341]. The patent literature describes a variety of inorganic supports [342]. The most common ones, however, are based on $MgCl_2$ treated with various Lewis bases, like ethyl benzoate. One such catalytic system is described as being prepared by treating a complex, $TiCl_3 \bullet 3C_5H_5N$, with diethyl aluminum chloride in the presence of highly dispersed $MgCl_2$. The product of that reaction is then combined with triethylaluminum [355]. The reaction between an electron donor, a Lewis base, and $MgCl_2$ is a two step exothermic reaction [343]. The first one is a rapid adsorption to the inorganic surface and the second one, a slower one, is formation of the complex. The most commonly used Lewis bases are ethyl benzoate, di-*n*-butyl phthalate, and methyl-*p*-toluenate. Amines, like 2,2,6,6-tetramethylpiperidine, and some phenols are also used.

A common practice is to ball mill the Lewis base with the support material first. The transition metal component is then added and the mixture is milled some more or thoroughly mixed. This Lewis base is called the *internal* Lewis base. This is followed by addition of Group I–III metal-alkyl component with an additional Lewis base. The base that is added the second time may be the same or a different one from one used in the original milling. In either case it is called the *external* Lewis base. It is not uncommon to use an ester as the internal base and an organosilane compound, like phenyltriethoxysilane, as the external one.

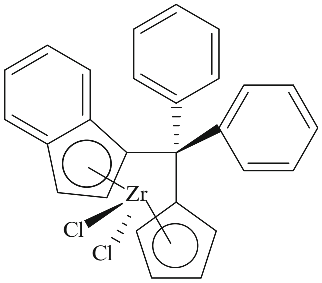
Initially, a series of soluble, highly isospecific catalysts were developed for propylene polymerization [168]. These materials are zirconium, titanium, or hafnium based ***metallocenes***, such as racemic 1,1-ethylene-di-η^5-indenylzirconium dichloride. The term metallocene applies to complexes of transition metals sandwiched between two aromatic rings, usually two cyclopentadienyl. They are rigid structures, due to ethylene bridges between the two five-membered rings. Syntheses of these compounds yield racemic mixtures of two enantiomers. Both produce isotactic polypropylene:





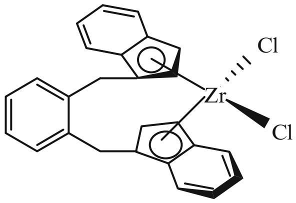
Methylaluminoxane co catalyst is required by these metallocenes to become highly isospecific catalysts capable of very high isotactic placement. They are also very active, yielding very large quantities of polypropylene per each gram of zirconia.

Catalysts that yield highly syndiotactic polypropylene (86% racemic pentads) were also developed. One of them is *i*-propylene(η^5-cyclopentadienyl-η^3fluorenyl)zirconium dichloride [291]. Initial disclosures of metallocene catalysts were followed by numerous publications in the literature that described similar materials for the polymerizations of either ethylene or propylene, or both, and for formation of various copolymers. Thus, for instance, Kaminsky et al. [292], reported preparation of a zirconium dichloride-type catalyst for copolymerization of cyclic olefins with ethylene. These cyclic olefins are cyclopentene, norbornene, and the hindered cyclopentadiene adducts of norbornene [292]. The catalytic system consists of a bridged indene derivative that is combined with methylaluminoxane:

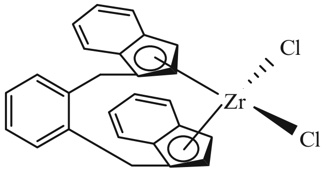


It is interesting that the copolymers of some of these cycloolefins with ethylene were reported to be transparent, amorphous, and oxidatively stable materials. In addition, it is claimed that they have glass transition temperatures in excess of 200°C, are melt processable, solvent stable, and possess high mechanical strength [292].

Another example is work by Han et al. [293], who synthesized *ansa*-dichloro[*o*-phenylenedimethylenebis(η^5-1-indenyl)]zirconium. Both *racemic* and *meso* forms were obtained and separated:



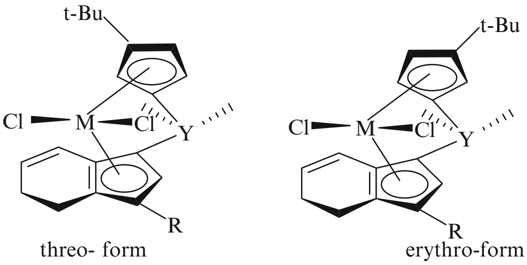
racemic - 1



meso - 1

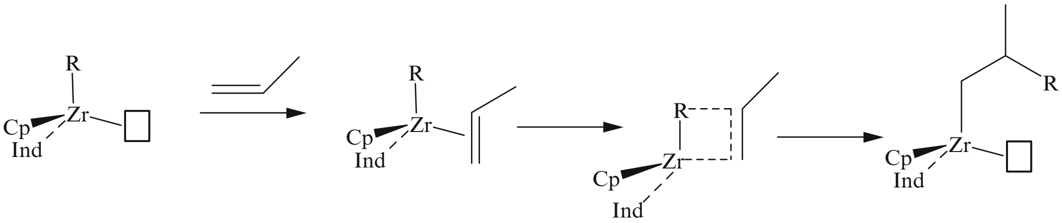
These catalysts also polymerize ethylene and propylene in the presence of methyl-aluminoxane [293]. The *meso*-1/MAO analog was found to be more active than the *rac*-1/MAO in ethylene polymerization. In propylene polymerization, however, the racemic one is active and the meso is inactive. Ethylene polymerization activity with *rac*-1/MAO increases as the temperature increases. An inverse temperature effect is observed for propylene polymerization with the *rac*-1/MAO catalyst system. The stereoregularity of polypropylene formed with this racemic catalyst is low [293]. This led Han et al. to conclude [293] that the α-olefin polymerization is influenced by changes in the structure of *ansa* chiral metallocene catalysts such as variation of the transition metal, the steric and electronic properties of π- and σ-ligands, and the length and rigidity of the bridging groups. The activity and the stereoselectivity of α-olefin polymerization reactions can be significantly affected by slight structural variations of the bridging group in metallocene catalysts. The length of the bridging chain affects the angle between the cyclopentadienes and the metal atom. The chiral metallocenes having π-ligands bridged with one atom (carbon or silicon) or two carbon atoms have either C_2 (*racemic*) or C_8 (*meso*) symmetry, if the *ansa*-ligand is enantiotropic [293].

The mechanism of monomer insertion and steric control in polymerizations of α-olefins by the metallocene catalysts received considerable attention [293–297]. There is no consensus on the mechanism of polymerization. Many studies of chain propagation tend to support the Cossee-Arleman mechanism [293–297]. An example is work by Miyake et al. [294] who synthesized unsymmetrical *ansa*-metallocenes and separated them into *threo* and *erythro* isomers. Both isomers coupled with methylaluminoxane polymerize propylene in toluene to highly isotactic polymers of $M_w = 105{,}000$. The isotactic placement is greater that 99.6% and the polymer melting point is 161°C.



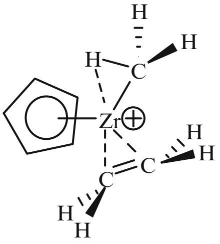
Based on experimental evidence obtained with the above catalysts, it was concluded by Miyake et al., that the isotactic propylene polymerization with zirconium catalysts takes place by a regioselective 1,2-insertion of the propylene monomer into the metal-polymer bond [294]. Monomer insertion is believed to take place at two active sites on the metal center in an alternating manner. In addition, it was shown [295] that the substituents on the cyclopentadiene rings determine the conformation of the polymer chain end, and the fixed polymer chain end conformation in turn determines the stereochemistry of olefin insertion in the transition state as a form of indirect steric control.

With the above catalysts, however, because the stereochemistry of the two sites is different, Miyake et al. [294], suggest that monomer insertion takes place at the same active site on the metal center:



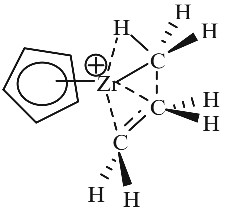
Lohrenz et al. reported [296] quantum mechanical calculations on model systems [297] support the Cossee-Arleman mechanism. Insertion of ethylene into Cp_2Zr^+-Me is preceded by an initial olefin complexation with the vacant coordination site and formation of π-complex 1 as shown below:

complex 1



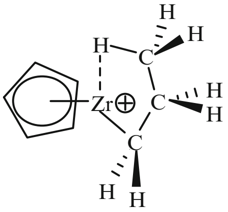
-96 kJ/mol

complex 2



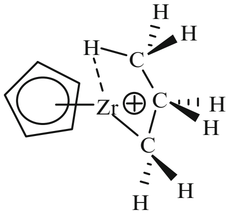
-93 kJ/mol

complex 3



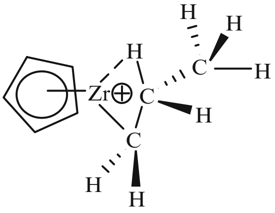
-128 kJ/mol

complex 3a



0.0 kJ/mol

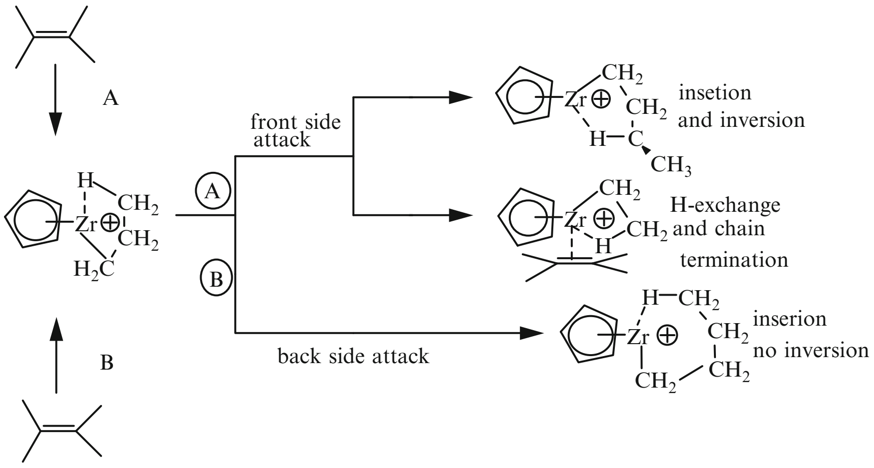
complex 3b



-22 kJ/mol

After the formation of complex 1, the insertion follows a low activation barrier ($E_{act} = 3$ kL/mol), yielding the γ-agostic product 3a. These calculations also led to the conclusion about the importance of agostic interactions present in the product [296]. The most stable conformation is the β-agostic structure (3b) at 22 kJ/mole that is more stable than the primary insertion product (3a). It is assumed that this conformation serves as a model for the resting state of the growing chain attached to the cationic group-4 metallocenes between insertions [297].

To shed additional light on complex 3b, shown above, calculations were carried out [296] on the reaction of ethylene with a model complex, Cl_2Zr + Et. Two reaction paths (A) and (B) are possible as illustrated below:



Front-side attack leads to the formation of a π-complex that in turn can undergo two possible reactions. Insertion of the olefin into the Zr–C_α bond may take place after rotation around Zr–C_α that moves C_β out of plane. The β-hydrogen can be transferred from the polymer chain to the olefin. This leads to chain termination and formation of a vinyl-terminated polymer and an ethyl-zirconocene that can start a new polymer chain [296].

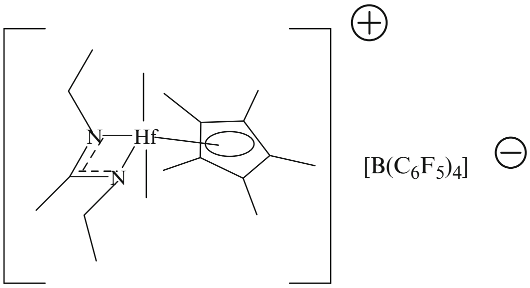
The backside attack on the other hand allows insertion of the olefin without rotation around Zr–C_α bond. The front-side insertion is accompanied by chain migration from one side to the other whereas backside attack does not involve inversion at the metal center.

Lohrenz et al. [296] concluded that insertion into the metal-polymer bond takes place exclusively from the backside. That means that no inversion takes place. They also feel that in propylene polymerization two orientations occur. In the first step the polymer chain points to the larger ligand side and the propylene methyl group points away from the large ligand and the polymer chain. The next step is governed by a stronger interaction of propylene with the polymer chain than with the ligand [296].

An analysis of molecular mechanics using model metallocene complexes, as possible intermediates for propylene polymerization was also reported by Guerra et al. [298]. The two coordination positions available for the monomer and the growing chain are diastereotopic. The conclusion was that the energy difference between the corresponding diastereoisomeric pre-insertion intermediates appear to be relevant for the model complexes [298]. It was also concluded [391] that energy differences can be related to an increased probability of a back-skip of the growing chain toward the outward coordination position after the monomer insertion and prior to the coordination of a new olefin molecule.

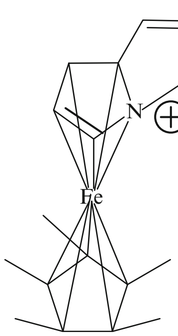
Busico et al., on the other hand, came to a conclusion [299] that the stereoregularity of polypropylene produced with C2-symmetric group 4 *ansa*-metallocene catalysts is a result of the interplay of two competing reactions. These are: isotactic monomer polyinsertion and a side process of epimerization of the polymer chain at its active end. That makes this class of homogenous catalysts different from the typical Ziegler–Natta catalyst, because with these catalysts enantioselectivity and stereoselectivity are not necessarily coincidental [96].

Zang et al. reported [300] that they achieved highly efficient, rapid, and reversible chain transfer reactions between active transition-metal based propagating centers with catalysts derived from {Cp*Hf (Me)[N(Et)C(Me)N(Et)]} $[B(C_6F_5)_4]$ (Cp* $= \eta^5$-C_5Me_5) or {Cp*Hf (Me)[N(Et)C(Me)N (Et)]} $[B(C_6F_5)_3Me]$



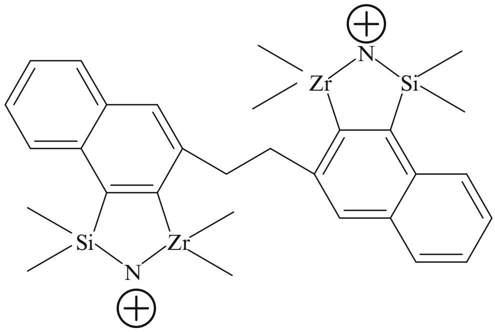
with multiple equivalents of dialkylzinc (ZnR_2) acting as "surrogate" chain-growth sites. This was done to achieve *living* coordinative chain-transfer polymerization of ethylene with α-olefins, and α,ω-non conjugated dienes. It is claimed by these investigators that these living coordinated chain transfer processes provide a work-around solution to the "one chain per metal" cap on product yield. In addition, they are claimed to provide access to practical volumes of a variety of unique new classes of precision polyolefins of tunable molecular weights and very narrow polydispersity ($M_w/M_n \leq 1.1$).

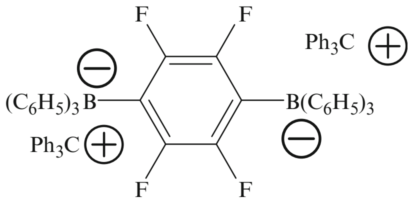
A Japanese patent issued to Watanabe and Okamoto [301] describes preparation and illustrates an iron containing catalyst for polyethylene preparation. It is shown here as an illustration:



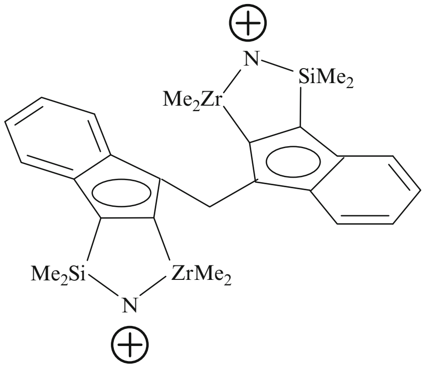
This catalyst was reported to yield 2.66 kg of polyethylene per one minimol of nickel.

Subsequent research efforts have been focused on discovering more efficient catalytic processes benefiting from cooperative effects between active centers in multinuclear complexes. The idea is to ultimately mimic the advantageous enzyme characteristics. Thus, for instance, Li, Stern, and Marks [303] reported that in their earlier work they demonstrated that the constrained geometry of binuclear catalyst + binuclear co catalyst combination



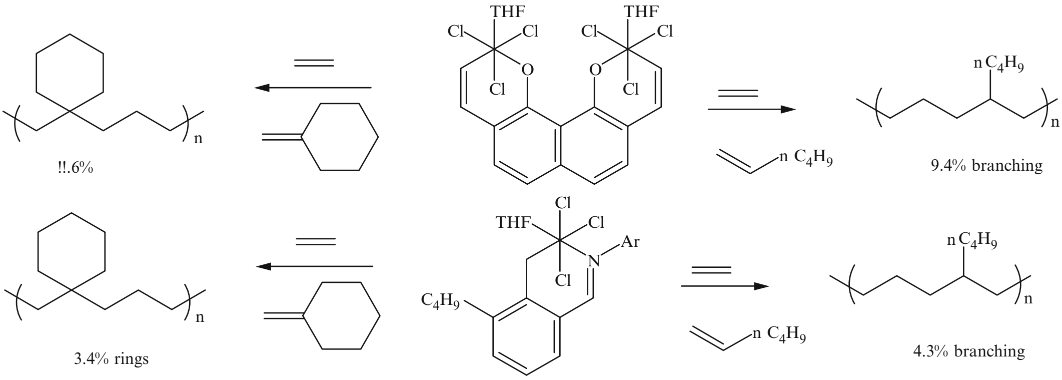


affords, via the modification of chain transfer pathway kinetics, significantly enhanced branching in ethylene homopolymerization and enhanced comonomer incorporation, as well as ethylene plus 1-hexene copolymerization. Such catalysts, however typically produce unacceptably low molecular weight polyolefins. Earlier, they reported preliminary results that showed that metal–metal proximity and cocatalyst structure have significant impact in terms of product molecular weight and comonomer enchainment selectivity. Following that they reported in the subject publication the synthesis of single methylene-bridged $(\mu\text{-CH}_2\text{-}3,3')\{(\eta^5\text{-indenyl})[1\text{-Me}_2\text{Si}(^t\text{BuN})](\text{ZrMe}_2)\}_2\text{Zr}$ based catalyst:



to examine achievable metal-metal proximity effects. They also reported preparing sterically encumbered naphthyl-derivatized catalyst {1-Me$_2$Si [3-(1)-naphthyl indenyl]-(^{t}BuN)}ZrMe$_2$ (N-Zn) to additionally probe catalytic center steric effects. Placing the two metals into closer proximity was shown by them to significantly increase polyethylene molecular weight in ethylene homopolymerizations and α-olefin enchainment in ethylene copolymerizations with 1-hexene. Additionally, they found that when methyl alumoxane is used as the co catalyst, the catalyst shown above, yields even greater enhancement in weight average molecular weight. Also, when they used a polar solvent, C_6H_5Cl in the reaction, it caused a weakening in the catalyst-cocatalyst ion pairing, a significant alteration in catalyst response and polymer product properties was observed. Their results showed that $Zr \cdots Zr$ spatial proximity, as modulated by ion pairing, significantly influences chain transfer rate and selectivity for comonomer enhancement. These proximity effects are highly cocatalyst and solvent sensitive.

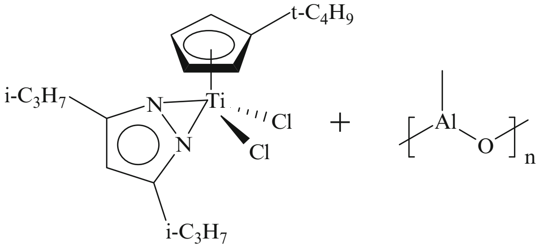
In a subsequent publication [304] they reported the synthesis and activity of binuclear catalysts 2,7-di[(2,6-isopropylphenyl) imino]-1,8-naphthalenediolato group 4 metal complexes and copolymerization of ethylene with various mono olefins. The bimolecular catalysts exhibited enhanced activity as compared to their mononuclear analogs. The polymerizations were illustrated as follows:



At the present time, in spite of all the research effort, there is still a need for catalyst systems that will enable preparation of low density polyethylene with controlled levels of both short and long branches.

Homura and coworkers [305] investigated a series of half-titanocenes containing pyrazole ligands that have been employed as catalyst precursors for ethylene polymerization, syndiospecific styrene polymerization, and copolymerization of ethylene with 1-hexene, styrene, and norbornene in the presence of methyl aluminoxane cocatalyst. The catalyst was $TiCl_2$ ($3,5R_2C_3HN_2$), where R was hydrogen, methyl, propyl, and phenyl. The ethylene/styrene copolymerization proceeds in a living manner, irrespective of the styrene concentration in toluene at 25°C and the same system exhibits relatively high catalytic activity for the ethylene/norbornene copolymerization with highly efficient norbornene incorporation [305].

The catalyst system can be illustrated as follows:

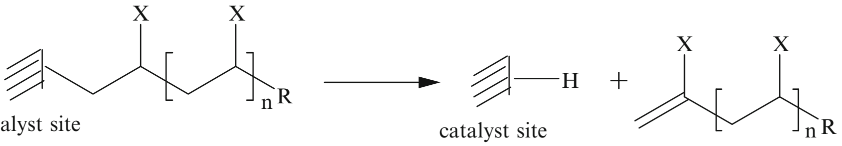


4.5.5 Effect of Lewis Bases

Many investigations were carried out to understand the role Lewis bases play in affecting stereospecificity of the Ziegler–Natta catalysts. One of them, for instance, included studies with optically active bases to determine the reactions with the active sites [252]. Nevertheless, the effect of Lewis bases like tertiary amines is not fully understood. Evidence, gathered to date, suggests that when they react with aluminum alkyl halides’ [306] they increase the number of stereospecific sites by assisting in the stabilization and/or dispersal of the catalyst on the support. They appear to alter the identities of the attached ligands. This might be due to increasing the steric bulk at these sites. The Lewis bases are also given credit for reducing the reactivity of the less stereospecific sites. Because both internal and external Lewis bases are used, the enhancement of stereospecificity by the external bases is attributed to displacing the internal base and/or augmenting its effect [307].

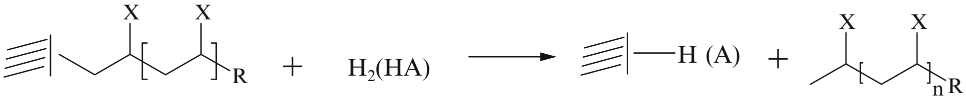
4.5.6 Terminations in Coordination Polymerizations

The terminations usually occur by chain transferring, either by an internal hydride transfer [261]:



or by a transfer to a monomer:

Terminal unsaturation in the products was confirmed by infrared spectroscopy. Hydrogen terminates the reactions and it is often added to control the molecular weights of the products. Protonic acids do the same thing:



4.5.7 Reduced Transition Metal Catalysts on Support

The catalysts that belong to this group are efficient in homopolymerizations of ethylene. They can also be used in some copolymerizations of ethylene with α-olefins. Such catalysts are prepared from TiO_2, V_2O_5, Nb_2O_5, Ta_2O_5, CrO_3, Cr_2O_3, and MoO_3. WO_3, NiO, and CoO. The supports are charcoal, silica, alumina, zinc oxide, or alumina-silica. These catalysts require higher temperatures and pressures for activity than do the typical Ziegler–Natta catalysts. The temperatures range from 140 to 230°C and pressures from 420 to 1,000 psi.

One of the original disclosures of such catalyst preparation was as follows [308]. A transition metal nitrate solution is used to saturate a charcoal bed, previously leached with nitric acid. The charcoal bed is then heated to temperatures high enough to decompose the nitrate to the oxide.

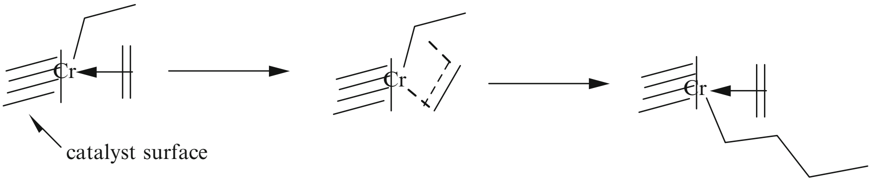
Following the heating, the oxide is reduced with H_2 or $NaBH_4$. Sometimes, powdered Al_2O_3 or MoO_3-Al_2O_3 is added prior to reduction.

For an Al_2O_3-SiO_2 support, a 3% metal nitrate solution is used. The saturated bed is heated to 500°C to decompose the nitrate. This is followed by a reduction. Many modifications of the above procedure developed since.

Preparations based on molybdenum oxide are called Standard Oil Co. catalysts, while those based on chromium oxide are known as the Phillips Petroleum Co. catalysts. Following is a description of a preparation of a molybdenum based catalyst. Alumina is saturated with a solution of ammonium molybdate and then subjected to heating in air at 500–600°C. The oxide that forms is reduced with hydrogen at 430–480°C. Reducing agents like CO, SO, or hydrocarbons are also used. Hydrogen, however, is preferred at pressures of approximately 75 psi. The catalyst may contain between 5 and 25% of the molybdenum compound dispersed on the surface [309].

A typical chromium based catalyst is prepared similarly. It is usually supported by a 9:1 of SiO_2: Al_2O_3 [347] carrier. Either $Cr(NO_3)_3 \bullet 9H_2O$ or CrO_3 solutions in nitric acid are used to impregnate the support. The nitrates are decomposed in air at 400–1,000°C [310]. Optimum chromium content in these catalysts is 2–3%.

The mechanism of polymerization was initially believed to be as follows [212]. Cr–O–Si bonds are present on the catalyst surface. Contact with ethylene results in an oxidation-reduction reaction and formation of an ethylene-chromium complex. The initiations are accompanied by gains of hydride ions and formations of terminal methyl groups. Polymer growth was pictured as follows:

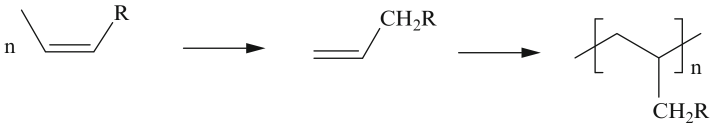


The termination reactions were believed to result from hydride-ion transfers [262]. Later, however, polyethylene, formed with these catalysts, was found to contain approximately equal numbers of saturated and unsaturated chain ends. This contradicts the above concept. It may also mean that the initiation involves π-complexes that disproportionate to yield coordination of the metal to $–CH{=}CH_2$ and to $–CH_2–CH_3$ groups [262].

Polymerization of propylene with these catalysts yields polymers with very little crystallinity. Higher α-olefins yield completely amorphous polymers. Formation of partially crystalline polymers was reported for vinylcyclohexane, allylcyclohexane, and 4-phenyl-1-butene. Styrene does not polymerize at all. Isoprene forms a *trans*-1,4-polymer [262].

4.5.8 Isomerization Polymerizations with Coordination Catalysts

Polymerizations of many internal olefins, like 2-butene, 2-pentene, 3-heptene, 4-methyl-2-pentene, 4-phenyl-2-butene and others, with Ziegler–Natta catalysts are accompanied by monomer rearrangements. The isomerizations take place before insertions into the chains [311–318]:



The double bonds migrate from the internal to the α-positions:

The products consist exclusively of poly(1-olefin) units. Polymerizations of 2, 3 and 4 octenes with $TiCl_3/Al(C_2H_5)_3$ at 80°C for instance, result in the same high molecular weight homopolymer, poly (1-octene) [319].

Also, it was reported that addition of some transition metal compounds of Group VIII to Ziegler–Natta catalysts enhances isomerization of 2-olefins [321, 329]. When nickel compounds are added to $TiCl_3–(C_2H_5)_3Al$ they react and form $TiCl_3–NiX_2–(C_2H_5)_3Al$. X can be a chloride, an acetylacetonate, or a dimethyl glyoximate [328]. The product is an efficient isomerization catalyst.

4.6 Polymerization of Aldehydes

Aldehyde polymers were probably known well over 100 years ago [322–324]. In spite of that, polyoxymethylene is the only product from aldehyde polymerization that is produced in large commercial quantities. Formaldehyde polymerizes by both cationic and anionic mechanisms. An oxonium ion acts as the propagating species in cationic polymerizations [322, 323]. In the anionic ones, the propagation is via an alkoxide ion.

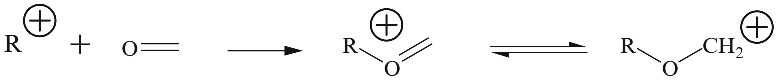
Most polymerizations of aldehydes are conducted in aprotic anhydrous solvents because proton-yielding impurities are very efficient chain transferring agents. Polymerization of formaldehyde can be looked upon as an exception [323]. When protonic solvents are used, however, the resultant polymer has a very wide molecular weight distribution. Usually, therefore, solvents with low dielectric constants are preferred. In all cases of aldehyde polymerizations, the polymers precipitate from solution as they form. Choice of low dielectric solvents contributes to this. In spite of that, the polymerizations often keep on going as rapidly as the monomers are added to the reaction mixtures. In addition, only low molecular weight polyoxymethylene forms in some high dielectric solvents, like dimethylformamide, and the reaction is quite sluggish. Higher aldehydes fail to polymerize in dimethylformamide.

As stated above, the propagation reaction continues after polymer precipitation. That is due to the fact that the precipitated macromolecules are highly swollen by the monomers. This was shown in polymerizations of *n*-butyraldehyde in heptane [326]. The physical state of the polymers and the surface areas of their crystalline domains, therefore, influence the paths of the polymerizations.

The solubility of the initiators in the solvents can affect strongly the molecular weights of the resultant products and their bulk densities [323]. The whole reaction can even be affected by small changes in the chemical structures of the initiators or by changes in the counterions [323]. Chain transferring is the most important termination step in aldehyde polymerizations.

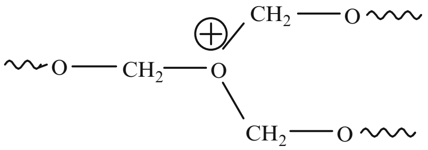
4.6.1 Cationic Polymerization of Aldehydes

The cationic polymerizations of formaldehyde can be carried out in anhydrous media with typical cationic initiators. Initiation takes place by an electrophilic addition of the initiating species to the carbonyl oxygens. This results in formations of oxonium ions [323]:

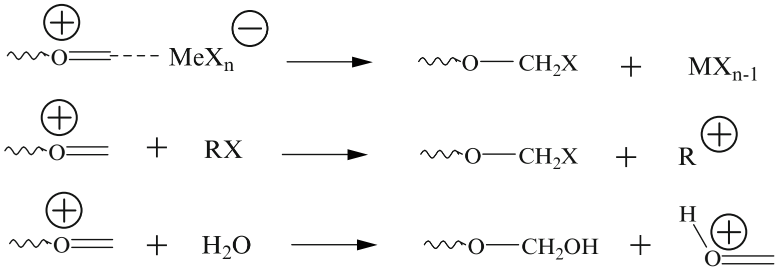


The oxonium ions may react as oxygen-carbon cations. The propagation steps consist of attacks by the electrophilic carbon atoms upon the carbonyl oxygens of the highly polar formaldehyde molecules:

In these polymerizations, the propagating oxonium ions are probably further solvated [226]:



Terminations of chain growths occur through recombinations, reactions with impurities, and by chain transfers:

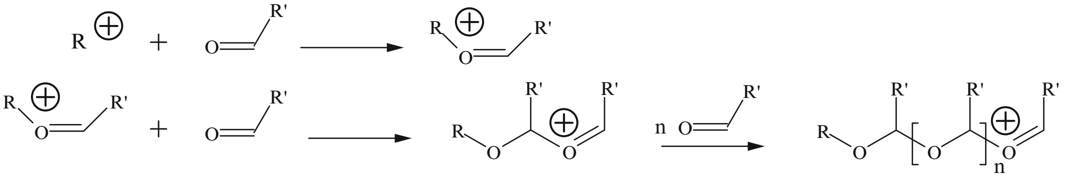


where, MnX_n is a Lewis acid.

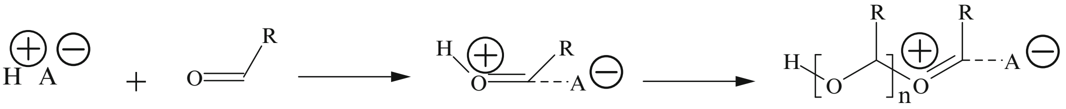
Formaldehyde can polymerize in an anhydrous form in all three physical states of matter: as a gas, as a liquid, or as a solid [322]. It also polymerizes in water with acid catalysts. Many Lewis acids are efficient catalysts for this reaction. In addition, some protonic acids are also effective. Among them are perchloric and sulfuric acids and monoesters of sulfuric acid [322].

The activity of the initiators is independent of the solvents in cationic polymerizations of formaldehyde [322]. There are, however, differences in the performance of the initiators. With BF_3 the reaction reaches equilibrium at 30% conversion and stops. Much higher conversions are achieved with $SnCl_4$ and $SnBr_4$ [322]. Both Lewis acids yield polyoxymethylenes that are very similar to those formed by anionic mechanism [324–327].

Higher aldehydes can be polymerized by Lewis acids, Bronsted acids, and acidic metal salts [322]. Initiation and propagation reactions consist of repeated nucleophilic attacks by the carbonyl oxygens on the electrophiles and formations of carbon-oxonium ions [328]:



The counterions are not shown in the above equations. When the initiators are protonic acids the reactions can be illustrated as follows (additional monomers are not shown):



Many aldehydes trimerize in acidic conditions. Paraldehyde and many other trimers fail to undergo further polymerizations to high molecular weight, linear polymers. The trimer of formaldehyde, trioxane, however, is unique. It polymerizes by a mechanism of ring opening polymerization. This is discussed in Chap. 5. To avoid trimer formations, low dielectric solvents must be used at low temperatures. In addition, the initiator must be carefully selected.

Potentially, atactic, isotactic, and syndiotactic polymers should form from higher aldehydes. Catalysts, like Al_2O_3, CrO_3, MoO_3 and SiO_2, form high molecular weight atactic polyacetaldehyde at −78°C [329]. These are solid catalysts that yield polymers under heterogeneous conditions [330]. Some alumina can be converted into efficient catalysts by treating the surface with HCl, F_3CCOOH, or BF_3 [331]· Acetaldehyde is polymerized by a variety of soluble initiators, such as H_3PO_4, HCl, HBO_3, F_3CCOOH, AsF_3, $AsCl_3$, $ZnCl_2$, $ZrCl_4$ and Cl_3COOH [332]. Polymerization reactions require good solvent if weak cationic initiators are used. When strong initiators are employed, the reactions are difficult to control. Low temperatures can be maintained by such techniques as boiling off low boiling solvents.

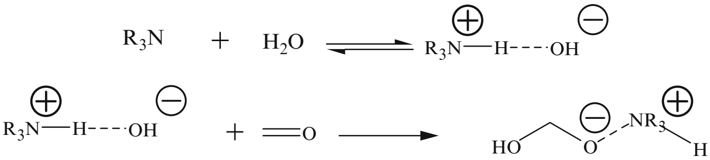
Formation of pure isotactic polyacetaldehyde was reported. It forms in small quantities in the presence of an atactic polymer obtained with crystalline BF_3-etherate [332].

4.6.2 *Anionic Polymerization of Aldehydes*

Many patents describe polymerizations of anhydrous formaldehyde by anionic mechanism. The initiators included amines, phosphines, and metal alcoholates. Kern pictured initiations of formaldehyde polymerizations by tertiary amines as direct addition reactions [332, 334]:

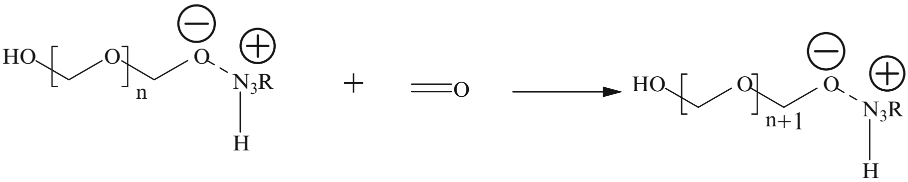
$$R_3N + CH_2O \rightarrow R_3N^{\oplus} - CH_2 - O^{\ominus}$$

Earlier, however, Machacek suggested [335–337] that the initiations take place with the help of protonic impurities:

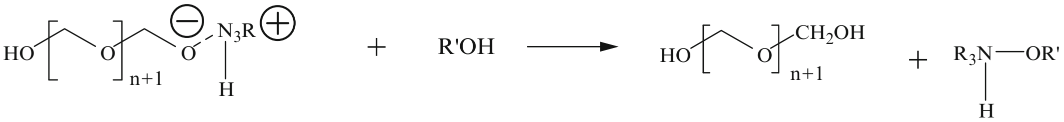


Much of the evidence presented since favors the Machacek mechanism of initiation [335]. By contrast, tertiary phosphines apparently do initiate such polymerizations by a zwitter ion mechanism [338]. This may, perhaps, be due to higher nucleophilicity and lower basicity than that of the tertiary amines. Phosphorus incorporates into the polymer [338] in the process.

The propagation reactions in tertiary amine initiated polymerizations can be pictured as follows [339]:

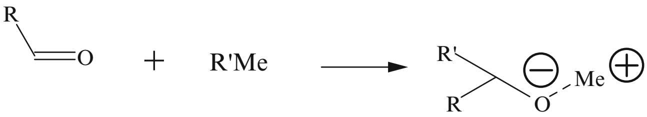


The terminations, probably, result from chain transferring [241]:

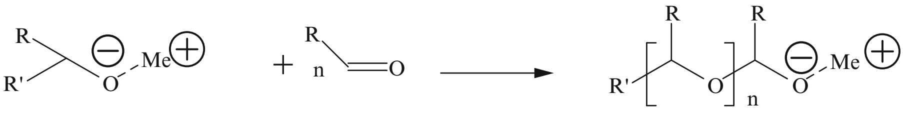


The newly formed active species can initiate new polymerizations.

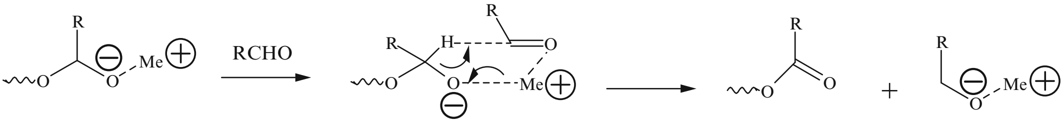
Metal alkyls and metal alcoholates are very effective anionic initiators for higher aldehydes. Aldol condensation can occur, however, in the presence of strong bases. Thus, while some such initiators yield high molecular weight polymers from formaldehyde, they only yield low molecular weight polymers from higher aldehydes. Initiations by metal alkyls result from additions to the carbonyl group:



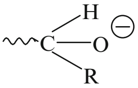
Where, Me represents a metal group. The propagation reaction is a series of successive nucleophilic additions [340], with the alkoxide ion as the propagating species:



There are indications that many aldehyde polymerizations result in formations of "living" polymers similarly to anionic polymerizations of vinyl compounds. Termination can occur through hydride transfer via a form of a crossed Cannizzaro reaction:



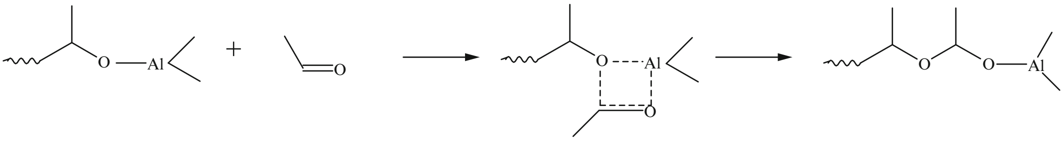
The alkyl substituent has a tendency to destabilize the propagating anion by increasing the charge density on the oxygen:



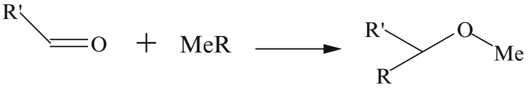
As a result, weak bases, like amines, fail to initiate polymerizations of higher aldehydes.

A ***stereospecific anionic polymerization*** of acetaldehyde was originally reported in 1960 [343, 344]. Two alkali metal compounds [341] and an organozinc [342] one were used as the initiators. Trialkylaluminum and triarylaluminum in heptane also yield crystalline, isotactic polymers from acetaldehyde, heptaldehyde, and propionaldehyde at −80°C [343]. Aluminum oxide, activated by diethylzinc, yields stereoblock crystalline polymers from various aldehydes [342, 344]. Lithium alkoxide formed polyacetaldehyde is insoluble in common solvents. It melts at 165°C [341].

The mechanism of stereoregulation is still debated. Some concepts are presented in the rest of this section. Natta [343] believed that polymerizations initiated by organoaluminum compounds proceed by coordinated anionic mechanism. The aluminum atoms were seen as forming complexes with the oxygen atoms on the penultimate units:

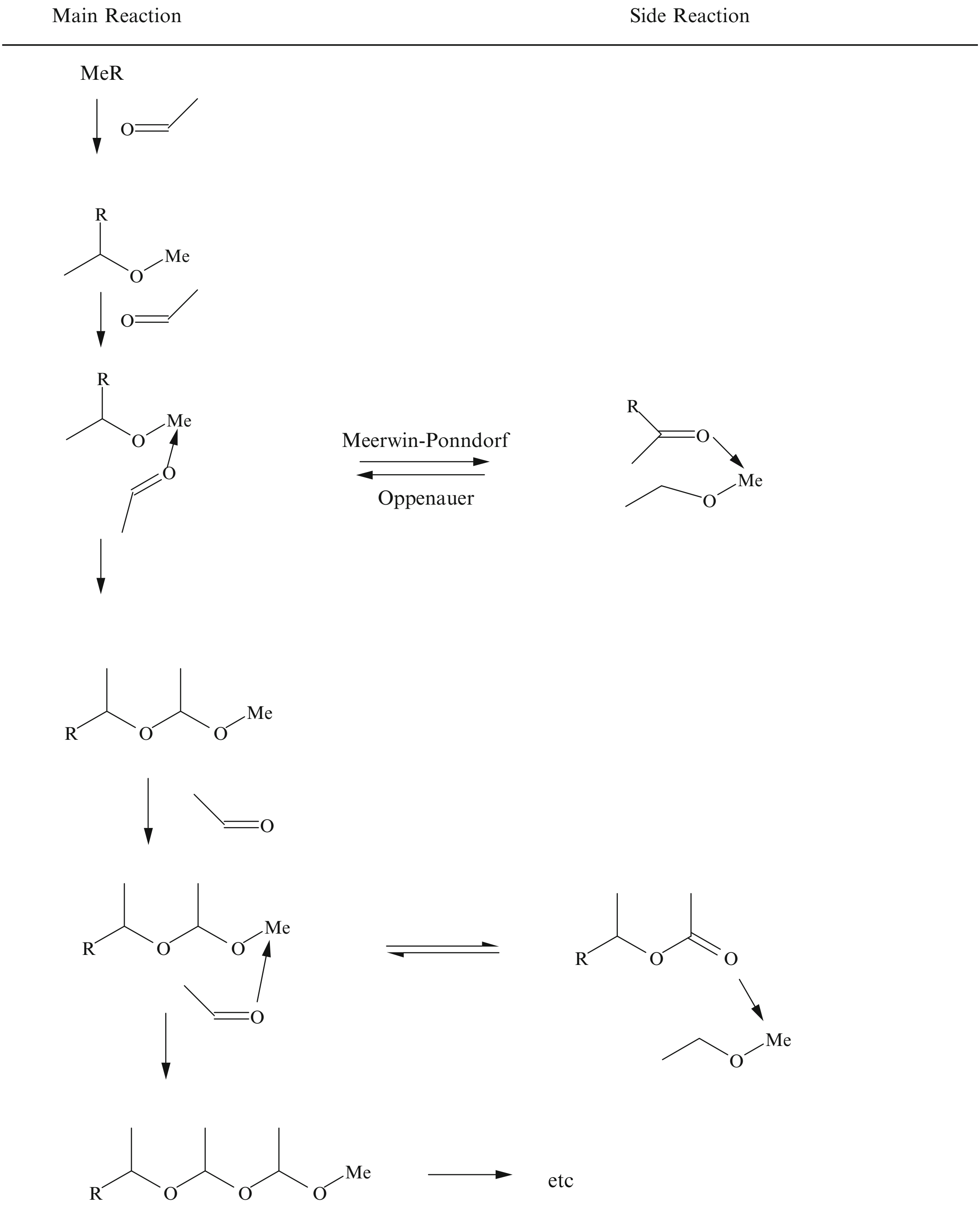


The activated complexes, which form, have steric configurations that allow minimum amounts of non-bonded interactions. Other mechanisms were proposed since. For instance, Furukawa et al. [344] concluded that metal alkyl compounds must become metal alkoxides through reactions with the aldehydes:



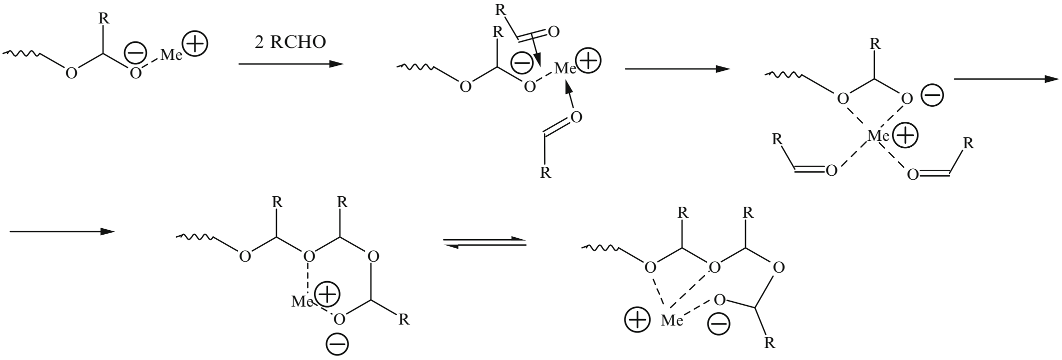
where, Me means metal.

His polymerization mechanism, therefore, is based on known reactions of metal alkoxides with carbonyl compounds. Side reactions, like a Meerwein-Ponndorf or a Tischenko, should be expected and were included into the reaction scheme:



Each monomer addition to the growing chain requires a transfer of the alkoxide anion to the carbonyl group. This results in a formation of a new alkoxide anion. (A hydride transfer from the alkoxide group to the carbon atom of the aldehyde can take place by the Meerwein-Ponndorf reduction.) Chain growth takes place by repetition of the coordination of the aldehyde, and subsequent transfer of the alkoxide anion.

In the Vogl and Bryant [345] mechanism, four oxygens are coordinated to the metal atom. These oxygens are from the penultimate and ultimate units of the growing chains and from two monomers:

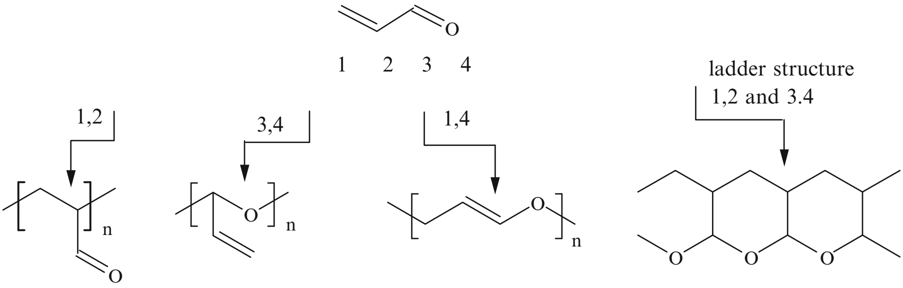


A simultaneous coordination of the two aldehydes prior to addition may explain the observed sequence of isotactic dyads.

Yashida and Tani derived their mechanism from investigations of isotactic aldehyde polymerizations by $[R_2AlOCR'NC_6H_5]$ catalysts [346–348]. The bulkiness of the substituent group is considered to be the most important factor in steric control. The catalyst enhances the degree of stereoregulation by controlling the mode of approach through coordination. Also, the Lewis acidity of the catalyst must be confined to a narrow range for each particular aldehyde to yield isotactic polymers [347, 348]. If the acidity is too strong, an amorphous polymer forms. If it is too weak, no polymerization takes place [348]. In addition, special techniques, like high pressures, for instance, can result in formations of isotactic butyraldehyde and heptaldehyde [349].

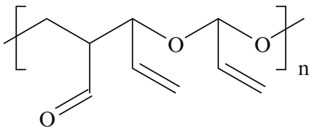
4.6.3 *Polymerization of Unsaturated Aldehydes*

Unsaturated aldehydes are unique, because they polymerize in special ways. Much of the effort in acrolein polymerizations is to form products with the aldehyde groups in tact. This means, the reactions must be confined to the carbon to carbon double bond portions of the molecules [350–356]. Organometallic catalysts like *n*-butylmagnesium bromide, however, are also initiators for polymerizations through the carbonyl groups. In fact, unsaturated aldehyde monomers can be polymerized in four ways similar to dienes. The placement can be through carbon to carbon double bond, or through the carbonyl group, or it can be 1,4:



Because acrolein polymerizes by free-radical and by ionic mechanisms, all of the above reactions are possible, and the products are quite complex. The structures of the materials include linkages from both vinyl and carbonyl groups. In addition, tetrahydropyran rings, as shown above, can also form [357].

Coordination complexes, like $CdI_2(pyridine)_2$, also initiate polymerizations of acrolein. Propagation reactions precede through both, vinyl and carbonyl groups [358]:



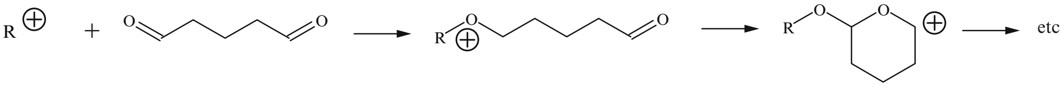
The ratio of vinyl to carbonyl placement depends upon the nature of the complex. Polymers formed by complexes of metallic salts with triphenylphosphine contain considerably less aldehyde groups than those formed with triphenylphosphine alone [358].

Polymerization of propionaldehyde ($CH{\equiv}C{-}CH{=}O$) is also unique. In dimethylformamide at 0°C with sodium cyanide or with tri-*n*-butyl phosphine catalysts the reactions yield polymers composed of two different structural units. One is a polyaldehyde and the other one is a polyacetylene [355]. The reaction in tetrahydrofuran, however, at −78°C with sodium cyanide catalyst results in a crystalline poly(ethynyl oxymethylene) [359]. Radical initiated polymerizations of this monomer at 60°C, on the other hand, proceed through the acetylenic group only.

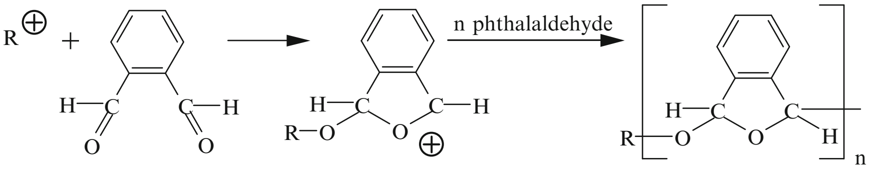
Crotonaldehyde, like acrolein can be expected to yield polymers with structures derived from 1,2; 3,4; or 1,4 additions. Anionic catalysts, however, yield predominantly polyacetal structures [360].

4.6.4 Polymerizations of Di Aldehydes

As one might expect, di aldehydes can be polymerized to yield polymers with cyclic ether linkages. This resembles polymerizations of non-conjugated dienes [361]:



Cationic polymerizations can take place by either one of three paths: stepwise additions, intermediate-type additions, and concerted additions. When phthalaldehyde is polymerized by cationic mechanism or by γ-irradiation at −78°C, the products consist of dioxyphthalan units [362]:

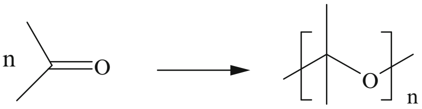


Aromatic aldehydes usually polymerize with difficulty. The enhanced polymerizability of phthalaldehyde is due to formation of intermediates from concerted propagation reactions [362].

In the above illustration, the anhydride rings can be either ***cis*** or ***trans*** in configuration. Cationic polymerizations yield polymers with high *cis* content. Anionic catalysts and particularly coordination catalysts, like triethylaluminum-transition metal halides, yield high *trans* polymers [363].

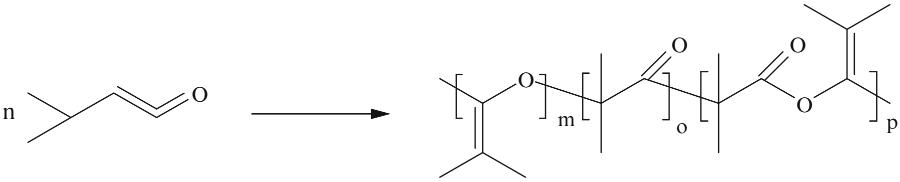
4.7 Polymerization of Ketones and Isocyanates

In spite of many attempts to prepare useful polymers from ketones, so far, this is not very successful. Acetone polymerizes with the aid of magnesium [364]. The reaction requires high vacuum. Vapors of magnesium metal and dry acetone condense simultaneously in vacuum on a surface cooled by liquid nitrogen. The white elastic polymer that forms possesses a polyketal structure:



Like low molecular weight ketals, the polymer is unstable and decomposes even at room temperature. Acetone also polymerizes upon irradiation in a frozen state under high vacuum. The product is a yellow, rubbery material [364]. Infrared spectra show presence of both, C–O–C linkages and carbonyl groups. Monobromoacetone polymerizes in the same manner, by irradiation in the frozen state. The hard resinous polymer that forms is more stable than polyacetone [364].

Polymerizations of ketenes yield varieties of structures because monomer placements are possible through either the carbon to carbon double bond or through the carbon to oxygen double bond. Dimethylketene polymerizes by anionic mechanism to a polymer with the following structures [46]:



Polar solvents increase formations of ether groups. Non-polar solvents, used with lithium, magnesium, or aluminum counterions, yield products that are high in ketones [46]. The same solvents, used with sodium or potassium counterions, form polymers with predominately polyester units [46].

Isocyanates polymerize through the carbon to nitrogen double bonds by anionic mechanism. Reactions can be catalyzed by sodium or potassium cyanide at −58°C [365]. *N*,*N*′-dimethylformamide is a good solvent for this reaction. Other anionic catalysts, ranging from alkali salts of various carboxylic acids [344] to sodium-naphthalene, are also effective [367]. In addition, polymerizations can be carried out by cationic [368], thermal [369], and radiation-induced [369] methods. Although anionic polymerizations yield very high molecular weight polymers, there is a tendency to depolymerize at high temperatures. The products of anionic polymerization are substituted polyamides [365] (for more information see Chap. 7).

4.8 Copolymerizations by Ionic Mechanism

Ionic copolymerizations are more complicated than free-radical ones. Various complicating factors arise from effects of the counterions and from influences of the solvents. These affect the reactivity ratios. In addition, monomer reactivity is affected by the substituents. They influence the electron densities of the double bonds and in cationic polymerizations the resonance stabilization of the resultant carbon cations. Also, the effects of the counter-ions, the solvents, and even the reaction temperatures can even be greater than that of the substituents in cationic polymerizations. There are only a few studies reported in the literature, where the reactivity ratios were determined for different monomers, using the same temperature, solvent, and counterion. One such study was carried out on cationic copolymerizations of styrene with two substituted styrenes. These were α-methylstyrene, and with chlorostyrene [370–372]. The relative reactivity ratios of these substituted styrenes were correlated with Hammett $\rho\sigma$ values. The effect of the substituents on reactivity of styrene falls in the following order:

$$p\text{ - OCH}_3 > p\text{ - CH}_3 > p\text{ - H} > p\text{ - Cl} > m\text{ - Cl} > m\text{ - OH}$$

This information, however, is useful only for copolymerizations of substituted styrene monomers.

Copolymerization studies demonstrated that steric factors are very important in cationic copolymerizations [373–375]. For instance, β-methyl styrene is less reactive than styrene. Also, *trans*-β-methylstyrene is more reactive than the *cis* isomer.

The effect of solvents on the reactivity ratios in cationic copolymerizations can be seen from copolymerizations of isobutylene with *p*-chlorostyrene, using aluminum bromide as the initiator [376]. The r_1 and r_2 values in hexane for isobutylene and chlorostyrene copolymerization are both equal to 1.0. In nitrobenzene, however, r_1 is equal to 14.7 and r_2 is equal to 0.15.

In copolymerization of styrene with *p*-methylstyrene catalyzed by $SbCl_5$, AlX_3, $TiCl_4$, $SnCl_4$, $BF_3 \bullet OEt_2$, $SbCl_3$, Cl_3COOH, and iodine, the copolymer composition depends upon the solvent and on the acid strength of the catalysts. There is no difference in copolymer composition in highly polar solvents, except when $SbCl_5$ is used [377]. Generally, the amount of styrene in the copolymer decreases as the solvent polarity increases. In solvents of low polarity, on the other hand, the amount of styrene in the copolymer decreases with a decrease in the strength of the Lewis acids. This depends upon the amount of solvation of the ion pair, and on the complexation of the solvent and monomer with the ion pair. With an increase in the tightness of the ion pairs in less polar solvents, selectivity increases. Because *p*-methylstyrene is more polar it complexes to a greater extent than does styrene. Polymerization temperature in cationic polymerizations affects monomer reactivity strongly. This effect is considerably greater in cationic copolymerizations than in free-radical ones. No general trend, however, appears to have been established, so far.

Electron withdrawing substituents in anionic polymerizations enhance electron density at the double bonds or stabilize the carbanions by resonance. Anionic copolymerizations in many respects behave similarly to the cationic ones. For some comonomer pairs steric effects give rise to a tendency to alternate [378]. The reactivities of the monomers in copolymerizations and the compositions of the resultant copolymers are subject to solvent polarity and to the effects of the counterions. The two, just like in cationic polymerizations, cannot be considered independently from each other. This, again, is due to the tightness of the ion pairs and to the amount of solvation. Furthermore, only monomers that possess similar polarity can be copolymerized by anionic mechanism. Thus, for instance, styrene derivatives copolymerize with each other. Styrene, however, is unable to add to a methyl methacrylate anion [379–381], though it copolymerizes with butadiene and isoprene. In copolymerizations initiated by *n*-butyllithium in toluene and in tetrahydrofuran at −78°C, the following order of reactivity with methyl methacrylate anions was observed [382]. In toluene the order is: diphenylmethyl methacrylate > benzyl methacrylate > methyl methacrylate > ethyl methacrylate > α-methylbenzyl methacrylate > isopropyl methacrylate > *t*-butyl methacrylate > trityl methacrylate > α,α′-di-methylbenzyl methacrylate. In tetrahydrofuran the order changes to: trityl methacrylate > benzyl methacrylate > methyl methacrylate > diphenylmethyl methacrylate > ethyl methacrylate > α-methylbenzyl methacrylate > isopropyl methacrylate > α,α′-dimethylbenzyl methacrylate > *t*-butyl methacrylate.

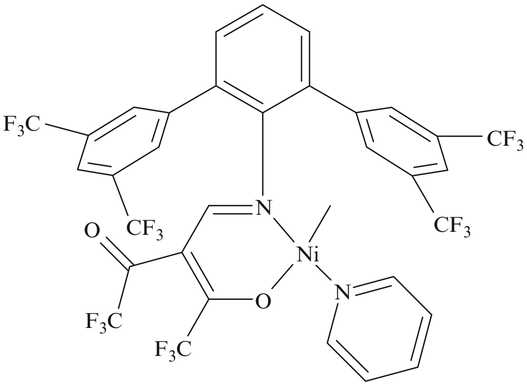
Copolymerizations of styrene with butadiene in hydrocarbon solvents, using lithium alkyls initiators initially yield copolymers containing mainly butadiene. The amount of styrene in the copolymer increases considerably, however, in tetrahydrofuran solvent.

Hashimoto and coworkers studied anionic living copolymerization by ionic mechanism of two monomers, styrene and isoprene in a dilute benzene solution with the aid of combined time-resolved measurements of small angle neutron scattering, NMR spectroscopy, size exclusion chromatography, and ultraviolet–visible spectroscopy [383]. They reported observing structural changes of living chains during the polymerization process. They also found that copolymerization process is divided into two time regions, defined by regions I and II. In region I, the copolymerization of styrene and isoprene monomers occurred and all I monomers were consumed at the end of region I, while in region II, pure polystyrene block chains were formed. In the beginning of region II, living polymers with terminal isoprenyl anion started to add styrene monomer rapidly and changed into chains with terminal styryl anions. This was followed by a slow change from polyisoprene to polystyrene in the latter part of region II. As a consequence of the polymerization of styrene monomers in the presence of polyisoprene and polystyrene, they found an increase in M_w/M_n. In addition. they also found that the conversion rate of styrene monomers at these conditions is slow compared with one in homopolymerization.

Anionic copolymerizations are very useful in forming block copolymers (see Chap. 9 for discussion). Ziegler–Natta catalysts also form block copolymers, similarly to anionic initiators. Much work on copolymerization with coordinated anionic initiators was done to develop ethylene propylene copolymers. Ethylene is considerably more reactive in these copolymerizations. To form random copolymers, soluble Ziegler–Natta catalysts are used. This is aided further by carefully controlling the monomer feed [384].

The 1,2-disubstituted olefinic monomers will usually not homopolymerize with the Ziegler–Natta catalysts. They can, however, be copolymerized with ethylene and some α-olefins [384]. Due to poorer reactivity, the monomer feed must consist of higher ratios of the 1,2-disubstituted olefins than of the other comonomers. Copolymers of *cis*-2 butene with ethylene, where portions of the macromolecules are crystalline, form with vanadium based catalysts. The products have alternating structures, with the pendant methyl groups in erythrodiisotactic arrangements [197]. Similarly, vanadium based catalysts yield alternating copolymers of ethylene and butadiene, where the butadiene placement is predominantly *trans*-1,4 [197].

Giuronett and Mecking carried out copolymerizations of ethylene with 1-olefins in supercritical carbon dioxide by electron poor nickel complexes [385]. The catalyst can be illustrated as follows:



They reported that the catalyst showed high activity in supercritical CO_2 yielding high molecular weight copolymers of ethylene with 1-hexene and with norbornene [385].

Copolymerizations of aldehydes take place by both anionic and cationic mechanisms. An elastic copolymer of formaldehyde and acetaldehyde forms with triisobutylaluminum. The rate of copolymerization is very rapid at −78°C. The reaction is complete within 30 min [364]. The product, however, is crosslinked. Aldehydes also copolymerize with some vinyl monomers [386]. An acetone block copolymer forms [387] with propylene when Ziegler–Natta catalysts are used at −78°C. Copolymers of acetone with other olefins and with formaldehyde were also prepared [388, 389]. Many initiators are effective in copolymerizations of aldehydes, ketones, and epoxies [387, 390].

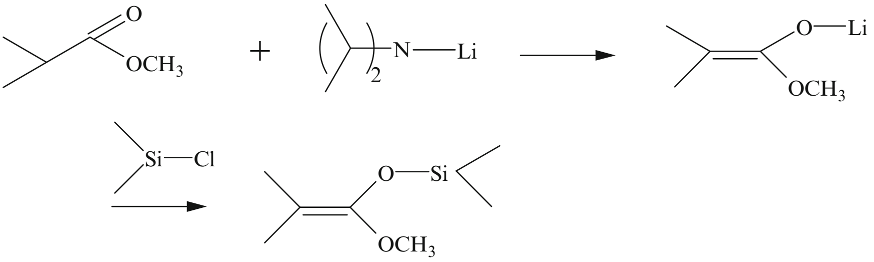
O'Driscoll [407] developed the kinetics of ionic copolymerization of dissimilar monomers. It is based on the assumption, that the ratio of monomers in the copolymer $d[M_1]/d[M_2]$ is directly proportional to the square of the initial monomer rate $([M_1]/[M_2])^2$ in the copolymerization reaction.

$$d[M_1]/d[M_2] = (k_1/k_2)(k_{11}/k_{22})([M_1]/[M_2])^2$$

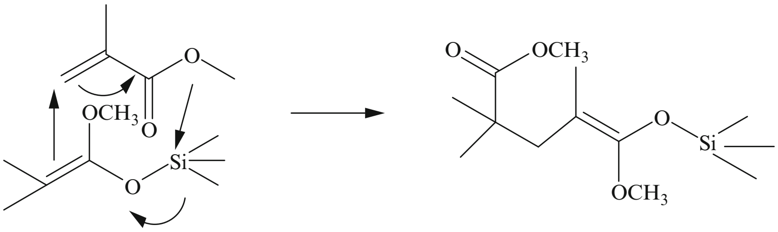
The above shown equation was derived on the assumption that initial homopropagation is fast, relative to the propagation. Also, that the crossover reaction is negligible at the beginning of the copolymerization.

4.9 Group Transfer Polymerization

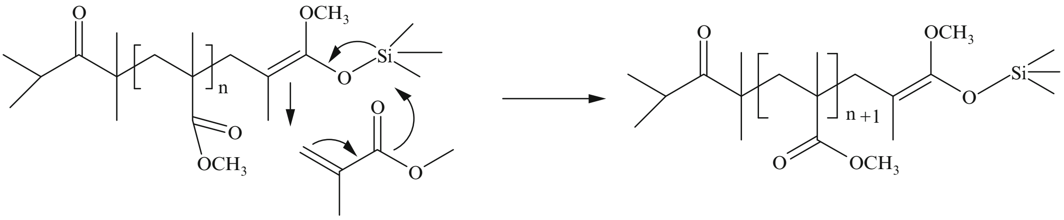
This technology offers considerable promise for commercial preparations of living polymers of methyl methacrylate without resorting to low temperature anionic polymerizations. Although the mechanism or polymerization is not completely explained, the propagation is generally believed to be ***covalent*** in character. A silyl ketene acetal is the initiator. It forms from an ester enolate [391]:



The initiation, that is catalyzed by either a nucleophilic or by a Lewis acid catalyst, was explained as consisting of a concerted attack by the ketene acetal on the monomer [392]:



This results in a transfer of the silyl ketene acetal center to the monomer. The process is repeated in each step of the propagation. The ketone double bond acts as the propagating center [391].



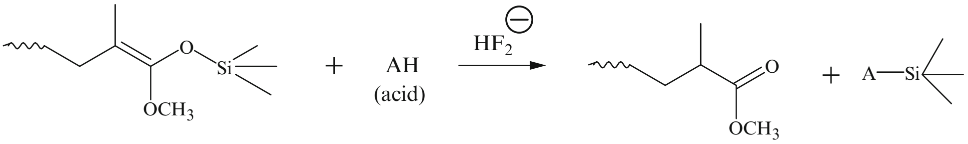
The above mechanism shows each step of chain-growth involving transfer of the trialkylsilyl group from the silyl ketene acetal at the chain end to the carbonyl group of the incoming monomer. This is disputed because it excludes silyl exchange between growing chains [393]. Such an exchange, however, was observed [392] and led to a suggestion that the mechanism can involve ester enolate anion intermediates. These are reversibly complexed with silyl ketene acetal chain ends, as the propagating species [394]. It should be noted, however, that the results do not exclude the possibility of transfer reactions occurring as well.

Difunctional initiators cause chain growth to proceed from each end [395]. Because group-transfer polymerizations are "living" polymerization, once all the monomer has been consumed, a different monomer can be added and block copolymers can be formed.

The most effective nucleophilic catalysts for this reaction are bifluoride (HF_2^-) and fluoride ions. They can be generated from soluble reagents like tris(dimethylamino)sulfonium bifluoride. Other nucleophiles, like CN^- and nitrophenolate have also been used. These nucleophilic catalysts function by assisting the displacement of the trialkylsilyl group. They are effective in concentrations below 0.1 mol% of the initiator. Among electrophilic catalysts are Lewis acids, like zinc chloride, zinc bromide, zinc iodide, and dialkylaluminum chloride. Such catalysts probably function by coordinating with the carbonyl oxygens of the monomers and increasing the electrophilicity of the double bonds. This makes them more reactive with nucleophilic reagents. They must be used, however, in much higher concentrations.

Water and compounds with active hydrogen must be excluded from the reaction medium. Oxygen, on the other hand, does not interfere with the reaction. Tetrahydrofuran, acetonitrile, and aromatic solvents are commonly used in polymerizations catalyzed by nucleophiles. Chlorinated solvents and dimethylformamide are utilized in many reactions catalyzed by electrophiles. Living polymerizations of methacrylate esters can be carried out at 0–50°C. The acrylate esters, however, require temperatures below 0°C for living, group-transfer polymerizations, because they are more reactive and can undergo side reactions.

Weakly acidic compounds, such as methyl α-phenylacetate or α-phenylpropionitrile, are added to terminate the reaction. They are effective with anionic catalysts [396]. The trialkylsilyl group is transferred from the chain end to the transfer agent:

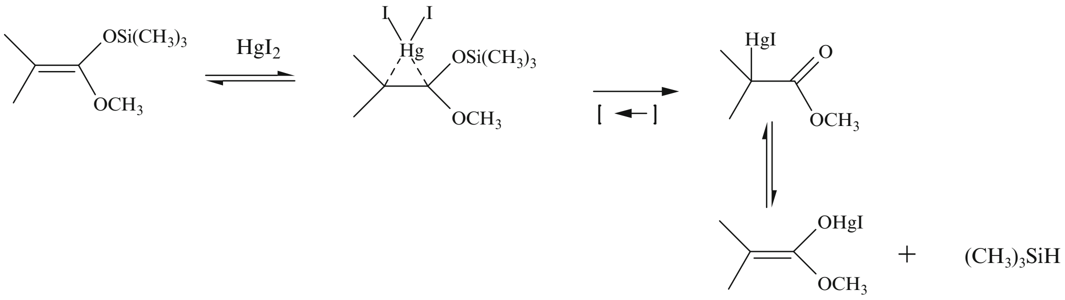


Group-transfer polymerizations yield very narrow molecular weight distribution polymers. When mixtures of monomers are used, random copolymers form. The polymerization reaction is very tolerant of other functional groups in the monomer. Thus, for instance, *p*-vinylbenzyl methacrylate is converted to poly(*p*-vinylbenzyl methacrylate) without the polymerization of the vinyl group [397]. In addition, it is possible to form polymers with high syndiotactic content.

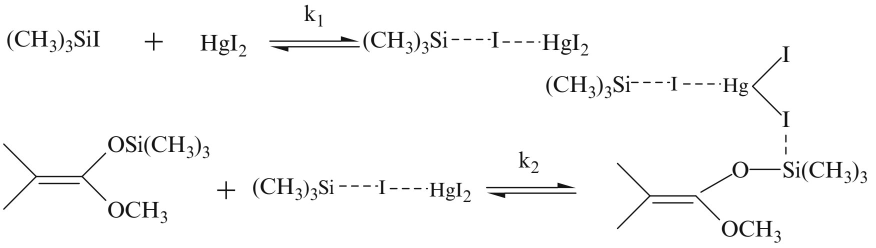
An example of copolymerization is that of methyl methacrylate with methyl α-phenylacrylate [398]. While no homopolymer formed from methyl α-phenylacrylate, alternating copolymers were obtained from mixtures of the two. Equimolar incorporation of monomers was reported even with methyl methacrylate in excess, as long as methyl α-phenylacrylate is present in the reaction mixture. The propagation constants were found to decrease in the order $k_{12} \gg k_{11} > k_{21} \gg k_{22}$. Block copolymers with an alternating block and a poly(methyl methacrylate) block are formed from a monomer feed having MMA in excess [398].

A variation on the group transfer polymerization of *n*-butyl acrylate was reported [399]. Here, 1-methoxy-1(trimethylsiloxy)-2-methyl-1-propene was used as an initiator and HgI_2 as a catalyst. This differs from the nucleophilic-catalyzed group transfer polymerizations described above.

The half-lives were reported to be in the range of minutes to hours. Induction periods were observed. Formation of trimethylsilyl iodide was proposed to be the cause of an induction period [399]. The polymerization follows first-order kinetics with respect to the concentrations of the initiator and the catalyst. With respect to concentration of the monomer the reaction is described as being first-order internally. It follows, however, an external reaction order of 1.52 due to the higher polarity of the reaction medium at higher monomer concentrations. The authors tentatively propose that the active species are formed from initiator, catalyst and trimethylsilyl iodide [399]:



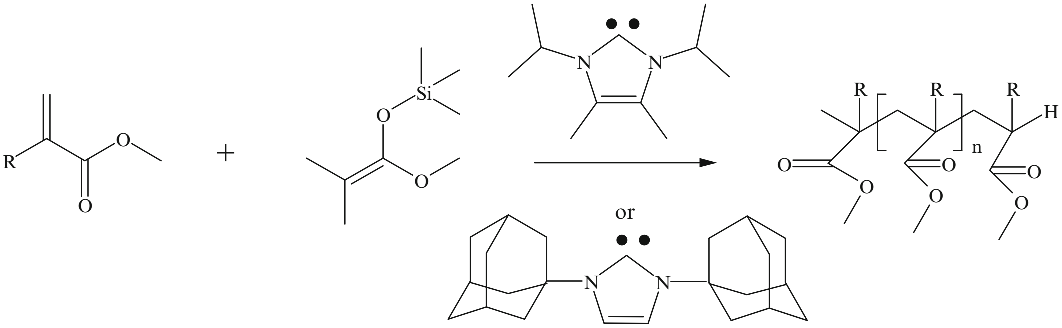
Part of the proposed mechanism is that TMSI forms from MTS and iodine. It is assumed, therefore, that TMSI forms a complex with HgI_2, which in turn activates MTS to form an active center capable of initiating the polymerization [399]:



Because group transfer polymerization is another form of a living polymerization, attempts have been made to write kinetic equations to include all forms of such polymerizations in one unified scheme. Livinenko and Muller [400] carried out a general kinetic analysis and compared molecular weight distributions for various mechanisms of activity exchange in living polymerizations. They concluded that molecular weight distributions in many living, e.g. anionic, group transfer, cationic, and radical polymerizations strongly depend on the dynamics of various equilibria between chain ends of different reactivity [400]. They also concluded that a very important special case is the equilibria between active and dormant centers [400]. Mechanisms that include uni- and bimolecular isomerizations (or activations/deactivations), aggregation, direct bimolecular activity exchange, and for both fast and slow monomer addition can be unified. The averages of the molecular weight distributions and polydispersity indexes, P_w/P_n were derived by them and the dependencies of these averages on three universal parameters were analyzed: (1) on the reactivity ratio of the two species, $\lambda = k'_p/k^*_p$, (2) on the fraction of the more active species, $\alpha = P^*/I_0$, which is determined by the initial concentrations of reagents, and (3) on a generalized exchange rate parameter, β, which quantifies the rate of exchange relative to that of propagation. The dependence of β on the initial concentrations of reagents is defined by the mechanism of exchange and can be used as a mechanistic criterion to distinguish between various possible mechanisms. Livinenko and Miller concluded that for the cases where $\beta > 1$, the polydispersity indexes decrease with monomer conversions. This is a common observation in many living polymerizations where, $10 < \beta < 100$. At full conversions, a simple relation, $P_w/P_n \approx 1 + \Theta/\beta$, is valid, where Θ depends on α and λ. For the common cases where one type of species are dormant this was simplified further to $P_w/P_n \approx 1 + 1/\beta$. Generally, the molecular weight distributions are narrower if the monomer is added slowly [400].

$$\Theta = \alpha^2(1-\alpha)(1-\lambda)/[\alpha + \lambda(1-\alpha)]^2, \quad \Theta < 1$$

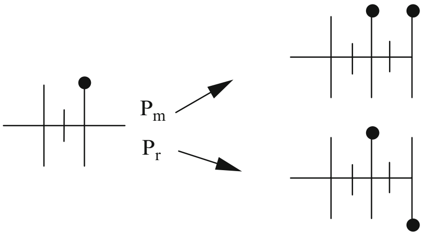
Scholten et al. [401] reported that *N*-heterocyclic carbenes are potent catalysts for group transfer polymerization of acrylic esters. The reaction is illustrated as follows:



0.1–0.5 moles of catalyst are used in tetrahydrofuran. The reaction is quenched with methyl alcohol. The product had a narrow molecular weight distribution.

4.10 Configurational Statistics and the Propagation Mechanism in Chain-Growth Polymerization

Analyses of polymers to determine stereosequence distributions and understand the propagation mechanism can be carried out with NMR spectroscopy aided by statistical propagation models [222, 402, 403]. A detailed discussion of the subject is beyond this book. The following is a brief explanation of the concepts. The Bernoulli, Markov, Colman-Fox, models describe propagation reactions with chain end control over monomer placement. The Bernoulli model assumes that the last monomer unit in the propagating chain end determines the stereochemistry of the polymer. No consideration is given to the penultimate unit or other units further back. In such an event, two modes of propagation are possible, meso and racemic:



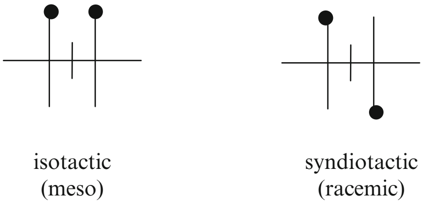
The statistical probabilities, P_m and P_r, which are called *conditional probabilities* or *transitions*, of forming meso or racemic dyads are defined by the following equations:

$$P_m = R_m/(R_m + R_r)$$

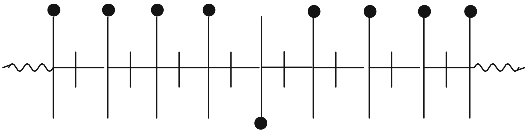
$$P_r = R_r/(R_m + R_r)$$

$$P_m + P_r = 1$$

where R_m and R_r are the rates of meso and racemic dyad placement. These dyads can be isotactic or syndiotactic to one another. Such dyads are more frequently called meso and racemic:



The probabilities represent the dyad tactic fractions m and r. The triad tacticity represent isotactic, syndiotactic, and heterotactic (or atactic) arrangements. They are designated as mm, rr, and mr respectively. One way to understand these definitions is by examining a representation of a section of a polymeric chain which has a total of 9 repeating units but only 8 dyads and 7 triads, as shown below:



In the above segment there are 2 racemic dyads and 6 meso dyads. In addition, there are also 4 isotactic, 1 syndiotactic, and 2 atactic dyads.

The triads are defined as follows:

$$(\mathrm{mm}) = P_\mathrm{m}^2$$

$$(\mathrm{mr}) = 2P_\mathrm{m}(1 - P_\mathrm{m})$$

$$(\mathrm{rr}) = (1 - P_\mathrm{m})^2$$

Note that the atactic triad can be produced in two ways, as mr and rm.

The tetrad probabilities can be defined as:

$$(\mathrm{mmm}) = P_\mathrm{m}^3, \quad (\mathrm{mrm}) = P_\mathrm{m}^2(1 - P_\mathrm{m})$$

$$(\mathrm{mmr}) = 2P_\mathrm{m}^2(1 - P_\mathrm{m}), \quad (\mathrm{rrm}) = 2P_\mathrm{m}(1 - P_\mathrm{m})^2$$

$$(\mathrm{rmr}) = P_\mathrm{m}(1 - P_\mathrm{m})^2, \quad (\mathrm{rrr}) = (1 - P_\mathrm{m})^3$$

The pentad probabilities are given as:

$$(\mathrm{mmmm}) = P_\mathrm{m}^4, \quad (\mathrm{rmrm}) = 2P_\mathrm{m}^2(1 - P_\mathrm{m})^2$$

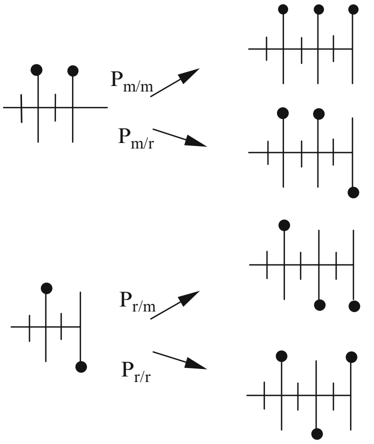
$$(\mathrm{mmmr}) = 2P_\mathrm{m}^3(1 - P_\mathrm{m}), \quad (\mathrm{rmrr}) = 2P_\mathrm{m}(1 - P_\mathrm{m})^3$$

$$(\mathrm{rmmr}) = P_\mathrm{m}^2(1 - P_\mathrm{m})^2, \quad (\mathrm{mrrm}) = P_\mathrm{m}^2(1 - P_\mathrm{m})^2$$

$$(\mathrm{mmrm}) = 2P_\mathrm{m}^3(1 - P_\mathrm{m}), \quad (\mathrm{rrrm}) = 2P_\mathrm{m}(1 - P_\mathrm{m})^3$$

$$(\mathrm{mmrm}) = 2P_\mathrm{m}^2(1 - P_\mathrm{m}), \quad (\mathrm{rrrr}) = (1 - P_\mathrm{m})^4$$

In the Bernoulli model there is no influence of the stereochemistry of the growing polymeric chain on the incoming monomer. The first order Markov model, on the other hand, is based on the concept that the adding monomer is influenced by the stereochemistry for the growing end. This end may by m or r. This means that there are four probabilities for characterizing the addition process. The monomer can add in *an m fashion to an m chain end, or m to an r chain end and so on. These* can be designated as $P_{\mathrm{m/m}}$, $P_{\mathrm{r/m}}$, $P_{\mathrm{m/r}}$, and $P_{\mathrm{r/r.}}$ These modes of propagation can be illustrated as follows:



There are four probabilities for propagation, $P_{\mathrm{m/m}}$, $P_{\mathrm{m/r}}$, $P_{\mathrm{r/m}}$, and $P_{\mathrm{r/r}}$. With conservation of the relationship we can write:

$$P_{\mathrm{m/m}} + P_{\mathrm{m/r}} = 1$$

$$P_{\mathrm{r/m}} + P_{\mathrm{r/r}} = 1$$

We can recast the dyads, triads, tetrads, and pentads in terms of $P_{\mathrm{m/r}}$ and $P_{\mathrm{r/m}}$. The dyads functions are:

$$(\mathrm{m}) = P_{\mathrm{r/m}}/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{r}) = P_{\mathrm{m/r}}/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

The triad fractions are:

$$(\mathrm{mm}) = (1 - P_{\mathrm{m/r}})P_{\mathrm{r/m}}/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mr}) = 2P_{\mathrm{m/r}}P_{\mathrm{r/m}}/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{rr}) = (1 - P_{\mathrm{r/m}})P_{\mathrm{m/r}}/(P_{\mathrm{m/r}} = P_{\mathrm{r/m}})$$

There are six tetrad functions,

$$(\mathrm{mmm}) = P_{\mathrm{r/m}}(1 - P_{\mathrm{m/r}})^2/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mmr}) = 2P_{\mathrm{m/r}}P_{\mathrm{r/m}}(1 - P_{\mathrm{m/r}})/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mrm}) = P_{\mathrm{m/r}}P_{\mathrm{r/m}}^2/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mrr}) = 2P_{\mathrm{m/r}}P_{\mathrm{r/m}}(1 - P_{\mathrm{r/m}})/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{rmr}) = P_{\mathrm{m/r}}^2 P_{\mathrm{r/m}}/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{rrr}) = P_{\mathrm{m/r}}(1 - P_{\mathrm{r/m}})^2/\left(P_{\mathrm{m/r}} + P_{\mathrm{r/m}}\right)$$

Ten pentad functions,

$$(\mathrm{mmmm}) = P_{\mathrm{r/m}}(1 - P_{\mathrm{m/r}})^3/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mmmr}) = 2P_{\mathrm{m/r}}P_{\mathrm{r/m}}(1 - P_{\mathrm{m/r}})^2/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{rmrm}) = 2P_{\mathrm{m/r}}^2 P_{\mathrm{r/m}}^2/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{rmrr}) = 2P_{\mathrm{m/r}}^2 P_{\mathrm{r/m}}(1 - P_{\mathrm{r/m}})/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{rmmr}) = P_{\mathrm{m/r}}^2 P_{\mathrm{r/m}}(1 - P_{\mathrm{m/r}})/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mrrm}) = P_{\mathrm{m/r}}P_{\mathrm{r/m}}^2(1 - P_{\mathrm{r/m}})/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mmrm}) = 2P_{m/r}P_{\mathrm{r/m}}^2(1 - P_{\mathrm{m/r}})/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mrrr}) = 2P_{\mathrm{m/r}}P_{\mathrm{r/m}}(1 - P_{\mathrm{r/m}})^2/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{mmrr}) = 2P_{\mathrm{m/r}}P_{\mathrm{r/m}}(1 - P_{\mathrm{m/r}})(1 - P_{\mathrm{r/m}})/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

$$(\mathrm{rrrr}) = P_{\mathrm{m/r}}(1 - P_{\mathrm{r/m}})^3/(P_{\mathrm{m/r}} + P_{\mathrm{r/m}})$$

The second order Markov model requires the specification of eight conditional probabilities. This is due to the influence of the last three pseudo asymmetric centers of the growing chain. The details of the second Markov were described by Bovey [403]. For details the reader is advised to consult the reference. For convenience the eight conditional probabilities are designated by Greek letters [403]:

$$P(\mathrm{mm/m}) = \alpha, \quad P(\mathrm{mm/r}) = \alpha'$$

$$P(\mathrm{mr/m}) = \beta, \quad P(\mathrm{mr/r}) = \beta'$$

$$P(\mathrm{rm/m}) = \gamma, \quad P(\mathrm{rm/r}) = \gamma'$$

$$P(\mathrm{rr/m}) = \delta, \quad P(\mathrm{rr/m}) = \delta'$$

In the above designation, P(mm/m) is the probability of a monomer adding to the chain end in the m manner. P(mm/r) is the probability of it adding to the chain in the r manner, and so on.

Because,

$$\alpha + \alpha' = 1, \quad \beta + \beta' = 1, \quad \gamma + \gamma' = 1, \quad \delta + \delta' = 1$$

there are four independent probabilities. When $\alpha = \gamma$ and $\beta = \delta$ the model reduces to the first order Markov model.

The Coleman-Fox model attempts to explain “block like” configurations that are exhibited in varying degrees by most propagating species that deviate from Bernoullian statistics. They proposed that “block” configurations are generated because the propagating chain ends might exist in two or more states. These states would correspond to chelation by the counterion and to interruption of chelation by solvation. Here too, for further details the reader is advised to go to the original literature [403].

The enantiomorphic site control is based on the probability of the monomer adding either to an R or to an S site of the catalyst. The propagation occurs through both faces of R and S monomers. The model is described in terms of a single parameter that is commonly designated as σ [404]. It is the probability of an R monomer adding at the R site and S monomer adding at an S site.

The dyads are described as,

$$(\mathrm{m}) = \sigma^2 + (1 + \sigma)^2, \quad (\mathrm{r}) = 2\sigma(1 - \sigma)$$

The triads functions are given as,

$$(\mathrm{mm}) = 1 - 3\sigma(1 - \sigma), \quad (\mathrm{mr}) = 2\sigma(1 - \sigma), \quad (\mathrm{rr}) = \sigma(1 - \sigma)$$

The tetrad fractions are:

$$(\mathrm{mmm}) = 2\sigma^4 - 4\sigma^3 + 6\sigma^2 - 4\sigma + 1$$

$$(\mathrm{mmr}) = (\mathrm{mrr}) = -4\sigma^4 + 8\sigma^3 - 6\sigma^2 + 2\sigma$$

$$(\mathrm{mrm}) = (\mathrm{rmr}) = (\mathrm{rrr}) = 2\sigma^4 - 4\sigma^3 + 2\sigma^2$$

and the pentad fractions as

$$(\mathrm{mmmm}) = 5\sigma^4 - 10\sigma^3 + 10\sigma^2 - 5\sigma + 1$$

$$(\mathrm{mrrm}) = -3\sigma^4 + 6\sigma^3 - 4\sigma^2 + \sigma$$

$$(\mathrm{mmmr}) = (\mathrm{mmrr}) = -6\sigma^4 + 12\sigma^3 - 8\sigma^2 + 2\sigma$$

$$(\mathrm{rmmr}) = (\mathrm{rrrr}) = \sigma^4 - 2\sigma^3 + \sigma^2$$

$$(\mathrm{mmrm}) = (\mathrm{rmrr}) = (\mathrm{rmrm}) = (\mathrm{mrrr}) = 2\sigma^4 - 4\sigma^3 + 2\sigma^2$$

NMR spectroscopy allows testing whether in a particular polymerization the propagation follows the Bernoulli, Markov, or enantiomorphic statistical form. Attempts are usually made to fit data for dyads, triads, tetrads, and higher sequence fractions to the equation for the different models. Spectral intensities can be associated with theoretical expression involving reaction probability parameters. Theoretical intensities are compared with the observed ones. This is optimized to obtain the best-fit values of reaction probability parameters and fully characterize the structure of the macromolecule. The fitting of data can be carried out with the aid of computers.

By determining which statistical model is followed in a polymerization, such as Bernoullian, or Markov, or others, it should be possible to understand better the mechanism of steric control. Thus the Bernoulli model describes those reactions in which the chain ends determine the steric arrangement. These are polymerizations that are carried out under conditions that yield mostly atactic polymers. The high isotactic sequences follow the enantiomorphic site model and the high syndiotactic ones usually follow the Markov models.

The dyads are described as,

$$(\mathrm{m}) = \sigma^2 + (1+\sigma)^2, \quad (\mathrm{r}) = 2\sigma(1-\sigma)$$

The triads functions are given as,

$$(\mathrm{mm}) = 1 - 3\sigma(1-\sigma), \quad (\mathrm{mr}) = 2\sigma(1-\sigma), \quad (\mathrm{rr}) = \sigma(1-\sigma)$$

The tetrad fractions are:

$$(\mathrm{mmm}) = 2\sigma^4 - 4\sigma^3 + 6\sigma^2 - 4\sigma + 1$$

$$(\mathrm{mmr}) = (\mathrm{mrr}) = -4\sigma^4 + 8\sigma^3 - 6\sigma^2 + 2\sigma$$

$$(\mathrm{mrm}) = (\mathrm{rmr}) = (\mathrm{rrr}) = 2\sigma^4 - 4\sigma^3 + 2\sigma^2$$

and the pentad fractions as

$$(\mathrm{mmmm}) = 5\sigma^4 - 10\sigma^3 + 10\sigma^2 - 5\sigma + 1$$

$$(\mathrm{mrrm}) = -3\sigma^4 + 6\sigma^3 - 4\sigma^2 + \sigma$$

$$(\mathrm{mmmr}) = (\mathrm{mmrr}) = -6\sigma^4 + 12\sigma^3 - 8\sigma^2 + 2\sigma$$

$$(\mathrm{rmmr}) = (\mathrm{rrrr}) = \sigma^4 - 2\sigma^3 + \sigma^2$$

$$(\mathrm{mmrm}) = (\mathrm{rmrr}) = (\mathrm{rmrm}) = (\mathrm{mrrr}) = 2\sigma^4 - 4\sigma^3 + 2\sigma^2$$

NMR spectroscopy allows testing whether in a particular polymerization the propagation follows the Bernoulli, Markov, or enantiomorphic statistical form. Attempts are usually made to fit data for dyads, triads, tetrads, and higher sequence fractions to the equation for the different models. Spectral intensities can be associated with theoretical expression involving reaction probability parameters. Theoretical intensities are compared with the observed ones. This is optimized to obtain the best-fit values of reaction probability parameters and fully characterize the structure of the macromolecule. The fitting of data can be carried out with the aid of computers. Cheng published a very useful program in Basic language that applies the model-fitting approach to various polymeric systems [405]. Many other programs in various computer languages are available today.

By determining which statistical model is followed in a polymerization, such as Bernoullian, or Markov, or others, it should be possible to understand better the mechanism of steric control. Thus the Bernoulli model describes those reactions in which the chain ends determine the steric arrangement. These are polymerizations that are carried out under conditions that yield mostly atactic polymers. The high isotactic sequences follow the enantiomorphic site model and the high syndiotactic ones usually follow the Markov models.

4.11 Thermodynamics of Equilibrium Polymerization

The effect of solvents on the equilibrium constants in anionic polymerization in solution has been considered in thermodynamic terms [407].

Sawada [407] expressed the change in free energy for converting one mole of liquid monomer in an anionic polymerization to one base-mole of an amorphous polymer, ΔF_{1c}, as follows:

$$\Delta F_{1c} = \Delta F_m - \Delta F_p$$

where, ΔF_m is the partial molar free energy of the monomer (per mole) in the equilibrium mixture, relative to that of the pure liquid monomer, and ΔF_p is the partial molar free energy of the polymer (per base mole) in the equilibrium mixture, relative to that of the amorphous polymer.

Flory [409] described ΔF_m and ΔF_p in a three component system of polymer, monomer, and solvent as follow:

$$\Delta F_m/RT = \ln\ \varphi_m + (1 - \varphi_m) - \varphi_s(X_m/X_p) - \varphi_p(X_m/X_p) + (\chi_{ms}\varphi_s + \chi_{ms}\varphi_p)(\varphi_s + \varphi_p) \\ - \chi_{sp}(X_m/X_p)\varphi_s\varphi_p$$

$$\Delta F_p/RT = 1/n[\ln\ \varphi_p + (1 - \varphi_p) - \varphi_m(X_p/X_m) - \varphi_s(X_p/X_m) + (\chi_{pm}\varphi_m + \chi_{ps}\varphi_s)(\varphi_m + \varphi_s) \\ - \chi_{ms}(X_p/X_m)\varphi_m\varphi_s$$

where, φ_i is the volume fraction of component i, X_i is the number of segments per molecule for component i, n is the degree of polymerization, R is the gas constant, T is the temperature, and χ is the free energy parameter between any two components. The subscripts m, s, and p indicate monomer, solvent and polymer, respectively. Flory puts the ration of molar volume as,

$$v_i/v_j = X_i/X_j$$

assuming that $v_p/v_m = n$ and expressing χ_{pm} and χ_{ps} in terms of molecular weight-independent quantities χ_{mp} and χ_{sp} through the relationship:

$$\chi_{pm} = \chi_{mp}(V_p/V_m) = V_{mp}n$$

$$\chi_{ps} = \chi_{sp}n(V_m/V_s)$$

The free energy of polymerization can then be written:,

$$\Delta F_{1c}/RT = \ln\ \varphi_m + 1 + (\chi_{ms}\varphi_s + \chi_{ms}\varphi_p)(\varphi_s + \varphi_p) - \chi_{sp}(V_m/V_s)\varphi_s\varphi_p - (1/n)\ \ln\ \varphi_p - 1/n \\ - (\chi_{mp}\varphi_m + \chi_{sp}\varphi_s V_m/V_s)(\varphi_m + \varphi_s) + \chi_m\varphi_m\varphi_s$$

where, φ_m is now the equilibrium volume fraction of monomer and the volume fraction of the polymer is φ_p.

Sawata points out [407] that by neglecting terms $1/n$ when n is large, and by replacing ($\varphi_s + \varphi_p$) by ($1 - \varphi_m$) and ($\varphi_m + \varphi_s$) by ($1 - \varphi_p$) one gets a more general expression:

$$\Delta F_{1c}/RT = \ln\ \varphi_m + 1 + \varphi_s(\chi_{ms} - \chi_{sp}V_m/V_s) + \chi_{ms}(\varphi_p - \varphi_m)$$

Review Questions

Section 4.1

1. Explain the differences and similarities m anionic and cationic chain growth polymerizations.

Section 4.2

1. Write chemical equations for cationic initiation, propagation, and termination steps and show what the kinetic expressions are.
2. Write the cationic kinetic expression for the degree of polymerization and the rate of propagation.
3. Repeat questions 1 and 2 for anionic polymerizations.

Section 4.3

1. Explain what is meant by the expression that initiation in cationic polymerization results from transposition of either one or two electrons. What type of initiating species is involved?
2. Summarize the initiation process in cationic chain-growth polymerization.
3. Show by chemical equations the initiation process by protonic acids, by Lewis acids complexed with water and or with alkyl halides.
4. What is the proposed mechanism of initiation of polymerization, by the Lewis arid like aluminum chloride or bromide through an auto ionization process?
5. What are the several proposed mechanisms of initiations by stable cations?
6. Explain how some cationic polymerizations can be initiated by metal alkyls and substances that generate cations.
7. Show the mechanism of one electron transposition initiation with chemical equations based on a free-radical oxidation by diphenyliodonium hexafluorophosphate (let the source of the free-radicals be photo decomposition of methyl benzoin ether).
8. Discuss briefly the role of charge transfer complexes in initiations of cationic polymerizations.
9. What is the mechanism of electro initiation of cationic polymerization?
10. How does the tightness of the ion pairs affect propagation in cationic polymerization?
11. What is the mechanism of chain growth with a tight ion pairs in cationic polymerization?
12. Discuss the Kunitake and Takanabe mechanism for steric control in homogeneous cationic polymerizations.
13. What is the Nakano et al. mechanism for steric control in heterogeneous cationic polymerizations?
14. What is pseudo-cationic polymerization? Explain and illustrate on polymerization of styrene initiated by perchloric acid.
15. Describe and give examples of chemical reactions of isomerization polymerization where the propagation is accompanied by bond or electron rearrangement.
16. Give two examples of chemical reactions where the propagation in isomerization polymerization is accompanied by migration of one or more atoms.
17. Illustrate the termination reactions in cationic polymerizations.
18. What are the important aspects of living cationic polymerization? Can you give examples?

Section 4.4

1. What are the two types of initiations in anionic polymerization?
2. Describe and illustrate by chemical equations the initiation mechanism m a homogeneous polymerization by addition of an butyllithium to an olefin in a polar solvent What is the effect of heteroatoms. such as oxygen present in the monomers? illustrate.
3. Describe and illustrate one electron transfer initiations of anionic polymerization and give several examples.
4. Describe initiations and propagation by Alfin catalysts.
5. Discuss electoinitiation of anionic polymerization.
6. How does the propagation reaction in anionic polymerization differ in the presence of polar and non-polar solvents?
7. How do structures of monomers influence propagation rates in anionic polymerizations? Illustrate.
8. Discuss steric control *m* homogeneous anionic polymerization of methyl methacrylate in non-polar solvents.
9. Discuss steric control in homogeneous anionic polymerization of isoprene on none-polar solvents.
10. Discuss steric control in homogeneous anionic polymerizations in polar solvents.
11. Discuss and illustrate hydrogen transfer polymerization of acrylamide.
12. How do termination reactions take place in anionic chain-growth polymerization?
13. Discuss living anionic polymerizations.
14. How are living monodisperse methyl methacrylate polymers prepared with the aid of enolate aluminum porphyrin intermediates? Explain and illustrate.

Section 4.5

1. What metals form catalysts in Ziegler–Natta coordinated anionic polymerization.
2. Illustrate the reactions that takes place between aluminum alkyls and transition metal compounds, like titanium chloride, in formations of Ziegler–Natta catalysis.
3. Describe the bimetallic polymerization mechanism of G. Natta.
4. Describe the Cossee and Arlman mono metallic mechanism.
5. Describe steric control in heterogeneous coordinated anionic polymerizations.
6. What are the homogeneous Ziegler–Natta catalysts?
7. Discuss steric control with homogenous catalysts.
8. Describe the currently used industrial Ziegler–Natta catalysts on support and soluble ones.
9. Discuss effects of Lewis bases on Ziegler–Natta typo coordinated anionic polymerizations.
10. What is the termination reaction in coordinated anionic polymerizations. Illustrate.
11. Describe the transition metal oxide on support catalysts, how they are prepared and used.
12. Describe the metallocene catalysts.
13. How does isomerization polymerization take place by coordinated anionic mechanism?

Section 4.6

1. Describe cationic polymerization of aldehydes.
2. Describe anionic polymerizations of aldehydes

3. What is the mechanism control in anionic polymerization of aldehydes polymerizations?
4. Describe polymerization of unsaturated aldehydes such as crotonaldehyde or acrolein.
5. Describe polymerization of dialdehydes.

Section 4.7

1. Discuss polymerization of ketones and isocyanates.

Section 4.8

1. Discuss copolymerization by ionic mechanism. What am some of the problems that are encountered?

Section 4.9

1. Discuss the proposed mechanisms of group transfer polymerization.

Section 4.10

1. What are Bernoulli, Markov, and Colman-Fox statistical models for the propagation reactions? Can you describe each?

Recommended Reading

H.L. Hsieh and R.P. Quick, *Anionic Polymerization - Principles and Practical Applications*, M. Dekker, New York, 1996

K. Matyjaszewski, ed., *Cationic Polymerization - Mechanism, Synthesis and Application,* M. Dekker, New York, 1996

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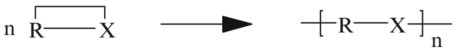
Chapter 5

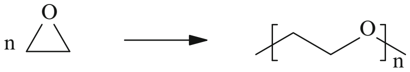
Ring-Opening Polymerizations

5.1 Chemistry of Ring-Opening Polymerizations

Formation of polymers through ring-opening reactions of cyclic compounds is an important process in polymer chemistry. In such polymerizations, chain-growth takes place through successive additions of the opened structures to the polymer chain:



An example of the above is a ring-opening polymerization of ethylene oxide that results in formation of poly(ethylene oxide), a polyether:



The cyclic monomers that undergo ring-opening polymerizations are quite diverse. Among them are cyclic alkenes, lactones, lactams, and many heterocyclics with more than one heteroatom in the ring. Such polymerizations are ionic in character and may exhibit characteristics that are typical of ionic chain-growth polymerizations (e.g., effect of counterion and solvent). It would, however, be wrong to assume that these polymerizations necessarily take place by chain-propagating mechanisms. Actually, many such reactions are step-growth in nature, with the polymer size increasing slowly throughout the whole course of the process. There are, on the other hand, some cyclic monomers that do polymerize in a typical chain-growth manner.

5.2 Kinetics of Ring-Opening Polymerization

There is general similarity between the kinetics of many ring-opening polymerization and those of step-growth polymerizations that are discussed in Chap. 7. Some kinetic expressions in ring-opening polymerizations, on the other hand, resemble ionic chain-growth reactions.

There are several forms of the rate law that describe the cationic ring-opening polymerization. For living or polymerizations without termination, one can write

$$R_p = k_p[M^*][M]$$

A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_5,

where [M*] is the concentration of the propagating oxonium ions. Such ions could be oxonium, sulfonium, and others. When, however, there is propagation–depropagation equilibrium, it can be expressed as follows:

$$\mathrm{M}_n^* + \mathrm{M} \underset{K_{\mathrm{Dp}}}{\overset{K_{\mathrm{P}}}{\rightleftharpoons}} \mathrm{M}_{n+1}^*$$

The rate expression can be written as propagation–depropagation

$$R_{\mathrm{p}} = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = K_{\mathrm{p}}[\mathrm{M}^*][\mathrm{M}] - K_{\mathrm{DP}}[\mathrm{M}^*]$$

At condition of equilibrium, if we designate the monomer concentration $[\mathrm{M}]_{\mathrm{C}}$, and the polymerization rate is zero, we can write

$$K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}} = K_{\mathrm{DP}}$$

Hirota and Fukuda [1] described the quantitative dependence of the degree of polymerization on various reaction parameters for an equilibrium polymerization. The equilibrium can be described as

$$\mathrm{I} + \mathrm{M} \overset{K_{\mathrm{I}}}{\rightleftharpoons} \mathrm{M}^*$$

where, I is the initiating species. It is assumed that the equilibrium constants for the initiation and propagation are independent of the size of the propagating species. The concentration of the propagating chains [M*] of size *n* at equilibrium *c* then can be written as:

$$[\mathrm{M}^*] = K_{\mathrm{I}}[I]_{\mathrm{C}}[\mathrm{M}]_{\mathrm{C}}(K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}})^{n-1}$$

The total concentration of molecules size *N* can be expressed as follows

$$[N] = \sum [\mathrm{M}_n^*]K_{\mathrm{I}}[\mathrm{I}]_{\mathrm{C}}[\mathrm{M}]_{\mathrm{C}}/(1 - K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}})$$

The total concentration of monomer segments that are incorporated into the polymer can also be expressed as follows:

$$[\mathrm{W}] = \sum_n [\mathrm{M}^*] = K_{\mathrm{I}}[\mathrm{I}]_{\mathrm{C}}[\mathrm{M}]_{\mathrm{C}}/(1 - K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}})^2$$

This allows us to express the average degree of polymerization that is [*W*]/[*N*] as follows:

$$\mathrm{DP} = \frac{1}{1 - K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}}}$$

We can describe the rate of polymerization in terms of $-\mathrm{d}[M]/\mathrm{d}t$ as

$$R_{\mathrm{p}} = -\mathrm{d}[M]/\mathrm{d}t = K_{\mathrm{p}}([\mathrm{M}^*]\mathrm{M}) - [\mathrm{M}])$$

The expression can be integrated to yield:

$$\mathrm{In}\left(\frac{[\mathrm{M}]_0 - [\mathrm{M}]_\mathrm{C}}{[\mathrm{M}] - [\mathrm{M}]_\mathrm{C}}\right) = k_{\mathrm{p}}[\mathrm{M}^*]t$$

where $[\mathrm{M}]_0$ is the initial monomer concentration

5.3 Polymerization of Oxiranes

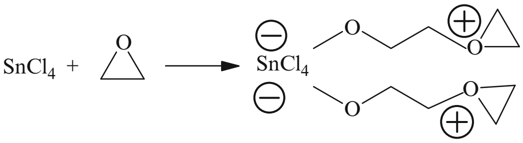
Polymerizations of oxiranes or epoxides occur by one of three different mechanisms: (1) cationic, (2) anionic, and (3) coordination. In this respect the oxiranes differ from the rest of the cyclic ethers that can only be polymerized with the help of strong cationic initiators. It appears, though, that sometimes coordination catalysis might also be effective in polymerizations of some oxetanes. The susceptibility of oxirane compounds to anionic initiation can be explained by the fact that these are strained ring compounds. Because the rings consist of only three atoms, the electrons on the oxygen are crowded and are vulnerable to attack [2].

5.3.1 *Cationic Polymerization*

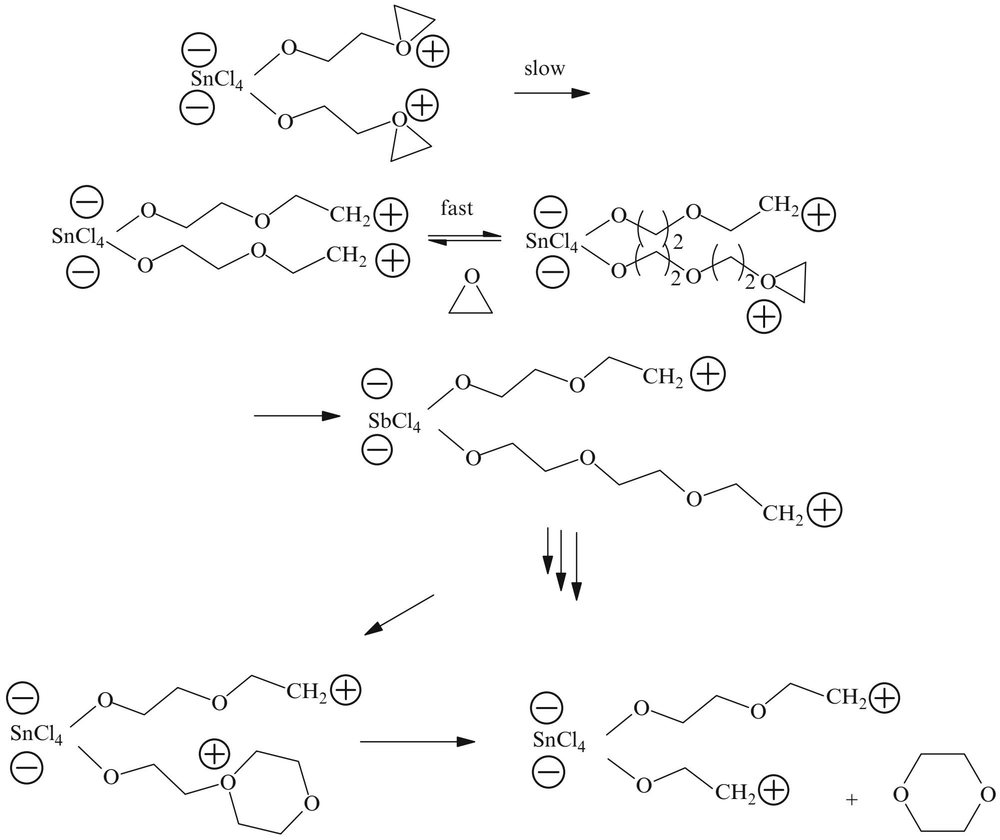
Various Lewis and protonic acids are capable of initiating cationic polymerization of epoxies. Among them, the following metal salts are effective in polymerizations of ethylene and propylene oxides [3, 4]: $ZnCl_2$, $AlCl_3$, $SbCl_5$, BF_3, BCl_3, $BeCl_2$, $FeCl_3$, $SnCl_4$, and $TiCl_4$. Often these polymerizations can be carried out in bulk without any solvent, particularly in the laboratory. The mechanism of these reactions can be complex, however, depending upon the particular Lewis acid used. In fact, not all of these polymerizations can even be treated in general terms as cationic. For instance, ferric chloride initiated polymerizations of epoxides initially proceed by a mechanism that has all the superficial features of cationic polymerization. After the initial stages, however, the polymerizations proceed by a coordination mechanism. This is discussed further in this section.

Stannic chloride yields only low molecular weight poly(ethylene oxide) from ethylene oxide (molecular weight below 5,000) when the reaction is carried out in ethylene chloride at room temperature. Some dioxane and dioxolane also form in the process. Following reaction scheme was proposed [2–6]:

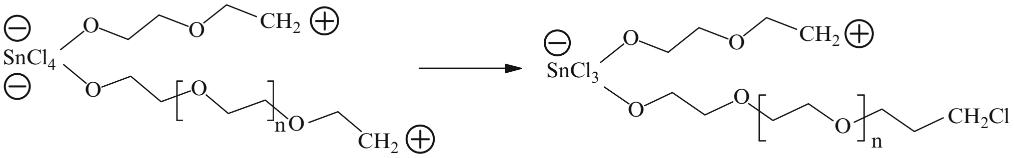
Initiation



Propagation

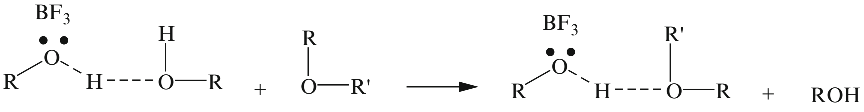


Termination

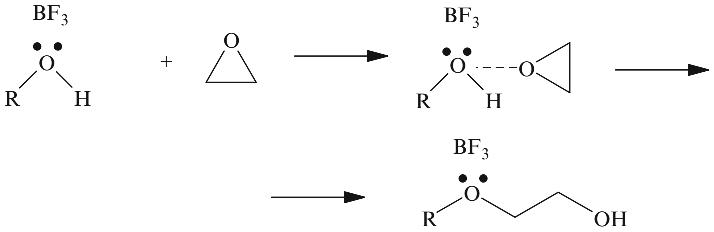


The initiation step depends upon formation of oxonium ions. Because a carbon cation intermediate is indicated, it was suggested [4] that the propagation probably occurs by ether exchange that results from a nucleophilic attack by the monomer on the oxonium ion.

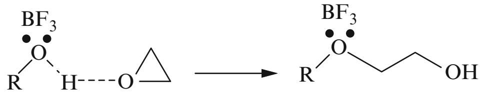
Boron trifluoride forms complexes with oxygen-containing compounds, like water, alcohols, and ethers. When it initiates the polymerization of epoxides, it can associate simultaneously with several different moieties. These are the monomeric cyclic ethers, as well as the open-chain polymeric ether groups, and the hydroxy groups on the chain ends. In addition it can also associate with the hydroxy groups of water. The following illustration shows the type of equilibrium that can take place [2]:

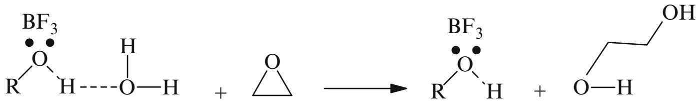


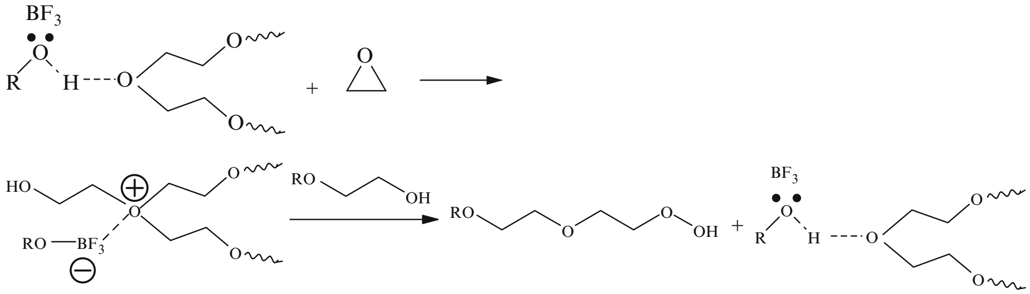
The alcohols and open-chain ethers have comparable basicities toward the coordinated acid ROH: BF_3. Ethylene oxide, on the other hand, is much less basic than the open-chain ethers [6]. In the initiation step, therefore, the monomer reacts with the coordinated acid [1]:



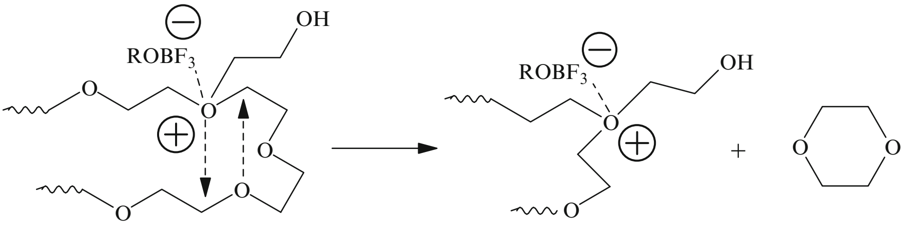
During propagation three different reactions can occur [2]:

1.


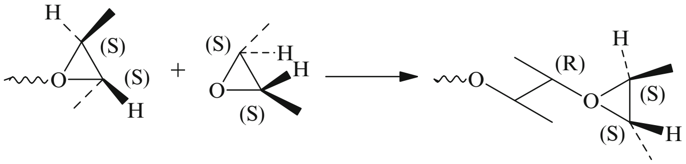
2.


3.


This reaction is also accompanied by formation of dioxane. It is actually a step of depolymerization:

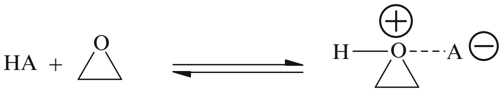


The ring-opening reaction, a nucleophilic substitution, usually takes place with an inversion of configuration at the carbon atom that undergoes the nucleophilic attack [8, 9, 11]. This can be illustrated as follows:

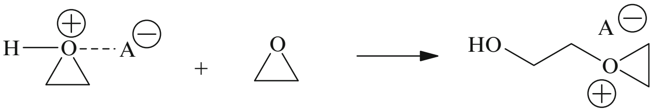


Alkyl substituents on the ethylene oxide ring enhance the process of cationic polymerization. For instance, ethylene oxide yields only low molecular weight oils with strong Lewis acids. Tetramethylethylene oxide, on the other hand, is converted readily by BF_3 into high molecular weight polymers that are insoluble in common solvents [10].

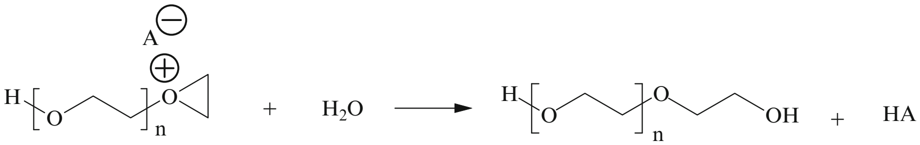
When proton donors initiate the polymerizations of epoxides, only low molecular weight products result. The reaction is quite straightforward. Oxonium ions form during the initiation step as follow:



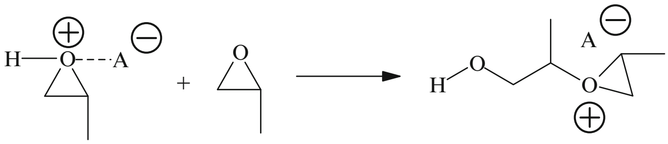
Propagation is the result of a ring-opening attack by a monomer:



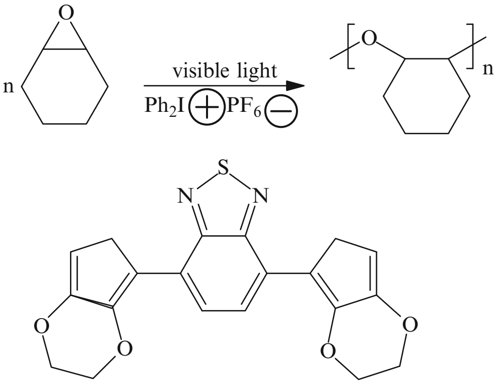
Chain-growth can terminate by a reaction with water:



In cationic polymerizations of propylene oxide the ring-opening step involves a direct attack on the oxonium ion at the carbon that bears a more labile bond to the oxygen:



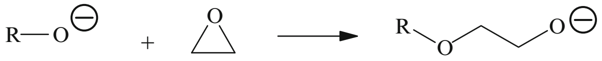
Cationic ring-opening polymerization of oxiranes can also be carried out photochemically (photochemical reactions are discussed in Chap. 10). Yagci and coworkers reported polymerizations of cyclohexene oxide with the aid of highly conjugated thiophene derivatives [12]. The reaction is illustrated as follows:



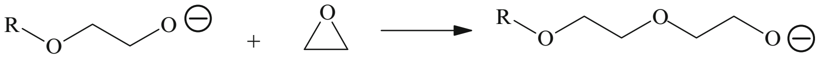
The cationic polymerization was initiated at room temperature upon irradiation with light in the visible region in CH_2Cl_2 solutions in the presence of diphenyliodonium hexafluorophosphate and the thiophene derivative. According to the suggested mechanism, Ayodgan et al. [12] discuss the formation of *exciplex* (see Chap. 10) by the absorption of light. Subsequent electron transfer from excited Photosensitizer to iodonium ion yields radical cations of the thiophene derivatives. The resulting strong Bronsted acid derived from this process catalyzes the cationic polymerization.

5.3.2 *Anionic Polymerization*

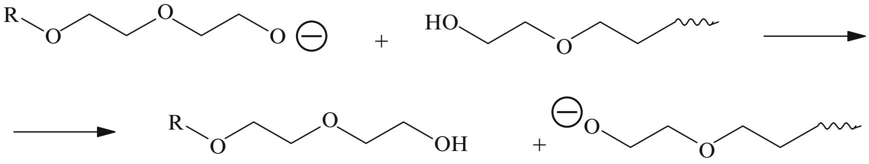
Anionic polymerizations of ethylene oxide were originally observed as early as 1894 [13]. A step-growth mechanism for these polymerizations was proposed later [14]. This mechanism is now well established [14]. The conversion increases linearly with time and the molecular weight also increases with conversion. Reactions with bases like sodium or potassium hydroxides or alkoxides yield only low molecular weight polymers. The initiation, an S_N2 displacement, results in formation of an alkoxide ion:



Subsequent propagation may occur by nucleophilic displacement involving a new alkoxide ion formation in each addition:

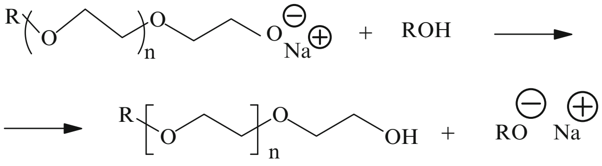


Termination takes place by a transfer to a hydroxy group of another molecule. It can also take place to a terminal hydroxyl group of a formed polymer, which starts new chain-growth from the second unit:



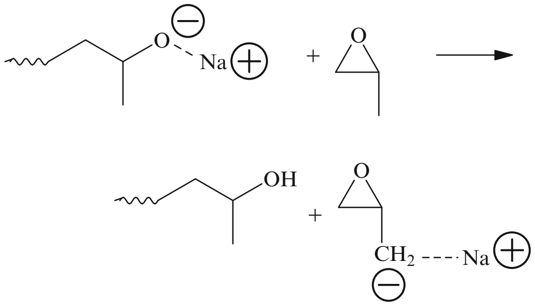
The chain ends remain active and higher molecular weights can be obtained by further additions of the monomer.

The reaction is often more complex than is shown above, because many such polymerizations, catalyzed by alkali hydroxides or alkoxides, are carried out in the presence of alcohols. This is done to achieve a homogeneous system. Such conditions, however, lead to exchange reactions:

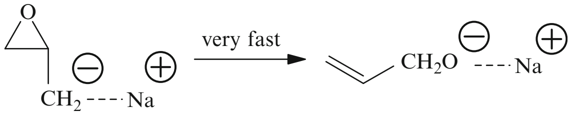


Of course, the exchanges, as shown above, affect the kinetics of the process. The extent of these reactions is subject to the acid strength of the alcohols present, including the terminal hydroxyl groups of formed polymers. If their acidities are approximately equal, the exchange reactions take place throughout the whole course of the polymerization [2].

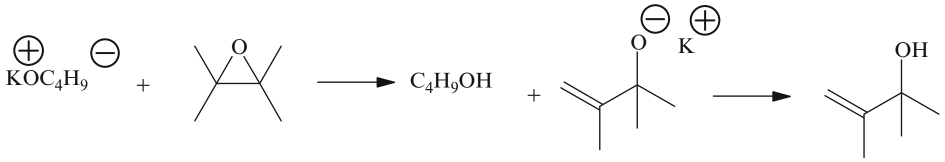
One of the reasons for the relatively low molecular weights of the products is the low reactivity of the epoxide ring toward anionic propagation. Another reason is the tendency to chain transfer to monomers, particularly in polymerizations of substituted ring structures, like, for instance, in propylene oxide:



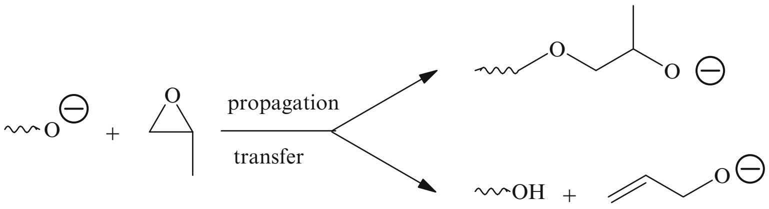
The newly formed species rearranges rapidly:



Such transfer reactions are E-2 type eliminations. This was shown on tetramethylethylene oxide that undergoes the reaction when treated with catalytic amounts of potassium *t*-butoxide [5]:

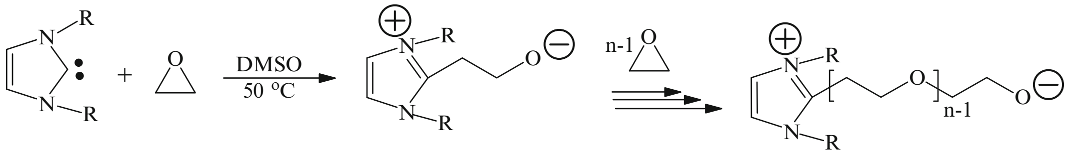


In propylene oxide polymerization, therefore, the E-2 type elimination reaction is in competition with propagation:



There are both allyl and propenyl ether end groups in the products, according to the infra-red spectra [5]. This suggests that in addition to the E-2 type elimination, an intramolecular transfer takes place by allylic hydrogen.

Raynaud et al. reported carrying out ring-opening polymerizations of ethylene oxide initiated by heterocyclic carbene [15]. The reaction yields high molecular weight polymers. It is illustrated as follows:



where *R* can be a propyl or a tertiary butyl group.

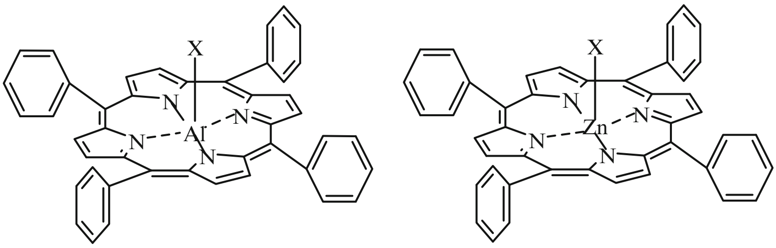


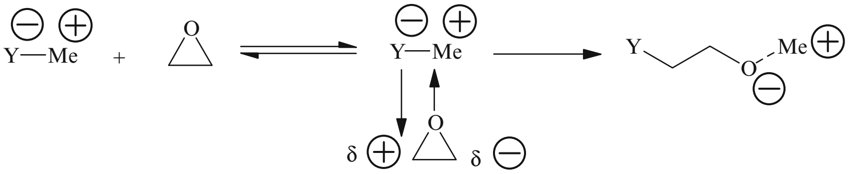
Fig. 5.1 Metalloporphyrin catalysts. X = methyl, methoxy, or other groups

5.3.3 Polymerization by Coordination Mechanism

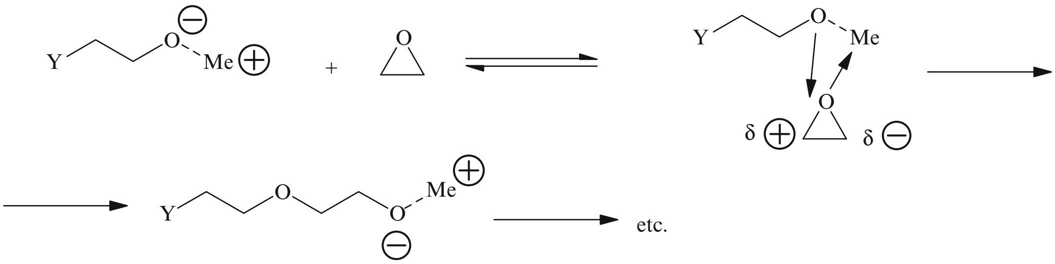
The coordination catalysts for these reactions are diverse. They can be compounds of alkaline earth metals, like calcium amide, or calcium amide-alkoxide. They can also be Ziegler–Natta type catalysts. These can be alkoxides of aluminum, magnesium, or zinc combined with ferric chloride. Others are reaction products of dialkylzinc with water or alcohol. They can also be bimetallic μ-oxoalkoxides, such as $[(RO)_2AlO_2]Zn$. Other catalysts are aluminum or zinc metalloporphyrin derivatives (see Fig. 5.1).

From propylene oxide these catalysts yield crystalline, isotactic polymers [16]. Living polymerizations with metalloporphyrin derivatives are difficult to terminate and are, therefore, called by some ***immortal*** [18]. Catalysts like, $(C_6H_5)_3$–$SbBr_2$–$(C_2H_5)_3N$ in combination with Lewis acids also yield crystalline poly(propylene oxide). Others, like pentavalent organoantimony halides are useful in polymerizations of ethylene oxide [19].

Polymerizations of epoxides by ***coordination*** mechanism result in high molecular weight products. The details of the reaction mechanism have not been fully resolved yet, but it is commonly believed to involve coordination of the monomers to electrophilic centers of the catalyst. This is followed by activation for an attack by the anion [2]. Such mechanism [1] can be illustrated by the following reactions:

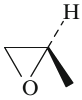


where Me means metal.

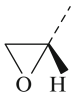


where, Me represents the metal catalyst.

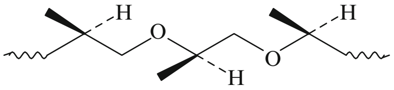
Ferric chloride polymerizes propylene oxide, a monomer with an asymmetric carbon atom, with retention of asymmetry in the backbone [3]. The products of polymerization contain either optically active polymers or racemic mixtures, depending upon the monomers used. When only a pure optical isomer monomer is used the products are crystalline polymers composed of the same optically active units:



(R)

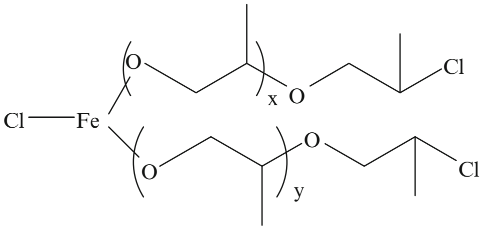


(S)

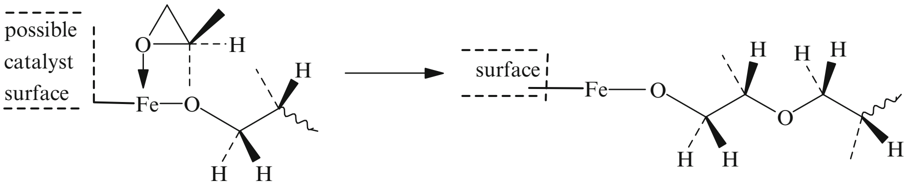


section of polymer

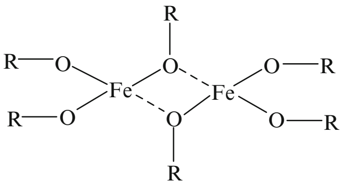
The polymers are fairly high in molecular weight, approximately 100 times greater than the products from KOH initiations. Propylene oxide initially reacts with ferric chloride to form an oligomer, a chloropolyalkoxide. The material contains approximately four or five propylene oxide repeat units. This forms two different halogen sites. It can be illustrated as follows:



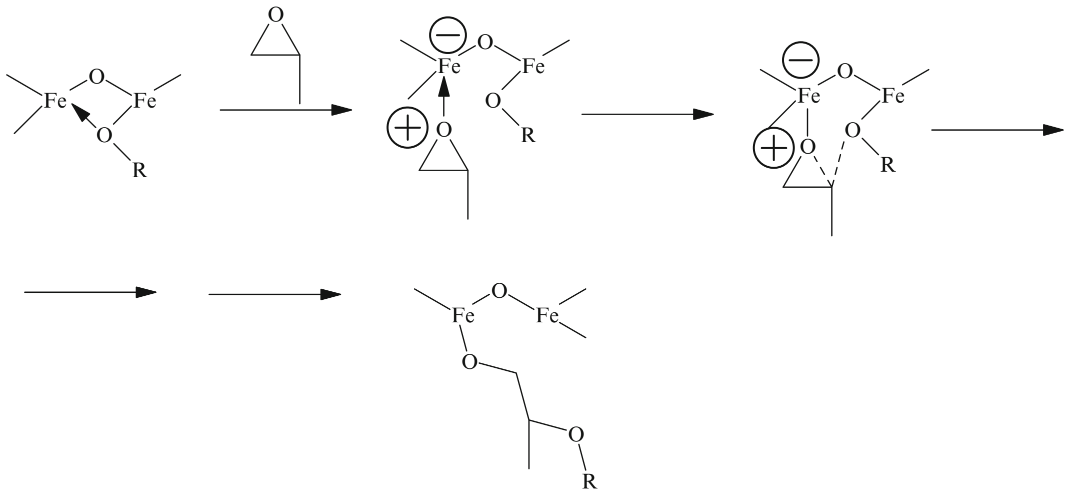
The above compound may be the catalyst or one closely related to it for forming stereoregular polymers. Water appears to play a role, because the proportion of crystallinity increases with addition of water. When water is added in a molar ratio of 1.8:1.0 of water to iron, the proportion of crystalline to amorphous fraction increases from 0.13 to 0.86. Price and Osgen [17] suggested that the polymerization proceeds in a step-growth mechanism as follows:



The solid surface of the catalyst causes the transition state to be more compressed. Steric repulsions between the incoming monomer and the ultimate unit are minimized if the incoming monomer molecule is forced to be ***trans*** to the methyl group of the previous unit. Such a conformational approach also results in minimum repulsion between the incoming monomer and the bulky growing polymer chain [18–20]. Also, ferric alkoxides are associated in nonpolar solvents. A dimer may have the following structure:



By comparison, intramolecular chelation can be expected to reduce the degree of association of the catalyst. Addition of water results in increased association after hydrolysis of the ferric alkoxide. This may explain the effect of promoting stereoregularity by addition of water [20]. The ferric alkoxide catalyst can also be made highly stereospecific by partial hydrolysis and still remain soluble in ether, the polymerization medium [21]. This led to a suggestion [22] that the catalyst may contain active Fe–O–Fe bonds. Such bonds would be formed from condensation of partially hydrolyzed alkoxide derivative. The monomer insertion between the iron–oxygen bonds can be illustrated as follows:

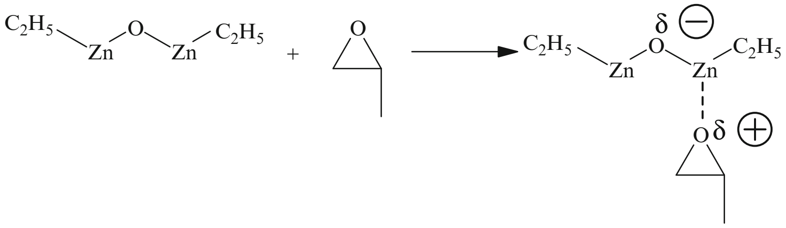


The forces of interaction between the iron atoms and the various oxygen atoms as shown above assure a *cis* opening of the epoxide ring. The mechanism of the reaction of the ferric alkoxide is an S_N2 type. There is, therefore, increased restriction on the conformation of the monomer unit as it approaches the reaction center [22].

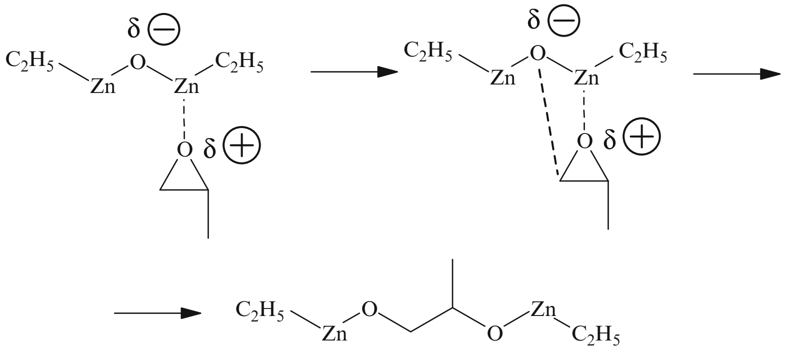
Many other coordinated anionic catalysts that are *metal alkoxides* or *metal alkyls* are also much more reactive in the presence of water or alcohols. The function of these co reactants is to modify the catalyst itself. For instance, diethylzinc combined with water in a ratio of 1:1 yields a very reactive species. The exact nature of the catalyst is still not fully established, however, the reaction product is pictured as follows [23, 24]:

$$C_2H_5 - \mathrm{Zn} - \mathrm{O} - \mathrm{Z}n - C_2H_5$$

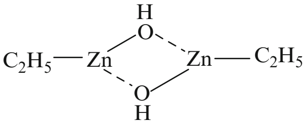
Several reaction mechanisms were proposed. One suggested pathway for propylene oxide polymerization pictures an initial coordination of the monomer with a cationically active center [25]:



The propagation is preceded by an intramolecular rearrangement:

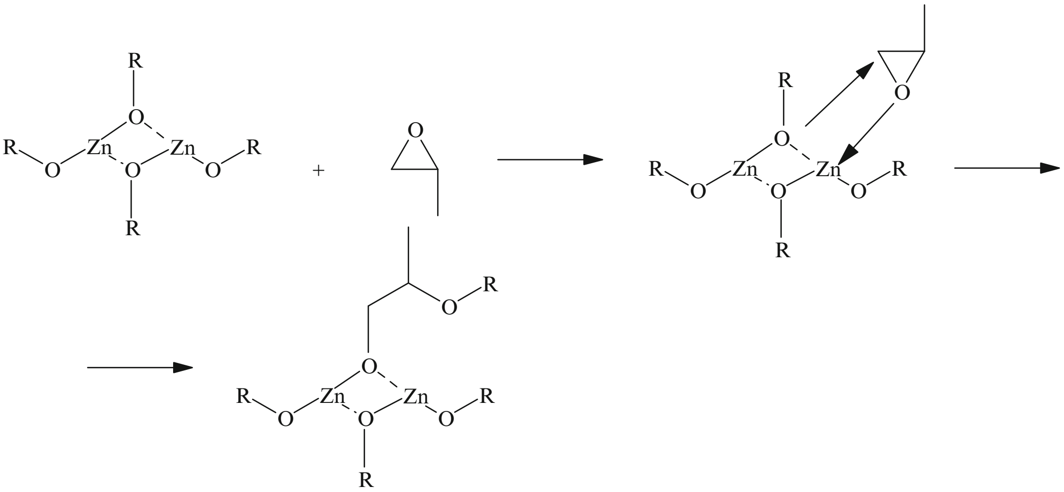


Another mechanism is derived from the structure of the diethylzinc–water catalyst [25] that is visualized as a dimer:



A similar structure pictured can be shown for diethylzinc–alcohol. The asymmetric induction is suggested to takes place during coordination of the monomer to the catalyst site. This is a result of indirect regulation that results form interactions between the monomer and the penultimate unit [25].

In yet another mechanism the initial coordination and subsequent propagation steps are pictured as follows [26]



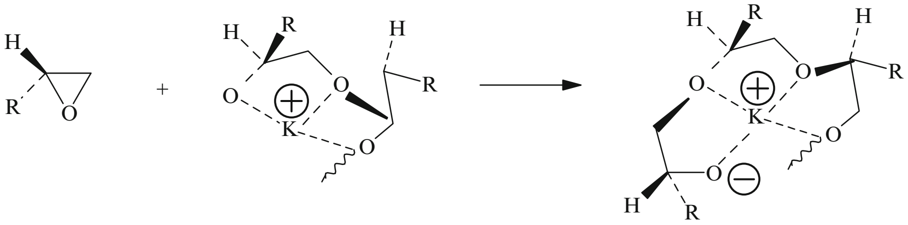
While the detailed structures of most catalyst sites are still unknown, it was established that stereoselectivity does not come from the chirality of the growing chain end. Rather it is built into the catalyst site itself [27, 28]. Normal preparations of the catalysts give equal numbers of (*R*) and (*S*) chiral catalyst sites. These coordinate selectively with (*R*) and (*S*) monomers respectively in the process of catalytic-site control [23].

5.3.4 Steric Control in Polymerizations of Oxiranes

Cationic polymerizations of oxiranes are much less isospecific and regiospecific than are anionic polymerizations. In anionic and coordinated anionic polymerizations, only chiral epoxides, like propylene oxide, yield stereoregular polymers. Both pure enantiomers yield isotactic polymers when the reaction proceeds in a regiospecific manner with the bond cleavage taking place at the primary carbon.

In all polymerizations of oxiranes by cationic, anionic, and coordinated anionic mechanisms, the ring-opening is generally accompanied by an inversion of the configuration at the carbon where the cleavage takes place. A linear transition state mechanism involving dissociated nucleophilic species has been proposed [15]. Yet, there are some known instances of ring-opening reactions of epoxies that are stereochemically retentive. For instance, ring opening of 2,3-epoxybutane with $AlCl_3$ results in formation of 3-chloro-2-butanol, where the *cis* and *trans* epoxides are converted to the *erythro* and *threo*-chlorohydrins. Inoue and coworkers [19] found, however, that polymerizations of *cis* and *trans* 2,3-epoxybutanes take place with inversion of configuration when aluminum 5,10,15,20-tetraphenylporphine and zinc 5,10,15,20-tetraphenyl-21-methylporphine catalysts are used. To explain the inversion, Inoue and coworkers proposed a linear transition state mechanism that involves a simultaneous participation of two porphyrin molecules [19]. One porphyrin molecule accommodates a coordinative activation of the epoxide and the other one serves as a nucleophile to attack the coordinated epoxide from the back side.

Potassium hydroxide or *alkoxide* polymerizes racemic propylene oxide with better than 95% regioselectivity of cleavage at the bond between oxygen and the carbon substituted by two hydrogens. The product, however, is atactic. Both (*R*) and (*S*) propylene oxides react at the same rate. This shows that the initiator is unable to distinguish between the two enantiomers of propylene oxide. When *t*-butyl ethylene oxide is polymerized by KOH it yields a crystalline product. This product is different in its melting point, X-ray diffraction pattern, and solution-NMR spectra from the typical isotactic polymers. It contains alternating isotactic and syndiotactic sequences [31]. It was suggested [34] that this may be a result of the configuration of the incoming monomer being opposite to that of the penultimate unit. Chelation of the paired cation (K⊕) with the last and the next to the last oxygen is visualized. Geometry of such a chelate is dictated by the requirement that the penultimate *t*-butyl group be in an equatorial conformation. This makes it reasonable to postulate that the necessary preference for the incoming monomer is to be opposite to that of the penultimate unit [31]:

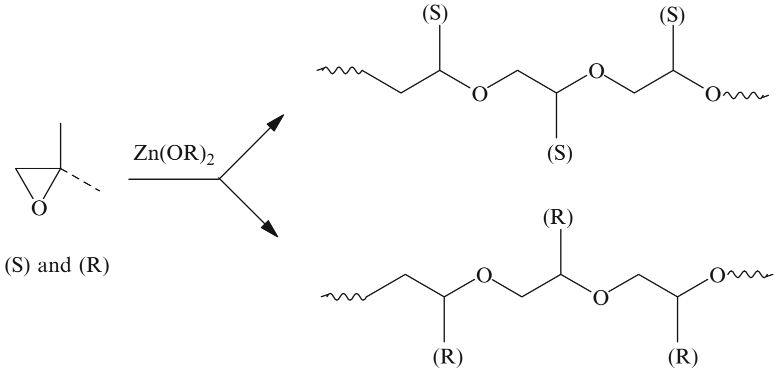


When phenyl glycidyl ethers are polymerized under the same conditions, the steric arrangement is all isotactic rather than isotactic–syndiotactic [31]. Price explained that on the basis of the oxygen in C_6H_6–O–CH_2 seeking to coordinate potassium ions in the transition state [31]. In the case of *t*-butylethylene oxide, on the other hand, the tertiary butyl group tends to be as far as possible away from the potassium ion [34]. This is supported by the observation that *p*-methoxy and *p*-methyl groups on phenyl glycidyl ether increase the crystalline portion of the polymer, while the *p*-chloro substituent decreases it [31].

Most stereoselective coordination catalysts polymerize propylene oxide to yield polymers that contain high ratios of isotactic to syndiotactic sequences. Large portions of amorphous materials, however, are also present in the same materials. These amorphous portions contain head to head units that are imperfections in the structures [29, 30]. For every head to head placement, one (*R*) monomer is converted to an (*S*) unit in the polymer [23]. This shows that at the coordination sites abnormal ring openings occur at the secondary carbon with an inversion of the configuration and results in head to head placements [23, 31]. Also, *erythro* and *threo* isomers units are present. The isotactic portion consists almost exclusively of the *erythro* isomer while other amorphous fraction contains 40–45% *erythro* and 55–60% *threo* [31]

All the above information is indirect evidence that a typical catalyst, such as $(C_2H_5)_2Zn$–H_2O contains isotactic and amorphous sites. The isotactic sites are very selective and coordinate either with (*R*) or with (*S*) monomers. The amorphous sites, on the other hand, coordinate equally well with both (*R*) and (*S*) monomers. In addition, there is little preference for attack on either the primary or the secondary carbons during the ring-opening reactions [23].

According to a Tsuruta mechanism [36] the first step in propylene oxide polymerization, with catalysts like zinc alcoholates, is the coordination of the ether oxygen onto a zinc atom. The second step is a nucleophilic attack at the oxirane ring by the alkoxy ion. Almost all the bond cleavage takes place at the CH_2–O bond. This results in retention of the steric configuration of the carbon atom at the C–H group. The next oxirane molecule repeats the process, coordinates with the same zinc atom and then undergoes the ring-opening reaction to form a dimer. Repetition of this process many times yields a high molecular weight polymer [36]:



The catalyst can also be ZnR_2–CH_3–OH.

Special catalyst complexes, like $[Zn(OCH_3)_2 \cdot (C_2H_5OCH_3)_6]$, form through carefully control of reaction conditions by adding 16 moles of methyl alcohol to 14 moles of diethylzinc in heptane under an argon atmosphere. X-ray analysis shows that two different structures [36]. One of them is a centrosymmetric complex of two enantiomorphic distorted cubes that share a corner Zn atom. The two would be equivalent if they were not distorted. Another structure, also centrosymmetric, consists of two enantiomorphic distorted structures that resemble “chairs without legs,” where the surfaces share a common seat. Both types of complexes are active initiators for polymerization of propylene oxide. Each has two enantiomorphic sites for polymerization. Based on that knowledge, NMR spectra and GPC curves, Tsuruta suggested the following mechanism of a monomer coordinating with the catalyst [36] (see Fig. 5.2). The bonds at the central zinc atom are loosened and coordination takes place with methyl-oxirane molecule at the central atom. Cleavage at the O–CH_2 bond of the oxirane takes place by a concerted mechanism. If the bond loosening takes place at the *d* cube and the nucleophilic attack takes place at one of the methoxy groups on that cube then chirality around the central zinc will favor *L* monomer over the *D* monomer. This is the origin of the *l** catalyst site. If the bond loosening takes place in the *l* cube the catalyst site will have *d** chirality. Because the probability of bond loosening in the *d* cube is exactly the same as in *l* cube, an equal number of *l** and *d** sites should be expected to form. These two cubes become a source of *d** and *l** chiral nature [35].

5.4 Polymerization of Oxetanes

Oxetanes (or oxacyclobutanes) are preferably polymerized in solution to maintain temperature and stirring control. It is necessary to purify both the monomer and the solvent, because impurities interfere with attainment of high molecular weight.

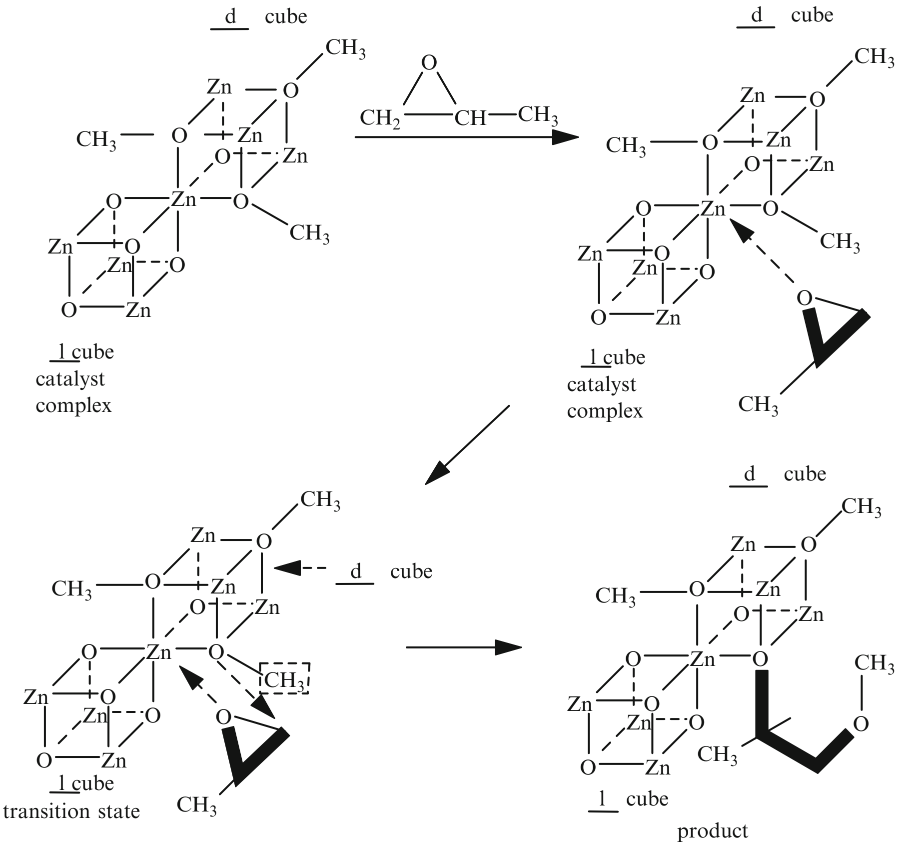


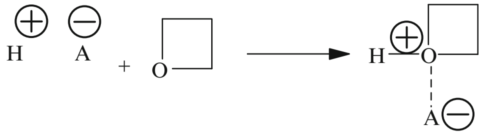
Fig. 5.2 Tsuruta mechanism

5.4.1 The Initiation Reaction

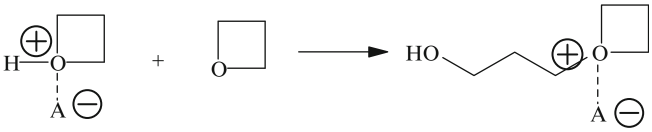
Theoretically, any Lewis acid can catalyze oxetane polymerizations. However, these acids differ considerably in their effectiveness. Boron trifluoride and its etherates are the most widely reported catalysts. Moisture must be excluded, as it tends to be detrimental to the reaction [35].

Chlorinated hydrocarbon solvents, like methylene chloride, chloroform and carbon tetrachloride, are common choices. The reactions are usually conducted at low temperatures and there are indications that the lower the reaction temperature the higher the molecular weight of the product

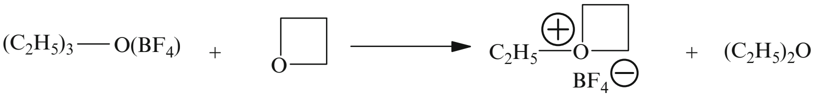
It was reported that when oxetane polymerizations are carried out with boron trifluoride catalyst in methylene chloride at temperatures between 0 and −27.8°C a cocatalyst is not required [32]. The product, however, is a mixture of linear polymer and a small amount of a cyclic tetramer. This is in agreement with an earlier observation that the polymerizations of oxetane are complicated by formations of small amounts of cyclic tetramers [33]. Other catalysts, like protonic acids, capable of generating oxonium ions, will also polymerize oxetane. Such acids are sulfuric, trifluoroacetic, and fluorosulfuric. The initiation reaction can be illustrated as follows:



The adduct reacts with cyclic ether:

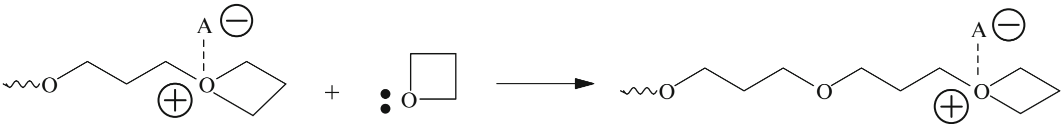


When complexes of Lewis acids with active hydrogen compounds initiate the polymerizations, such complexes acts as protonic acids. On the other hand, etherates initiate by forming oxonium ions and may involve alkyl exchange reactions with the monomer:



5.4.2 The Propagation Reaction

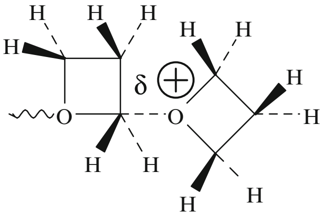
The propagation takes place via tertiary oxonium ions [37, 38]:



A cyclic oligomer forms in some instances in addition to the polymer [40]. For instance, in polymerizations with BF_3 in methylene chloride at low temperatures a cyclic tetramer forms, probably by a backbiting process [40].

The oxonium exchange reactions may occur with the polymer ether linkages as well as with cyclic tetramers that form, as shown above. The concentrations of the oxonium ions of the ether group on the polymer and on the cyclic tetramers, however, are very small [42]. Polymerizations with PF_5, on the other hand, or with $(C_2H_5)_3OPF_6$ either in bulk or in methylene chloride solutions, yield no significant amounts of cyclic oligomers [43].

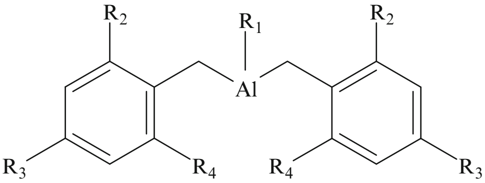
The activation energy of polymerizations of oxetane monomers is higher that that of tetrahydrofuran (see next section). This indicates that the orientation of the cyclic oxonium ion and the monomer is looser in the S_N2 transition state [42]:



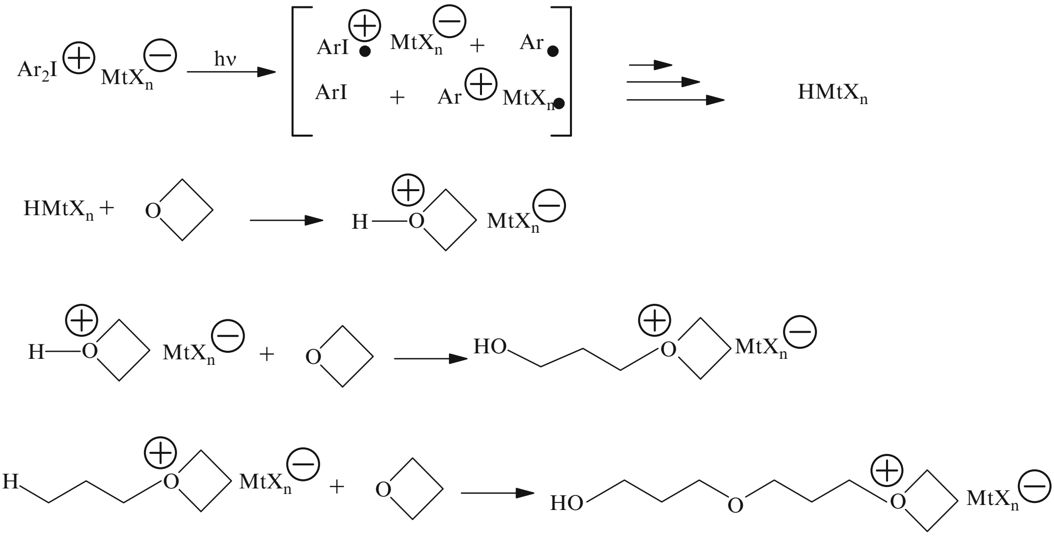
In principle, stereospecificity should be possible in substitute polyoxycyclobutanes, such as 2-methyl, 3-methyl, and others. The 2-methyl derivative however, yields amorphous polymers. This is due to the monomer's unsymmetrical structure [33] NMR studies of the microstructure of polymers from 3,3-dimethyloxetane [44] and 2-methyloxetane [43] led to no conclusions about the manner of ring opening. The predominant head to tail structures may result from attacks at either the methylene or the methine carbons next to the oxonium ions of the propagating species.

Oxetane compounds also polymerize with the aid of aluminum trialkyl–water acetylacetone catalysts [45, 46]. The reactions can take place at 65°C in heptane and yield very high molecular weight polymers. These polymerizations, however, are ten times slower that similar ones carrier out with propylene oxide, using the same catalyst. The reaction conditions and the high molecular weights of the products led to assumption that coordinated mechanisms of polymerizations take place [46].

Also, it was reported [218] that quaternary onium salts coupled wit bulky organoaluminum diphenolates initiate controlled (living) coordinate anion polymerizations of oxetane to give narrow molecular weight distribution polyethers The catalyst system consists of onium salts, such as quaternal ammonium phosphonium halides that are combined with sterically hindered methylaluminum diphenolates [47]



Crivello reported frontal photopolymerization of oxetane [48]. He proposed a mechanism for the polymerization that is shown in the following scheme:



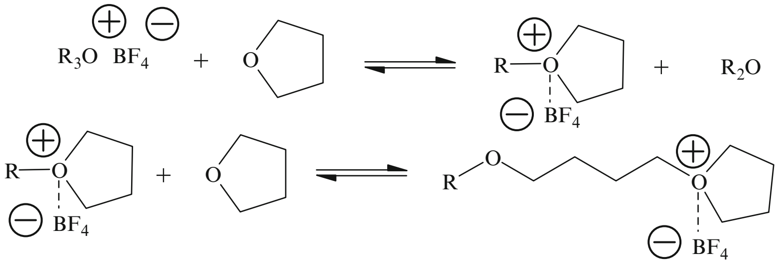
Crivello reported that only diaryliodonium salts were used as cationic photoinitiators in this study. Photo activation was carried out by UV irradiation prior to thermal initiation. Initiation was carried out using an electrically heated wire immersed in the monomer. The velocity of the resulting propagating front is quite high with the temperature of the front reaching 110°C.

5.5 Polymerization of Tetrahydrofurans

Lewis acids, carbon cations, salts of oxonium ions, and strong protonic acids initiate polymerizations of tetrahydrofuran. The reactions can be conducted in solution or without a solvent It was originally polymerized [49, 50] with a trialkyloxomum salt, $R_3O•BF_4$.

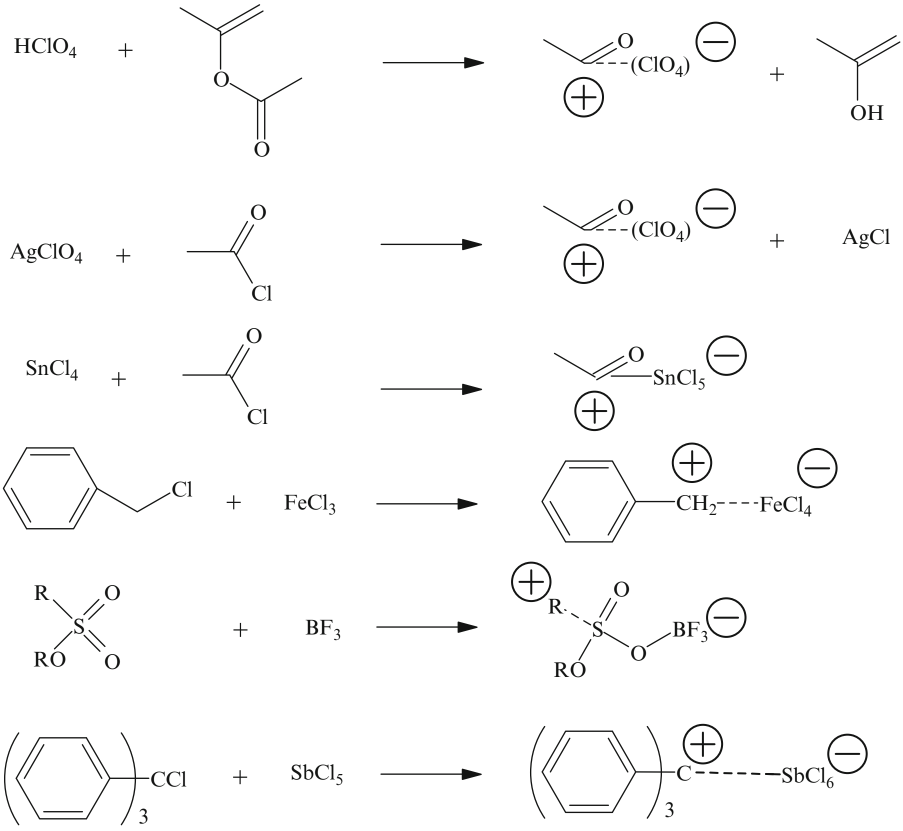
5.5.1 The Initiation Reaction

The initiations result from coordination of the cation catalysts with the oxygen of the monomers to form oxonium ions [48, 49]. This weakens the oxygen–carbon bonds and leads to ring openings after reactions with a second molecule of the monomer. New oxonium ions are generated in the process:

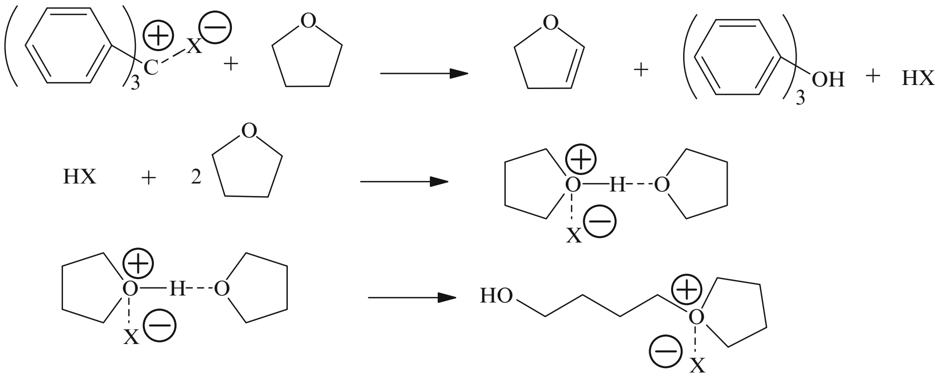


Some active oxonium salts are [48–50]: $[(C_2H_5O)_3O]^+$ $BF4^-$, $[(C_2H_5O)_3O]^+$ $SbCl_6^-$, $[(C_2H_5O)_3O]^+$ $FeCl_4^-$, and $[(C_2H_5O)_3O]$ $^+AlCl_4^-$

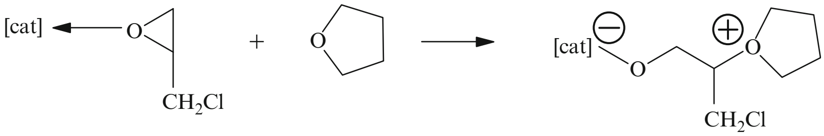
Examples of carbon cations that can initiate polymerizations of tetrahydrofuran, as well as some other cyclic ethers are:



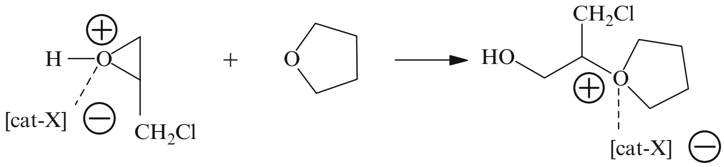
The initiation mechanisms, however, by many carbon cations as, for instance, by triphenylmethyl cations, are not straightforward. Initially, hydride ions are abstracted from the monomers to form triphenylmethanes [51–53]. Simultaneously, acids are released from the counterions. The acids become stabilized by complexing with monomers. After that, the complexes react slowly with additional monomers to form the propagating oxonium ions. This makes the acids the real initiators::



Other initiators for tetrahydrofuran polymerizations also include Lewis acids in combinations with “promoters.” These are complexes of Lewis acids, like BF_3, SnCL1, or $C_2H_5AlCl_2$ with epirane compounds like epichlorohydrin [42]. The small ring compounds are mote reactive toward many Lewis acids, or protonic acids, then tetrahydrofuran and act as promoters of the initiation reactions. The initiations in the presence of small quantities of oxirane compounds, for instance, can be illustrated as follows:



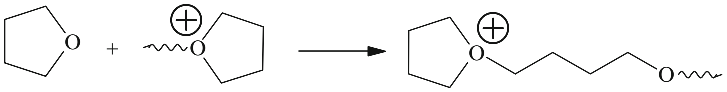
or



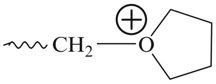
Strong Bronsted acids form when diaryliodonium salts. like BF_4^-, AsF_6^-, PF_6^- and SbF_6^- are reduced with compounds like ascorbic acid in the presence of copper salts. such acids also initiate the polymerizations of tetrahydrofuran, cyclohexene, and *s*-trioxane [54].

5.5.2 *The Propagation Reaction*

The propagation process is a succession of nucleophilic attacks by fn electrons on the oxygens of the monomers upon the α-carbons of the heteroatoms of the ultimate polymerizing species [1]:



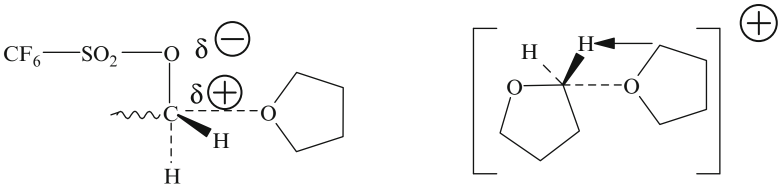
The products of these reactions are linear. Actually, this is common to polymerizations of many heterocyclics. The propagation reactions proceed by stepwise additions of monomer by S_N2 mechanism to the growing ends of the propagating chains. The NMR spectra of the growing chains only shows a presence of the oxonium ions [55, 56]:



The oxonium ions could, in principle, be in equilibrium with minute quantities of carbon cations, $–CH_2^+$ that are more active. All evidence, to date, however, shows that in tetrahydrofuran polymerizations the presence of carbon cations is negligible in the propagation process [57]. Also, the rate constant for propagation of free macroions with the counterions is equal, within experimental error, to the rate constant for macroions–counterion pairs. This does not appear to depend upon the stricture of the anion studied. The above information, however, was obtained on large anions. With smaller anions, differences in the rates of propagation of macrocations and those of macroion–counterion pairs has not be ruled out.

An S_N2 attack requires that the reaction occur at the oxygen carbon bond. In such an attack steric requirements are less restricted than they are in an anionic polymerization. In addition, positive and negative charges in the macroion-pairs that contain the oxonium ions are dispersed and the anions are large. This means that the electrostatic interactions are less important in cationic polymerizations of this type than they are in anionic ones.

When the polymerization of tetrahydrofuran is carried out with the aid of CF_3SO_3H, both covalent and ionic species are present They can be detected during propagation by means of NMR spectroscopy. Both species exist in a mobile equilibrium. Solvent polarity, apparently, influences the position of such equilibria. In nitromethane, 95% of the growing chains are macroions. In carbon tetrachloride 95% of them are macroesters. In methylene chloride both species are present in the reaction mixture, approximately in equal amounts [58–62]. The propagation rate of macroions, however, is 10^2 times faster than that of the macroesters. As a result; chain growth even in carbon tetrachloride is still by way of the ions. The macroesters, therefore, can be considered as dormant species [59], or, as some suggest, even cases of temporary termination [59]. The much higher reactivity of the macroions is attributed to the contribution of the partially released strain in ionic species [49]. Macroions and macroesters can be illustrated as follows:



5.5.3 The Termination Reaction

The termination reactions in tetrahydrofuran polymerizations can depend upon the choice of the counterion, particularly if the reaction is conducted at room temperature [60]. In many reactions, the chains continue to grow without any considerable termination or transfer [63, 64]. Some refer to this process as "**living**" polymerization. thus in polymerizations of tetrahydmfuran [65] with PF_6^- or

SbF_6^- counterions the molecular weights of the products can be calculated directly from the ratios of the initiators to the monomers. The molecular weight distributions of the polymers from such polymerization reactions with PF_6^- and, SbF_6^- however, start out as narrow, but then broaden. This is believed to be due to transfer reactions with ether oxygen. It is supported by evidence that with SbF_6^- initiation, both termination and transfer reactions take place [65]. In addition, polymerizations of tetrahydrofuran, like those of the epoxides, can be accompanied by formations of some macrocyclic oligomers. This is often the case [66, 67] when strong acids are used as initiators. The proposed mechanism involves backbiting and chain coupling and results in linear polymers with hydroxyl groups and oxonium ions at opposite chain ends as well as some macrocycles.

The absence of linear oligomers is due to rapid reactions of the hydroxyl and oxonium ion end groups. This mechanism is quite general [67, 68] for ring-opening polymerizations of cyclic ethers initiated with string protonic acids. Substituted tetrahydrofurans generally resist polymerizations.

5.6 Polymerization of Oxepanes

Oxepanes are polymerized by various cationic initiators like $(C_2H_5)_3C^+BF_4^-$, $(C_2H_5)_3C^+SbCl_6^-$, BF_3-epichlorohydrin, and $SbCl_6$-epichlorohydrin [42].The reactions take place in chlorinated solvents, like methylene chloride. The rates of these reactions, however, are quite slow [42]. In addition, these polymerizations are reversible. The rates of propagation of the three cyclic ether, oxetane, tetrahydrofuran, and oxepane at 0°C fall is in the following order [42]:

$$\text{oxetane} > \text{tetrahydrofuran} > \text{oxepane}$$

At the same temperature oxetane is about 35 times as reactive as tetrahydrofuran, which in turn is about 270 times as reactive as oxepane. This cannot be explained on the basis of ring strain, nor can it be explained from considerations of basic strength. Saegusa suggested [42] that the differences in the propagation rates are governed by nucleophilic reactivities of the monomers. They are also affected by the reactivities of the cyclic oxonium ions of the propagating species and also by the steric hindrances in the transition states of propagation. Higher activation energy of oxepane is explained by increased stability of the seven-membered oxonium ion. The oxepane molecule has puckered structure, and the strain that comes from the trivalent oxygen is relieved by small deformations of the angles of the other bonds [42].

5.7 Ring-Opening Polymerizations of Cyclic Acetals

The cationic polymerizations of cyclic acetals are different from the polymerizations of the rest of the cyclic ethers. The differences arise from great nucleophilicity of the cyclic ethers as compared to that of the acetals. In addition, cyclic ether monomers, like epirane, tetrahydrofuran, and oxepane, are stronger bases than their corresponding polymers. The opposite is tree of the acetals. As a result, in acetal polymerizations, active species like those of 1,3-dioxolane, may exist in equilibrium with the macroalkoxy carbon cations and tertiary oxonium ions [69]. By comparison, the active propagating species in the polymerizations of cyclic ethers, like tetrahydrofuran, are only tertiary oxonium ions. The properties of the equilibrium of the active species in acetal polymerizations depend very much upon polymerization conditions and upon the structures of the individual monomers.

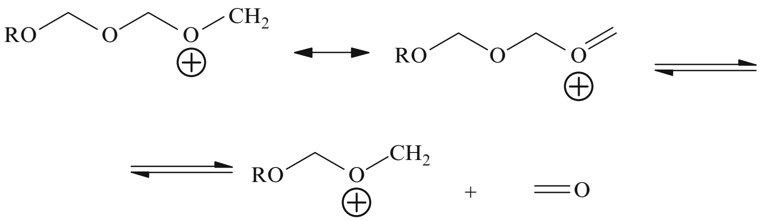
5.7.1 Polymerization of Trioxane

Trioxane is unique among the cyclic acetals because it is used commercially to form polyoxymethylene, a polymer that is very much like the one obtained by cationic polymerization of formaldehyde. Some questions still exist about the exact mechanism of initiation in trioxane polymerizations. It is uncertain, for instance, whether a cocatalyst is required with strong Lewis acids like BF_3 or $TiCl_4$.

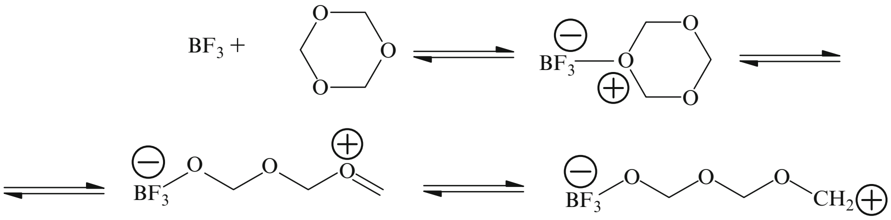
The cationic polymerization of trioxane can be initiated by protonic acids, complexes of organic acids with inorganic salts, and compounds that form cations [70]. These initiators differ from each other in activity and in the influence on terminations and on side reactions. Trioxane can also be polymerized by high-energy radiation [70]. In addition, polymerizations of trioxane can be carried out in the solid phase, in the melt; in the gas phase, in suspension, and in solution. Some of these procedures lead to different products, however, because variations in polymerization conditions can cause different side reactions.

Polymerizations in the melt above 62°C are very rapid. They come within a few minutes to completion at 70°C when catalyzed by ten moles of boron trifluoride. This procedure, however is only useful for preparation of small quantities of the polymer, because the exothermic heat of the reaction is hard to control.

Typical cationic polymerizations of trioxane are characterized by an induction period. During that period only oligomers and monomeric formaldehyde form. This formaldehyde, apparently, results from splitting the carbon cations that form in the primary steps of polymerization. The reaction starts after a temperature dependent equilibrium concentration of formaldehyde is reached [70].

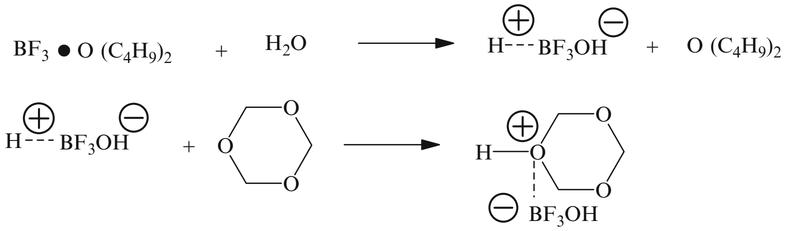


Several reaction mechanisms were proposed. One of them is based on the concept that Lewis acids, like BF_3 coordinate directly with an oxygen of an acetal. This results in ring opening that is induced to form a resonance stabilized zwiter ion [71]:



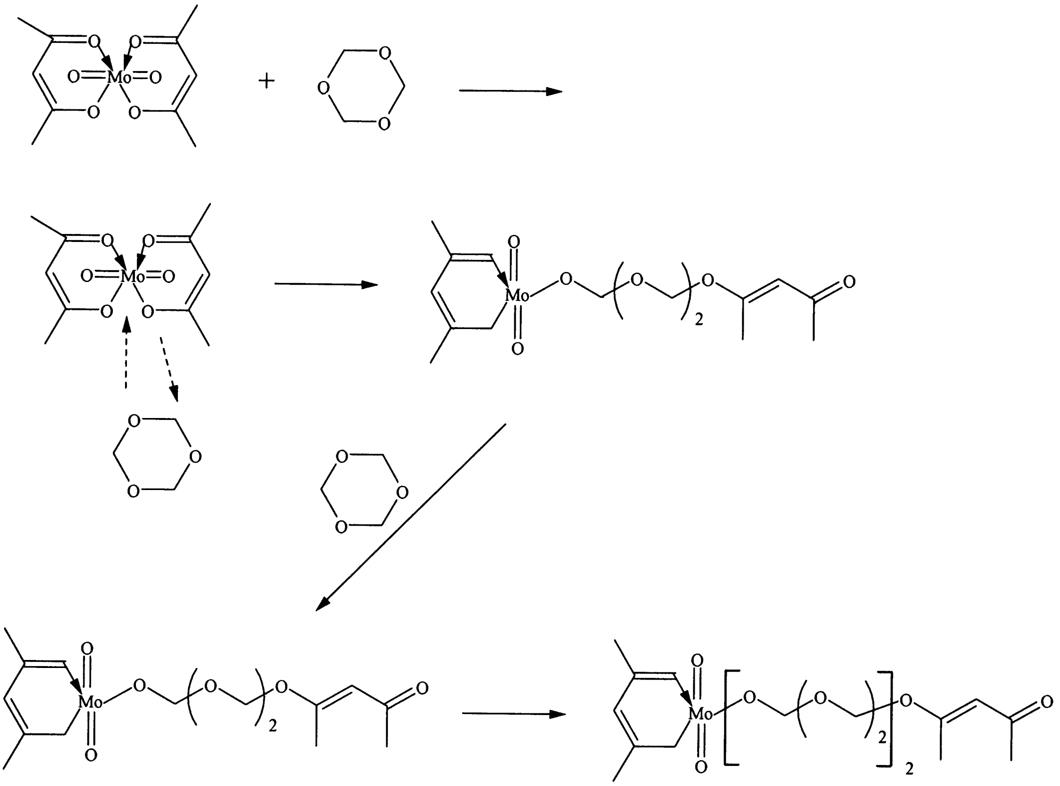
Resonance stabilizations of the adjacent oxonium ions lead to formations of carbon cations that are believed to be the propagating species. Propagations consist of repetitions of the sequences of addition of the carbon cations to the monomer molecules and are followed by ring opening. The above mechanism has to be questioned, however, because rigorously dried trioxane solutions in cyclohexane fail to polymerize with $BF_3{\cdot}O(C_4H_9)_3$ catalyst [72]. The same is true of molten trioxane [73]. It appears, therefore, that BF_3-trioxane complexes don't form as suggested and do not result in initiations of the polymerizations. Additions of small quantities of water, however, do result in initiations of the polymerizations.

Another mechanism, is based on a concept that two molecules of BF_3 are involved in the initiation process [69]. This also appears improbable since without water BF_3 fails to initiate the reaction. the following mechanism, based on water as the cocatalyst was developed [73]:



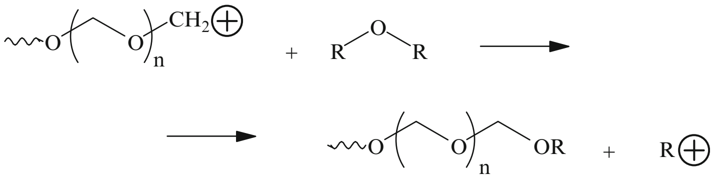
Chain growth in the reaction is accompanied by formations of tetraoxane and 1,3-dioxalane because of backbiting [71, 74].

Complex molybdenyl acetylacetones also act as catalysts for trioxane polymerization. The mechanism that is visualized involves formation of a coordinated intermediate [75]:

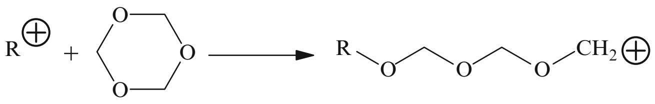


The termination mechanism and the catalyst requirement have not yet been fully explored.

Some transfer to water takes place during the reaction. As a result the polymer contains at least one terminal hydroxyl group [76]. Besides water, methyl alcohol and low molecular weight ethers also act as transfer agents [77].

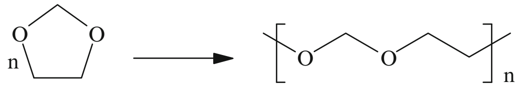


The new cation can initiate chain growth:

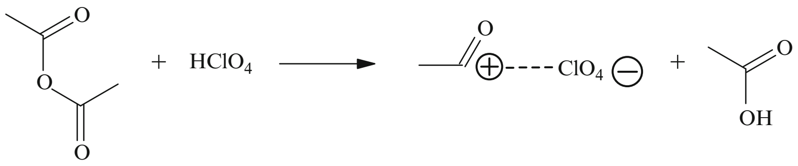


5.7.2 Polymerization of Dioxolane

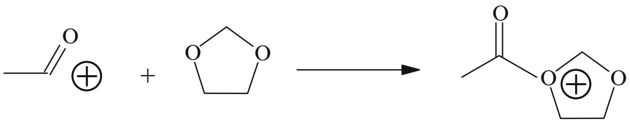
Polymerization of this cyclic monomer yields polymers that consists of strictly alternating oxymethylene and oxyethylene units [76]. the polymerization reaction can be induced by acidic catalysts, like sulfuric acid, boron trifluoride, *p*-toluenesulfonic, acid and phosphorous pentafluoride [76]:



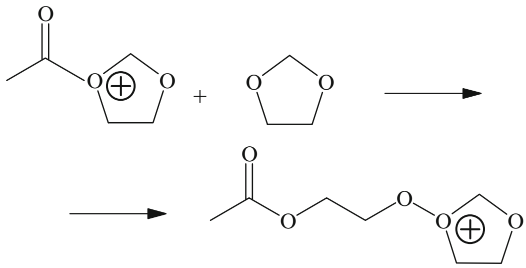
The polymers of molecular weight 10,000 or higher are tough solids that can he cold drawn. The following mechanism was proposed for the polymerizations that are initiated by reaction products of acetic anhydride with perchloric acid [78]:



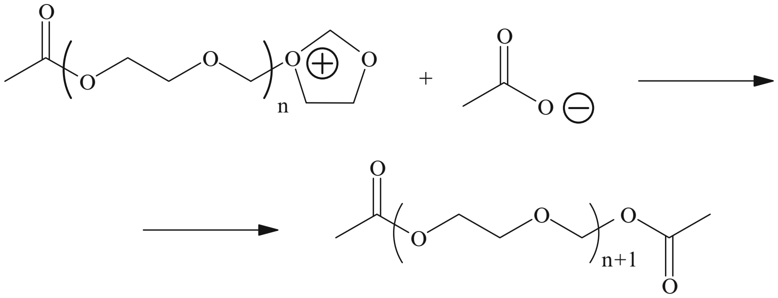
Initiation



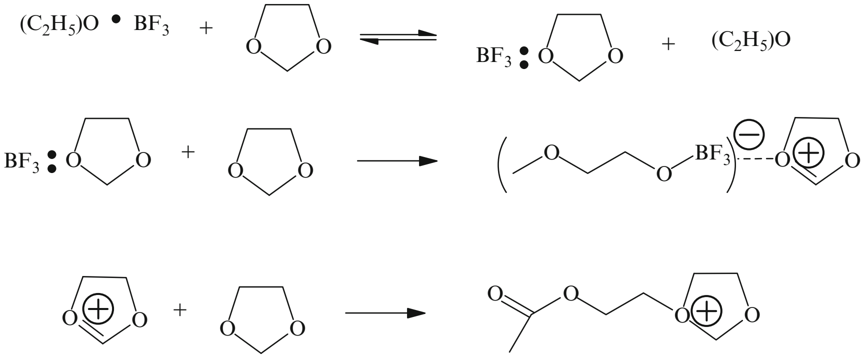
Propagation



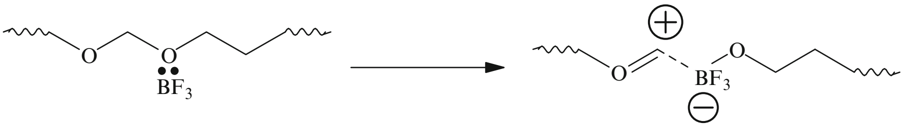
Termination



Acetate groups are present at both end of the polymer molecules as shown above [78]. This was confirmed by analytical evidence. The initiation of dioxolane polymerization is pictured differently [79, 80]:



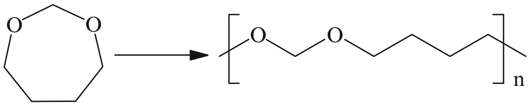
Chain cleavage can occur as a result of BF_3 complexation with an oxygen in a chain [80]:



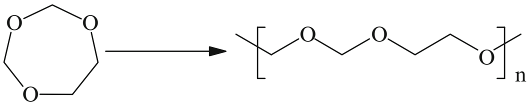
There is some disagreement about the nature of the end groups. and there are some speculations that the polymers might possess large cyclic structures. Nevertheless, polymerizations initiated with benzoyllium hexafluoroantimonate ($C_6H_5CO^+SbF_6^-$) and conducted at −15°C in nitromethane or methylene chloride result in mostly linear polymers. The terminal end groups come from terminating agents that are deliberately added [81]. These polymerizations proceed without any appreciable amounts of transfer reactions, affecting the DP.

5.7.3 *Polymerization of Dioxopane and Other Cyclic Acetals*

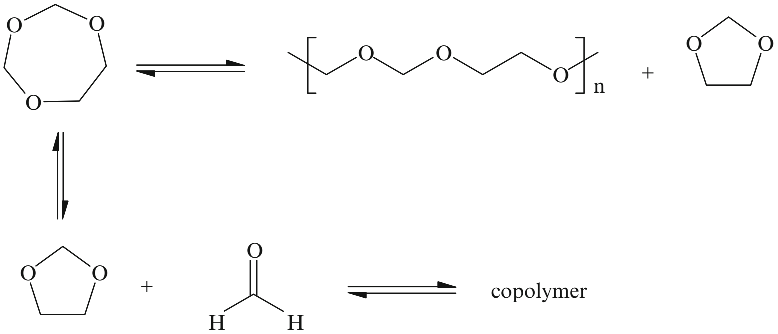
Polymerization of six membered cyclic formals has, apparently not been explored [1]. Polymerization of 1,3-dioxopane can be initiated by camphor sulfonic acid [82, 83]:



1,3-trioxopane, a product of condensation of trioxane with ethylene oxide, can be polymerized by cationic mechanism both in solution and in bulk [84]:

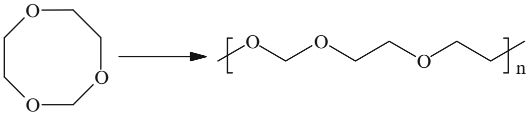


Polymerizations, carried out with boron trifluoride catalyst in dichloroethane solvent result in several reactions that occur simultaneously [84]:



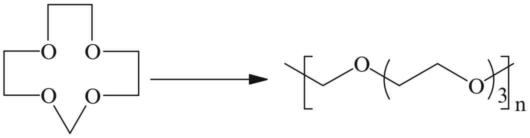
At low temperatures the amount of dioxolane that forms in the above reaction decreases considerably and can become zero.

Ring-opening polymerizations of trioxocane result in the following polymer [84, 85]:



So far, the nature of the end groups has not been established. Nor has it been shown that a macrocyclic structure does not form.

1,3,6,9-tetraoxacycloundecane (triethylene glycol formal) can be polymerized can be polymerized by several cationic initiators in solution or in bulk at varying temperatures from −30 to +150°C [84]:

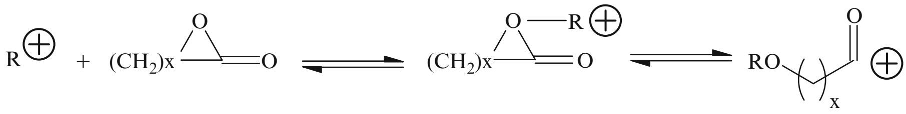


5.8 Polymerization of Lactones

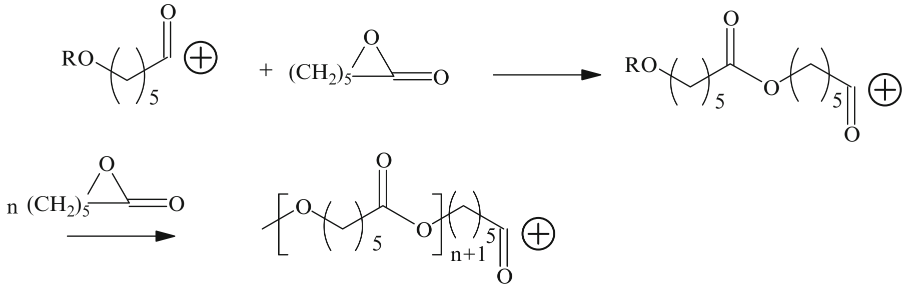
Polymerization of lactones can be carried out by three mechanisms, namely, cationic, anionic, and coordinated one. Often, the mechanism by which a specific lactone polymerizes depends upon the size of the ring.

5.8.1 Cationic Polymerization

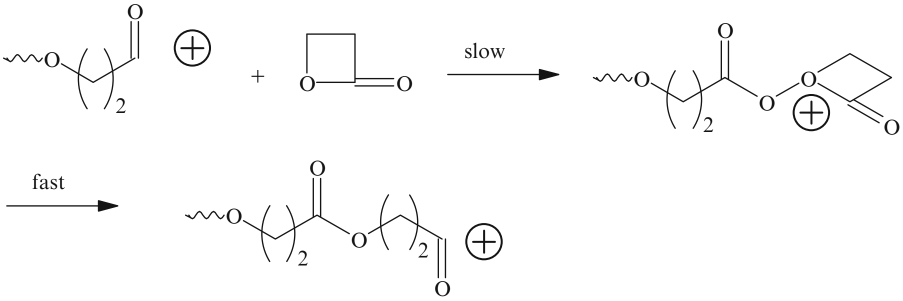
Cationic polymerizations of lactones has been carried out with the help of alkylating agents, acylating agents, Lewis acids, and protonic acids. Various reaction schemes were proposed to explain the cationic mechanism. They tend to resemble the schemes suggested for the polymerization of cyclic ethers [86, 87]. The initiation step involves an equilibrium that is followed by a ring-opening reaction:



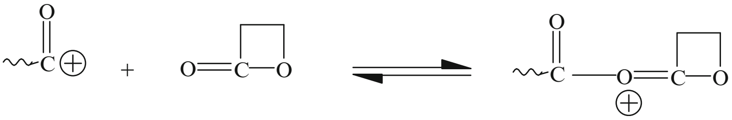
The propagation consists of many repetitions of the above step:



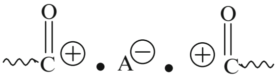
The polymerization of propiolactone in methylene chloride with an antimony pentachloride-dietherate catalyst was investigated [88]. The results show that the concentration of the active centers is dependent upon catalyst concentration and upon the initial concentration of the monomer. They also support the concept that opening of the lactone rings includes initial formation of an oxonium ions [88]:



Because the carbonyl oxygen is the most basic of the oxygens in the lactone molecule, a reverse reaction is

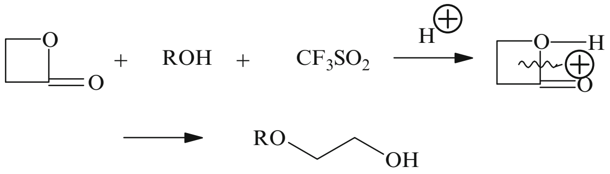


Conductivity measurements during polymerizations of β-propiolactone with antimony pentafluoride-etherate or *p*-toluenesulfonic acid show [89] that ion triplets form during the reaction. These are:



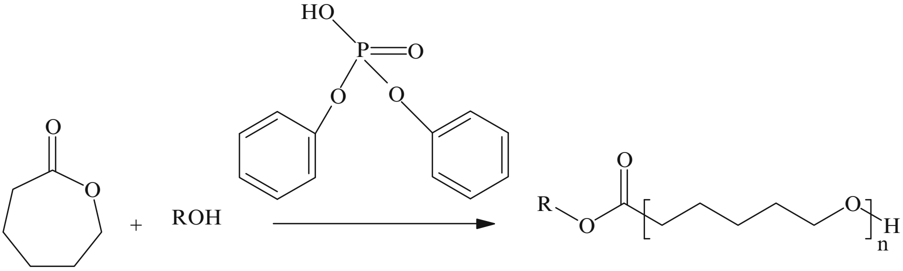
The triplets appear to be active centers throughout the course of the polymerizations. In addition, most of the growing chain ends exist as ion pairs, depending upon the concentration of the monomer [89].

Bourissou et al. reported recently controlled cationic polymerization of lactones using a combination of triflic acid with a protonic reagent as the initiators [90]. The reaction was carried out in CH_2Cl_2. Results indicated that the process is controlled is a linear relationship between the molecular weight of the product and the monomer to initiator ratio as well as to monomer conversion. The process is believed to proceed by protonation of the lactone by triflic acid and then followed by a nucleophilic attack by the initiating alcohol:



It is believed that the controlled cationic ring-opening polymerization proceeds by an “activated anionic mechanism” as suggested by Penczek [91]. According to his suggestion, the acid activates the cyclic ester and the alcohol subsequently initiates the polymerization.

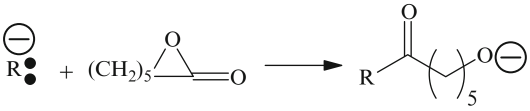
Kakuchi and coworkers reported controlled/living cationic ring-opening polymerizations of δ-valerolactone and ε-caprolactone with the aid of diphenyl phosphate [89]. The reaction was illustrated as follows:



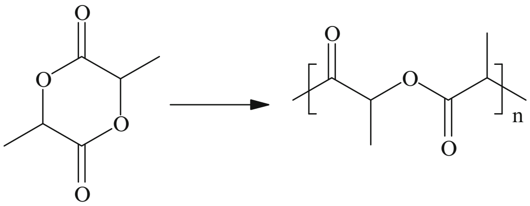
The ring-opening polymerization of δ-valerolactone and ε-caprolactone was carried out using 3-phenyl-1-propanol as the initiator and diphenyl phosphate as the catalyst in toluene at room temperature. They reported that the reaction proceeded homogeneously to yield poly(δ-valerolactone) and poly(ε-caprolactone) with narrow polydispersity indices. Analyses indicated a presence of residues of the initiator.

5.8.2 *Anionic Polymerization of Lactones*

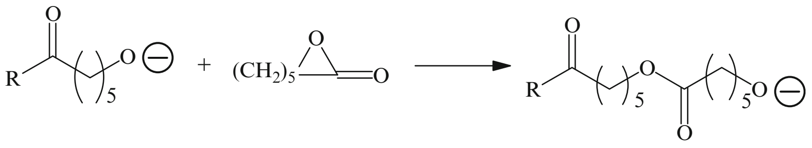
In anionic polymerizations the initiations result from attacks by bases upon the carbonyl groups:



Common initiators are Li and K alkoxides. In addition to that, it was reported that phosphazene bases can be used to carry out polymerizations of cyclic esters [92]. Also, commercially available materials, like *tert*-butoxybis(dimethylamino)methane and tris(dimethylamino)methane yield high molecular weight polylactic acid by ring-opening polymerization with narrow molecular weight distribution:



The propagations take place by a similar process:

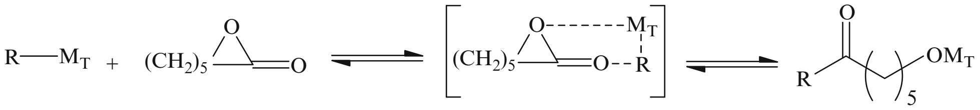


These steps repeat themselves until the chains are built up. Anionic polymerizations can yield optically active polymers. This was observed in formations of poly(α-methyl, α-ethyl-β-propiolactone) [193] that contains asymmetric carbon atoms.

5.8.3 Polymerization of Lactones by Coordination Mechanism

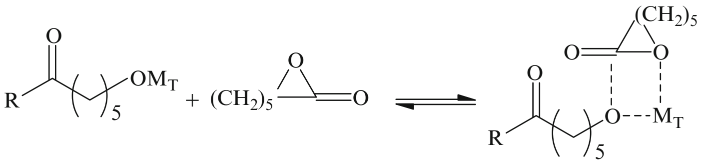
The mechanism of coordination polymerization was pictured by Yong, Malzner, and Pilato [90] as being an intermediate between the above two modes of polymerization (a cationic and anionic one):

Initiation



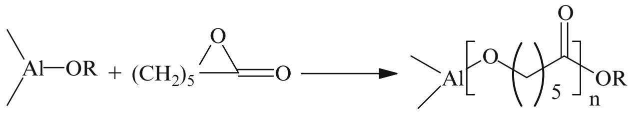
where, M_T means metal.

Propagation



The above shown mechanism, however, is incorrect when caprolactone is polymerized with tin compounds [95]. Yet, it appears to be correct for polymerizations of propiolactones with an ethylzinc monoxide catalyst [95].

The bimetallic oxoalkoxides are useful catalysts for the polymerizations of ε-caprolactone. The general course of the reaction is quite similar to one for oxiranes. A typical coordination mechanism is indicated from kinetic and structural data [97]. The molecular weight increases with conversion and the reaction exhibits a "living" character, because there is a linear relationship between DP and conversion. When the monomer is all used up, addition of fresh monomer to the reaction mixture results in increases in DP. By avoiding side reactions it is possible to achieve high molecular weights (up to 200,000) with narrow molecular weight distribution ($M_w/M_n \geq 1.05$) [97]. The reaction proceeds through insertion of the lactone units in the Al–OR bonds. The acyl–oxygen bond cleaves and the chain binds through the oxygen to the catalyst by forming an alkoxide link rather than a carboxylate one:

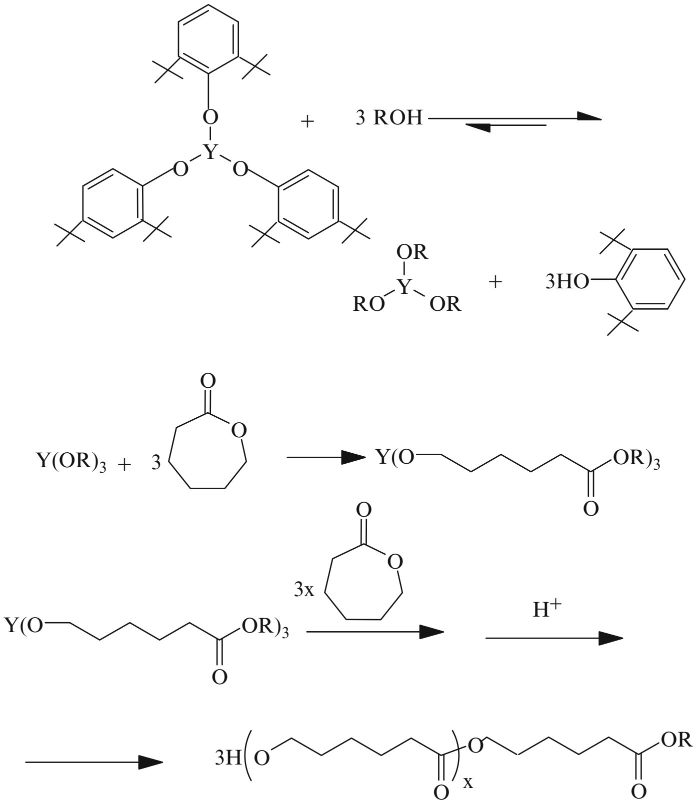


There are potentially four active sites per trinuclear catalytic molecule. The number of actual sites, however, depends upon the aggregation of the oxoalkoxides. Two different types of OR groups exist, depending upon the bridging in the aggregates. Only one is active in the polymerization. This results in a catalytic star-shaped entity. The fact that the dissociated catalysts generate four growing chains per each $Al_2(CH_2)_5CO_2(OR)_4$ molecule [97] tends to confirm this.

The commercially available aluminum triisopropoxide was reported to be a very effective initiator for the "living" ring-opening polymerizations of ε-caprolactone, lactides, glacolide, and cyclic anhydrides [98]. Based on kinetic and structural data, the ring-opening polymerization is believed to take place by a coordination-insertion mechanism. While the molecules of aluminum triisopropoxide are coordinatively associated in toluene, in the presence of lactones single isolated monomeric species form and are believed to remain unassociated during the propagation reaction [98].

Actually, ring-opening polymerizations of ε-caprolactone were achieved by various catalysts. Only a few, however, initiate "living" polymerizations. Among these are the aluminum alkoxides described above, bimetallic μ-alkoxides [99], porphynatoaluminum [100], mono(cyclopentadienyl) titanium complexes [101], and rare earth alkoxides [102, 103]. Examples of rare earth alkoxides are Ln, Nd, Y, or Nd isopropoxy diethyl acetoacetates and $(C_5H_5)_2LnOR$ and $[C_5(CH_3)_5]_2LnCH_3$ (donor) complexes. It was suggested that the steric effect of bulky groups of these catalysts is to suppress an interfering transesterification reaction by screening linear polymeric chains from the active centers during the reactions and yield "living" polymerizations [104]. These catalysts also are useful in formation of various block copolymers of lactones with other monomers [104, 105]. Among other lactones that were polymerized with the help of such rare earth catalysts are lactide [106–108], δ-valerolactone [109], β-propiolactone [109], and β-butyrolactone [107].

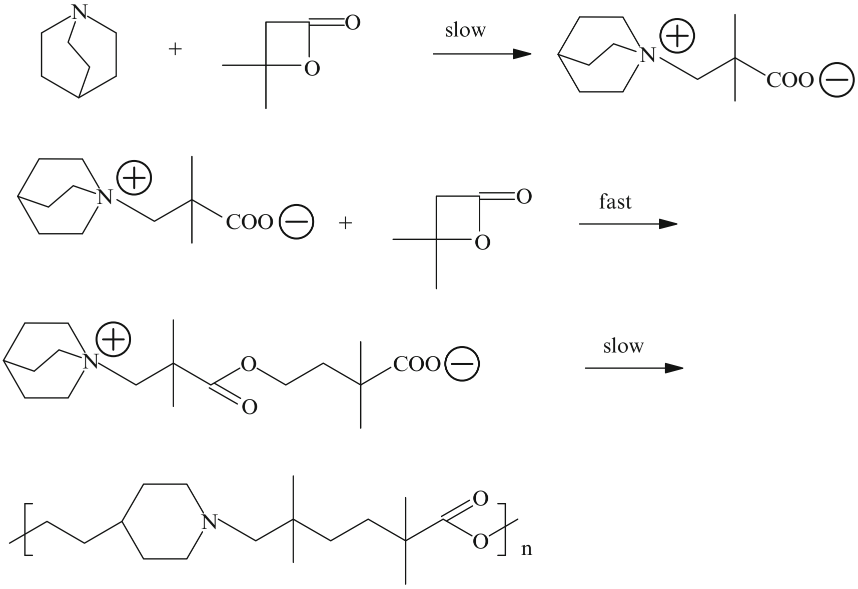
Polymerization of ε-caprolactone with a catalyst system consisting of tris(2,6-di-*tert*-butylphenoxy) yttrium and 2-propanol is first order with respect to the monomer and initiator [105]. This led to the conclusion that the reaction proceeds via a three-step mechanism that can be illustrated as follows [105]:



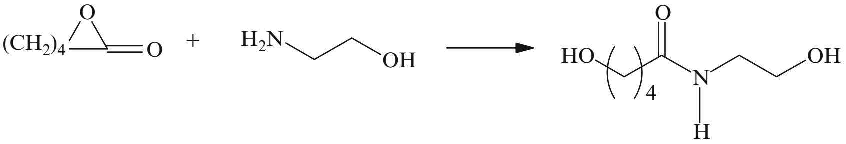
It was also reported that "living" ε-caprolactone polymerization can be carried with bis(acryloxy-) lanthanide (II) complexes based on samarium [110]. Thus, $(ArO)_2Sm(THF)_4$, (where ArO = 2,6-di-*tert*-butyl-4-methyl-phenoxy) yielded 98% conversion in toluene at 60°C in 1 h. The central ions and ligands appear to have an effect on the activity of the catalyst [110].

5.8.4 Special Catalysts for Polymerizations of Lactones

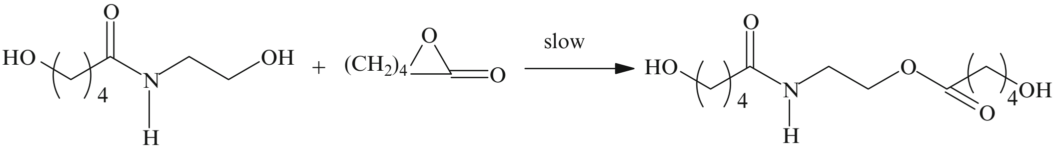
Some lactones can polymerize in the presence of compounds like alcohols, amines, and carboxylic acids without additional catalysts. The reactions, however, are slow and yield only low molecular weight polymers [95]. Exception is polymerizations of pivalolactone in the presence of cyclic amines that yield high molecular weight polyesters at high conversion [111]. The initiating steps result from formations of adducts, amine-pivalate betaines:



The above reaction appears to be restricted to highly strained lactones and may not work with larger lactones [95], For instance, when polymerization of δ-valerolactone is initiated with ethanolamine at temperatures up to 200°C there is initially a rapid reaction between the amine group and the monomer:



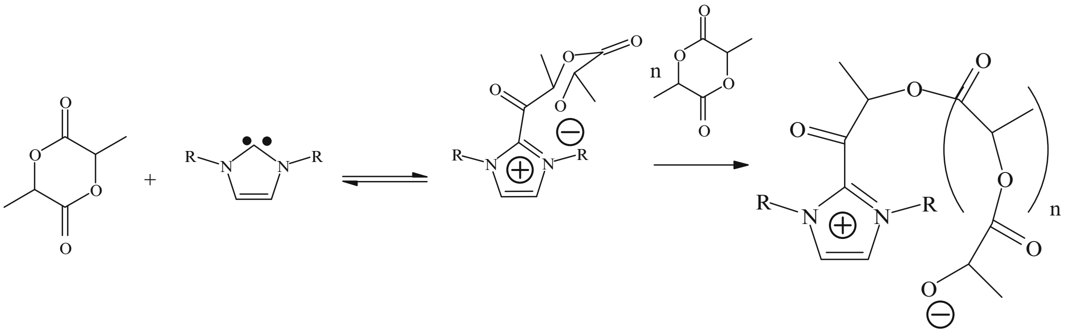
The subsequent reactions, however, are slow:



It was suggested that initiators, like dibutylzinc, that lack active hydrogens should be placed into a special category [96]. They can initiate polymerizations of some lactones. One of them is ε-caprolactone. Polymers form that are inversely proportional in molecular weights to the catalyst concentrations [112]. The same is true of stannic tetraacrylate. High molecular weight poly(ε-caprolactone), as high as 100,000 forms. Addition of compounds that may serve as source of active hydrogens is not necessary [95]. This group of initiators also includes dimethylcadmium, methylmagnesium bromide, and a few others that are effective in polymerizations of δ-valerolactone, ε-caprolactone, and their alkyl substituted derivatives. The polymers that form are high in molecular weight, some as high as 250,000 [113].

Another group consists of zinc and lead salts, stannous esters, phosphines, and alkyl titanates. This group does require additions of compounds with active hydrogens. Such additives can be polyols, polyamines, or carboxylic acid compounds [95]. Molecular weight control is difficult with the catalysts belonging to the first group. This second group, on the other hand, not only allows control over the molecular weights, but also over the nature of the end groups [95].

Weymouth and coworkers carried out kinetic and mechanistic studies of heterocyclic carbene mediated zwitterionic polymerization of cyclic esters [96]. Based on their results they proposed the following ring-opening mechanism:



From the kinetic studies they were able to conclude that in the heterocyclic carbene initiated polymerization of lactide, the rate of initiation is slower than the rate of propagation. Also, the rate of propagation is much faster than chain termination via cyclization.

5.9 Polymerizations of Lactams

Polymerizations of lactams produce important commercial polymers. The polymerization reactions, therefore, received considerable attention. Lactam molecules polymerize by three different mechanisms: cationic, anionic, and a hydrolytic one (by water or water releasing substances).

The lactam ring is strongly resonance stabilized and the carbonyl activity is low. Nevertheless, the ring-opening polymerizations start with small amounts of initiators through *trans*-acylation reactions. Fairly high temperatures, however, are needed, often above 200°C. In all such reactions, one molecule acts as the acylating agent or as an electrophile while the other one acts as a nucleophile and undergoes the acylation.

Generally, the initiators activate the inactive amide groups causing them to react with other lactams through successive transamidations that result in formations of polyamides. Both acids and bases catalyze the transamidation reactions. The additions of electrophiles affect increases in the electrophilicity of the carbonyl carbon of the acylating lactam. The nucleophiles, on the other hand, increase the nucleophilic character of the lactam substrate (if they are bases).

All initiators can be divided into two groups. To the first one belong strong bases capable of forming lactam anions by removing the amide proton. This starts the anionic polymerization reaction. To the second one belong active hydrogen compounds capable of protonating the amide bond and thereby affecting cationic polymerization [114].

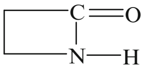
Side reactions are common in lactam polymerizations. Their nature and extent depends upon the concentration and character of the initiators, the temperatures of the reactions, and the structures of the lactams. When cationic polymerizations of lactams are initiated by strong acids, strongly basic amidine groups can be produced. These groups bind the strong acids, inactive the growth centers, and decrease the rate of polymerization. Use of strong bases to initiate polymerizations of lactams possessing at least one α-hydrogen also result in side reaction. Compounds form that decrease the basicity of lactams and polyamides and slow the polymerizations. Also, side reactions give rise to irregular structures, namely branching.

The ring-opening polymerization reactions depend upon thermodynamic and kinetic factors, and on the total molecular strain energies of the particular ring structures. Six-membered δ-valerolactam is the most stable ring structure and most difficult to polymerize. Also, presence of substituents increases the stability of the rings and decreases the ability to polymerize.

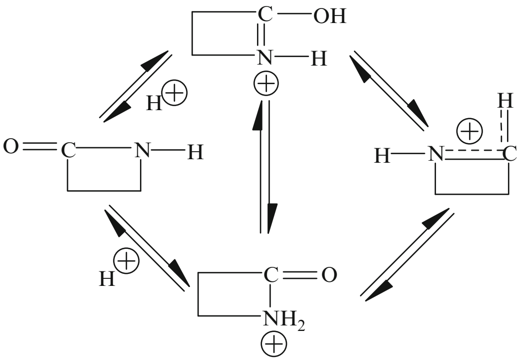
5.9.1 Cationic Polymerization of Lactams

The catalysts for cationic polymerization can be strong anhydrous acids, Lewis acids [115], salts of primary and secondary amines, carboxylic acids, and salts of amines with carboxylic acids that split off water at elevated temperatures [114]. The initiators react by coordinating with and forming rapid pre equilibrium lactam cations. These cations are the reactive species in the polymerizations. Initiations of this type are also possible with weakly acidic compound, but such compounds are not able to transfer protons to the lactam. They are capable, however, of forming hydrogen bonds with the lactams. The high reactivity of the lactam cations may be attributed to the decreased electron density at the carbonyl carbon atoms. This makes them more subject to nucleophilic attacks [114].

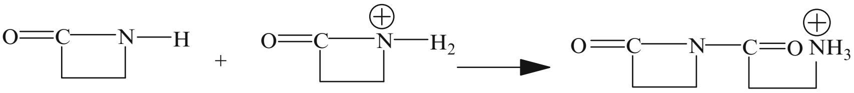
Protonations of the amides occur at the oxygens [116], but small fractions of N-protonated amides are also presumed to exist in tautomeric equilibrium. To simplify the illustrations, all lactams will be shown in this section as:



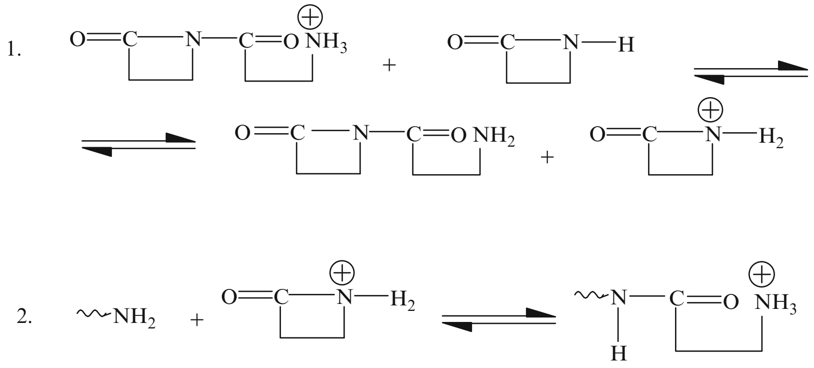
So, while the above structure commonly represents propiolactam, in this section it can mean any lactam, like a caprolactam, valerolactam, etc. Thus, the equilibrium can be shown as follows:



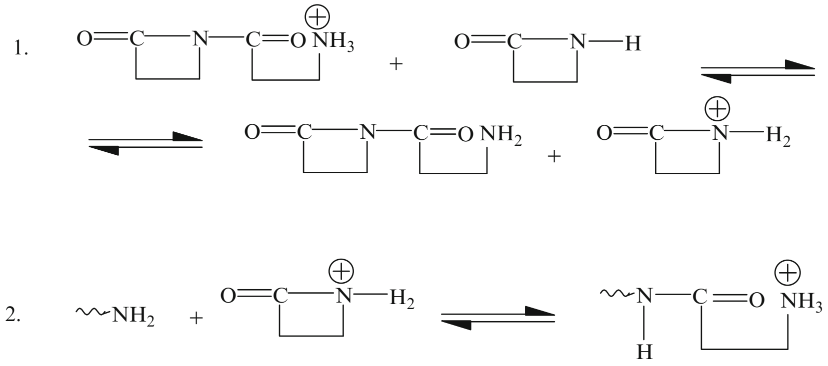
In a reaction mixture where the initiators are strong acids the strongest nucleophiles are the monomers. Acylations of the monomers with the amidinium cations result in formations of aminoacyllactams [113]:



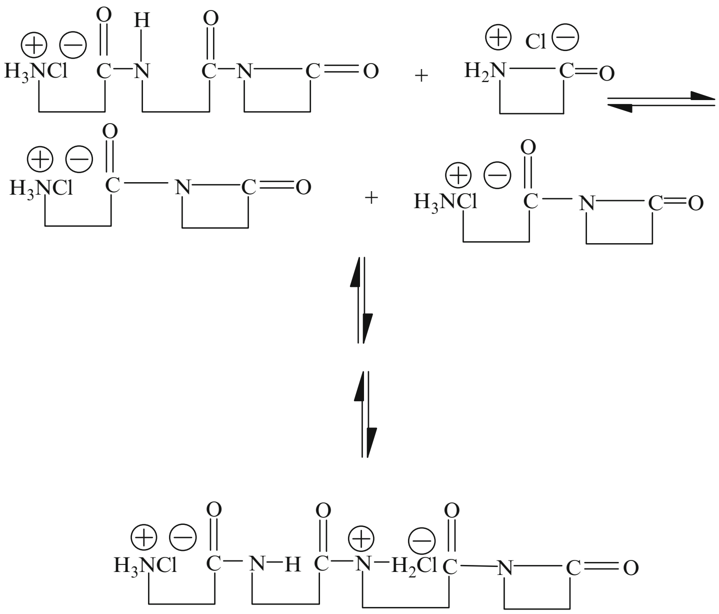
Acylation of these amine groups by molecules of other protonated lactams results in the monomers becoming incorporated into the polymers [117]. The growth centers are preserved and a molecule of lactam is protonated. This occurs in two steps [117]:



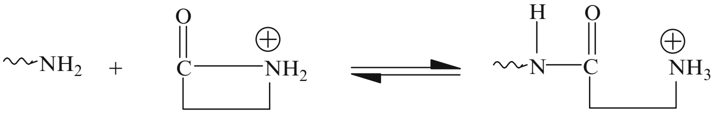
These reactions attain equilibrium quickly. Aminolyses of acyllactams, that are the reverse of the initiation reactions, precede rapidly [117–119]. Aminolyses of aminoacyllactams actually contribute to the propagation process [120, 121]:



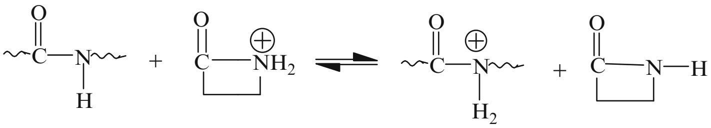
These reactions attain equilibrium quickly. Aminolyses of acyllactams, that are the reverse of the initiation reactions, precede rapidly [117–119]. The reaction, therefore, proceeds as follows [120, 121]:



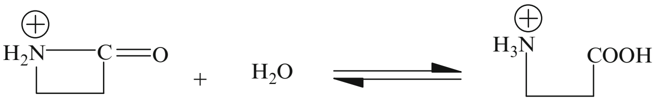
The above reaction results in the destruction of the equilibrium and a regeneration of the strongly acidic amide salt. Total lactam consumption results from repetitions of the above sequences and formations of new aminoacyllactam molecules [113–121]. Initiations of polymerizations with acid salts of primary and secondary amines result in chain growths that proceeds predominantly through additions of protonated lactams to the amines [113]:



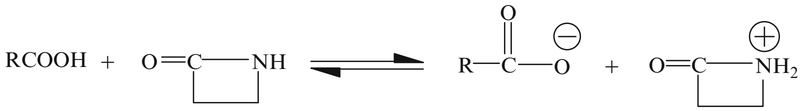
The rate at which the initiating amines are incorporated is proportional to the basicity. As the conversion progresses the concentration of protonated lactams in the reaction mixture decreases while that of the protonated polymer amide groups increases. The latter takes part in the initiation reactions with lactam molecules and in exchange reactions with polymer molecules [113]:



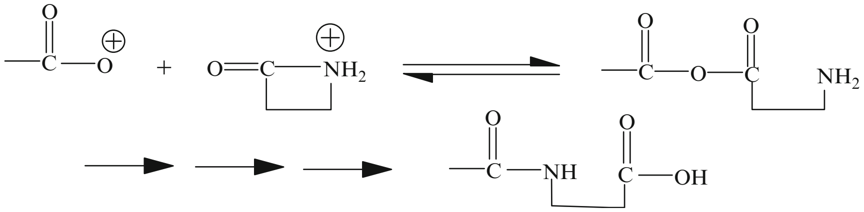
In each of the initiation steps the strongest nucleophile present reacts with the lactam cation. When strong anhydrous Bronsted acids initiate the polymerizations, the free lactams are acylated first with the formation of aminoacyllactams. When the polymerizations are initiated by amine salts, the initial steps are conversions of the amines to the amino acid amides. On the other hand, hydrolytic polymerizations start formations of unsubstituted amino acids [122]:



When weak carboxylic acids or acids of medium strength initiate lactam polymerizations at anhydrous conditions, there is an induction period [123]. In addition, the rates of these reactions are proportional to the pK_a of the acids [105]. It appears that different reaction mechanisms are involved, depending upon the acid strengths [113]. The nucleophiles are present in equilibrium:

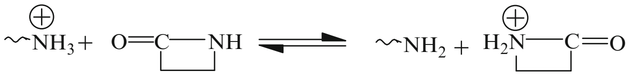


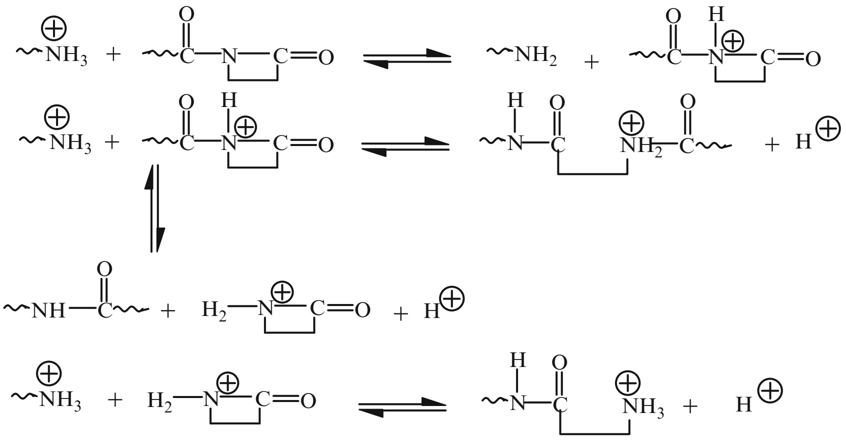
The acylation of the carboxylate anions is assumed to lead to formations of mixed anhydrides of the acids with amino acids [124] and subsequent rearrangements:



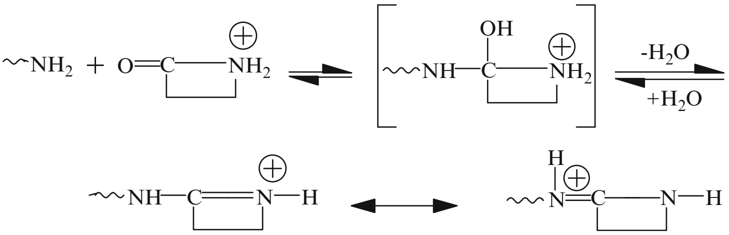
When strong acids, however, initiate the polymerizations, the strongest nucleophiles present are the lactam amide groups that undergo acylations. As a result, the acids are not incorporated into the polymers.

The propagation steps in cationic polymerizations of lactams occur by transamidation reactions between lactam rings and the ammonium groups formed during the steps of initiation. It is believed that during the reaction proton transfers take place first from the amine salts to the lactams or to the acyllactams to form cations. These in turn acylate the free amines that form with the regeneration of ammonium groups:



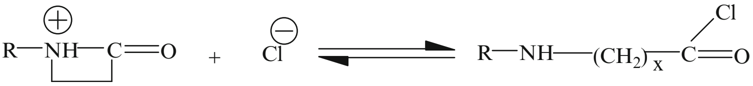


The propagation step is very rapid when aminolysis takes place at the carbonyl group of the activated acid derivative (like acyllactam or an acid chloride). It is slower, however, if it involves an amide group of the monomer [114]. As is typical of many carbonyl reactions, acylations are followed by eliminations [125]:



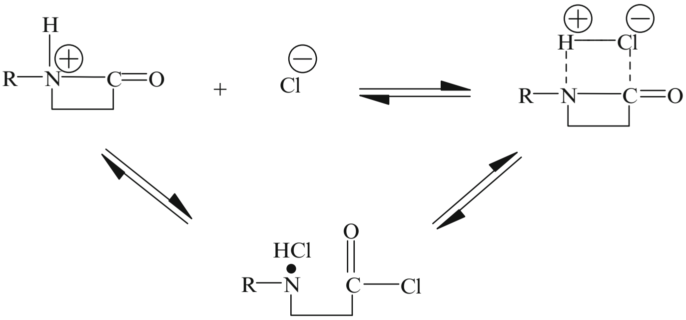
The above water elimination reaction results in formations of amidines. Acylamidinium ions can also result from dehydration of the tetrahedral intermediates during the reactions of amino groups with acyllactams. Such groups could also be present within the polymer molecules. The water that is released in these reactions hydrolyzes the acyllactams, acylamidine salts, and lactam salts to yield carboxylic acids [114].

In the cationic polymerization of lactams the ammonium and amidinium groups form N-terminal chain ends. The C-terminal chain ends are in the form of carboxylic acid groups or alkylamide residues. This is important, because the nature of the end groups and their reactivity determine the steps that follow in the polymerizations. This means that the different types of cationic polymerizations of lactams are the results of the different end groups that form during the initiation steps. Formation of amidines increases with increasing acidity and concentration of the initiator and with an increase in the temperature:

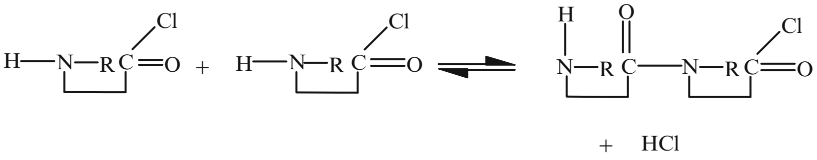


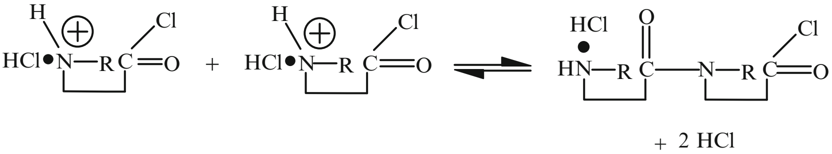
When strong acids or amine salts initiate the polymerizations, almost all amine salt groups become converted to amidine salts shortly after the start of the initiation reaction [108]. Formation of amidinium salts leads to a decrease in the reaction rate because they initiate polymerizations of lactams less effectively than do ammonium salts [125, 126]. Lewis acids act in a similar manner, unless a co-reactant is present, like water. In that case, the Lewis acids are transformed into protonic acids and the polymerizations proceed as if they were initiated by protonic acids [114].

N-substituted lactams can generally not be polymerized. Some exceptions, however, are known when cationic mechanisms are employed [122] and when strong carboxylic or inorganic acids are used as initiators. In such cases the anions of the initiating acids, like Cl^{-}, react with the lactam cations to yield amino acid chlorides [114]:



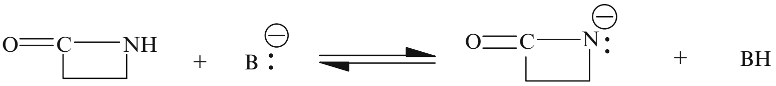
Only the more strained four-, eight- and nine-membered N-substituted lactams have so far been shown to be capable of polymerizations [113]. The 2,2-dimethylquinuclidone is highly strained and undergoes polymerizations at room temperature [127]. The propagation reaction of substituted lactams can be illustrated as follows [122]:



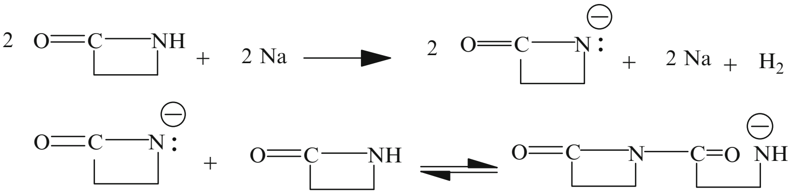


5.9.2 Anionic Polymerization of Lactams

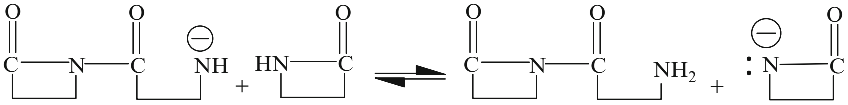
The anionic polymerizations of lactams are initiated by strong bases [128] capable of forming lactam anions:



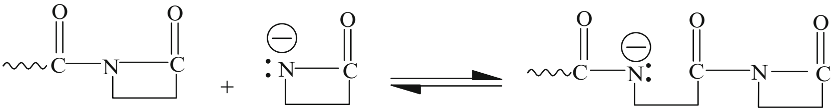
Such bases can be alkali metals, metal hydrides, organometallic compounds, and metal amides. The initiation step of ring-opening amidation can be shown as follows:



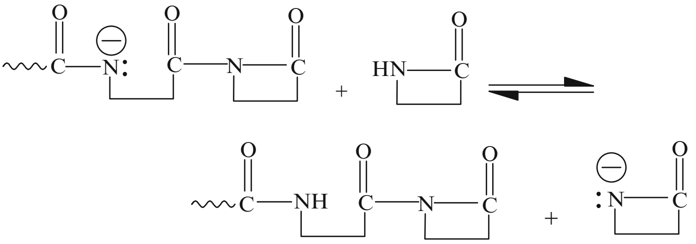
The primary amine anions abstract protons very rapidly from other molecules of lactams to form amino-acyllactams [130]:



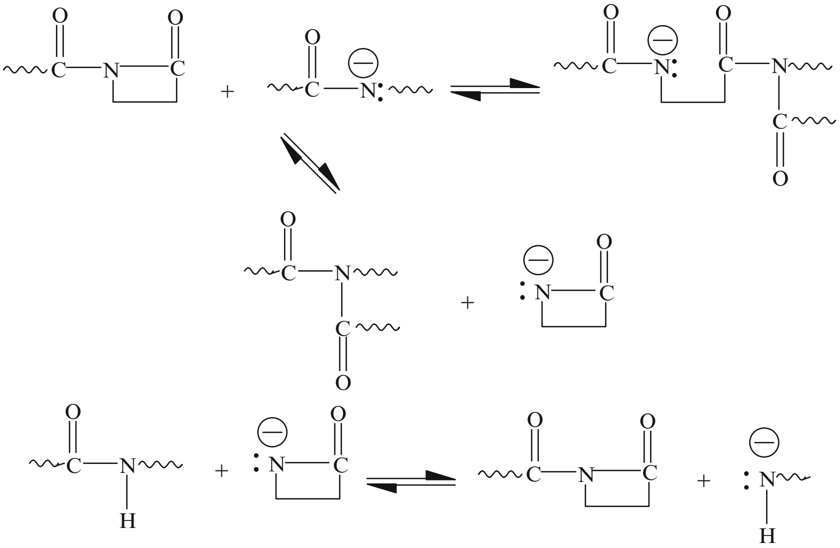
In these reactions, the propagation centers are the cyclic amide linkages of the N-acylated terminal lactam rings. Acylation of the amide nitrogens have the effect of increasing the electron deficiencies of these groups. This in turn increases the reactivities of the cyclic amide carbonyls toward attacks by the nucleophilic lactam anions [115]:

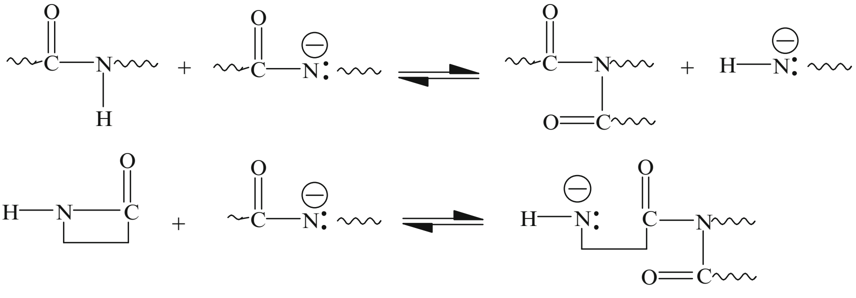


Very rapid proton exchanges follows. This results in equilibrium between the lactam and the polymeric amide anions [129]:



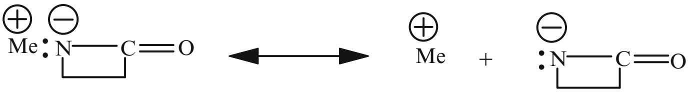
The polymer amide anions can undergo acylation by acyllactam groups with accompanying ring opening or with formation of lactam anions. In the first instance, it is an alternate path of propagation with formation of imide groups:





The acylation reactions shown above are much faster than the initiation reactions [129, 131] As a result, there are induction periods in anionic polymerizations of lactams [113]. In addition, steep increases in molecular weights take place at the beginning of the polymerizations. Bimolecular aminolyses may contribute to that, though their contributions to the total conversions are negligible [113].

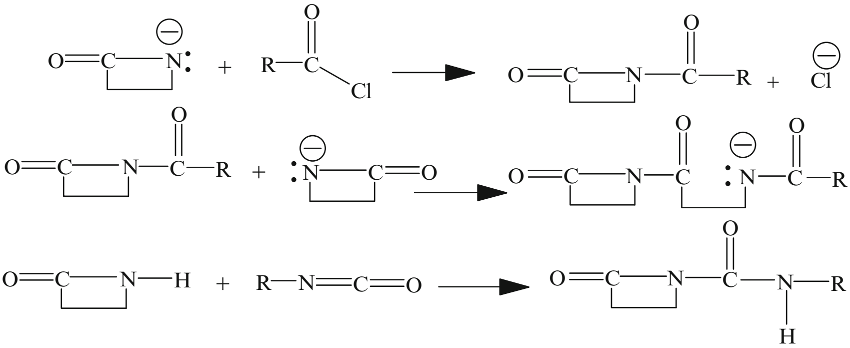
The overall rates of polymerizations depend on the concentrations of acyllactams and diacylamine groups as well as on the lactam anions. The latter result form dissociations of the lactam salts, depending upon the nature of the metal:



where Me means metal The alkali metals can be rated in the following order with respect to rates of initiations and propagations [113, 132]:

Li<Na<K<Ca

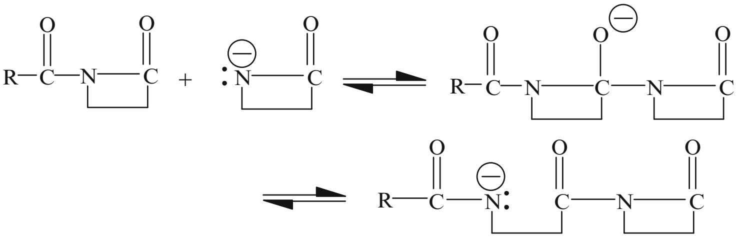
Additions of *activators* or cocatalysts, such as acyl halides, anhydrides, or isocyanates, can result in elimination of the induction period. These additives insure formations of stabilized adducts:



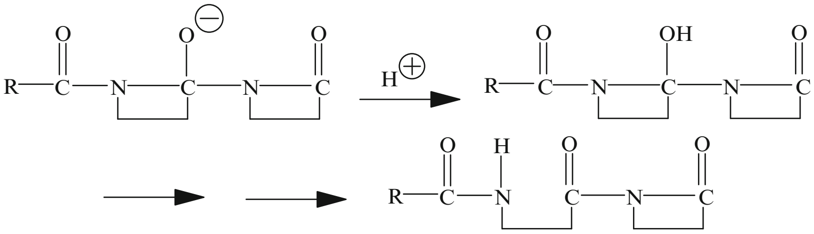
The structures of the activators can determine the rates of addition to the first lactam anion [113]. If, for instance, the acyl group is large, as in pivaloylcaprolactam, the decrease in the rate can be merely due to steric hindrance [113, 129]. On the other hand, substituents like the benzoyl group increase the rates of additions to the first lactam anions [113, 129]. In addition, the structures of the activators can also affect the course of the polymerization. This is because they become incorporated at the end of the polymeric molecules and may influence the basicity during the polymerization reactions.

Polymerizations in the presence of acylating agents are often called *activated* polymerization. If the acylating agents are absent from the reaction mixture the reactions may be called *nonactivated*. Sometimes the terms *assisted* and *nonassisted* are used instead.

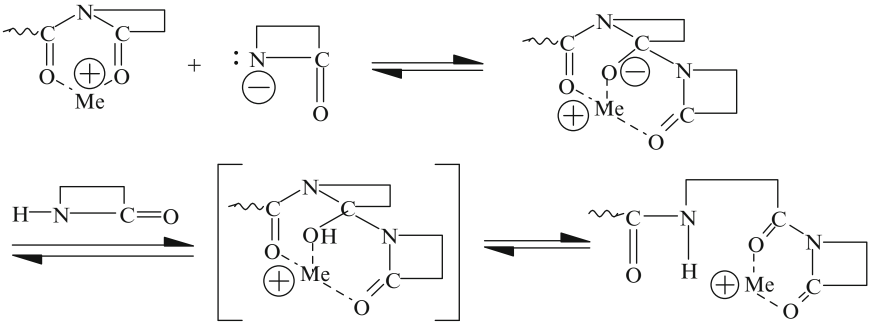
Several reaction mechanisms were offered to explain the mechanism of anionic ring-opening polymerizations of lactams. One mechanism is based on nucleophilic attacks by the lactam anions at the cyclic carbonyl groups of N-acylated lactams. This leads to formations of intermediate symmetrical mesomeric anions that rearrange with openings of the rings [133, 134]:



Champetier and Sekiguchi concluded that the intermediate anions are neutralized first by protons from the lactams or from the polymer amide groups. The neutral molecules subsequently rearrange with the openings of the penultimate units [135, 136].

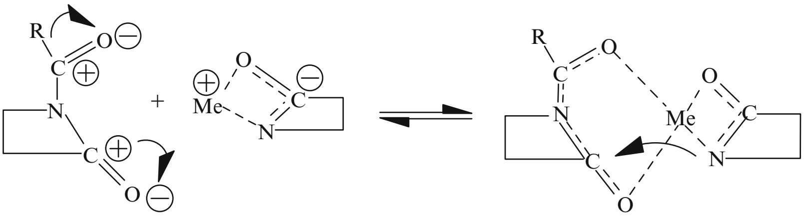


They also felt that the acylating strength of the acyllactams is enhanced by coordination of the cations with the imide carbonyl groups [135, 136]. This is based on an assumption that the incorporations of the lactam units proceed through additions of lactam anions. Protonations and subsequent rearrangements follow [135, 136]. This type of chain growth is termed *lactomolytic* propagation [137]:



The mechanism implies that the alkaline cation is fixed to the imide group and that a nucleophilic attack (that is the rate-determining step) by the lactam anion takes place on the endocyclic carbonyl group of the imide to give a “carbinolate” anion. Proton exchange takes place between this intermediate and a lactam monomer. Intramolecular rearrangement results in ring opening of the unit that is now in the penultimate position.

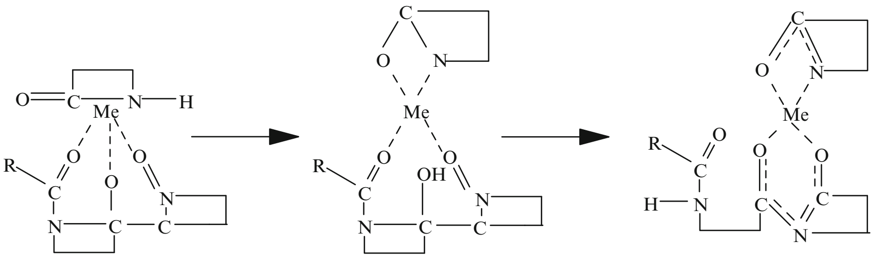
In anionic activated polymerization of ε-caprolactam chain growth involves both free anions and ion pairs [138]. Quantum-chemical calculations suggest that in the alkali metal lactamate molecule the negative charge is delocalized between the oxygen and the nitrogen heteroatoms. This led to a suggestion by Frunze et al [138]. that the acts of initiation are formations of activated intermediate chelate type complexes between the activators and the catalyst molecules [138]:



complex

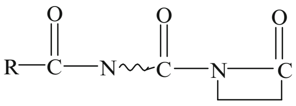
where Me is a metal like Li, K, Cs, etc.

The carbinol fragment of the resulting complex, shown above, undergoes an intramolecular rearrangement. It leads to opening of the heterocyclic ring and to growth of the polymer chain by one unit:

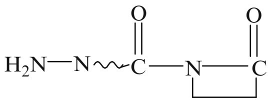


The Frunze et al. mechanism [138] has much in common with the “alkali lactomolytic” mechanism of Champetier and Sekiguchi [135], except for the formation of the above shown complex. Frunze et al. also believe that probably a single mechanism exists for the anionic polymerization of lactams that they describe as *ion-coordinative* [138]. The contributions of various mechanisms via ion pairs or via free ions depend upon the nature of the alkali metal counterion and upon their capacity to coordinate with electron donating compounds (activator and monomer). The growth of ion pairs may mainly be expected from a lithium counterion, while growth by free anions may be expected from potassium or cesium

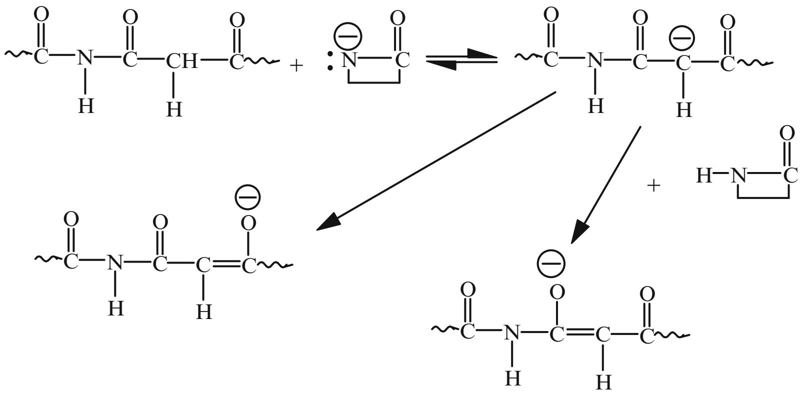
The products of anionic lactam polymerizations can vary, depending upon reaction conditions such as the temperatures, and upon the structures of the lactams themselves. Thus, five-, six-, and seven-membered lactams polymerize at different temperatures and the products differ in molecular weights. For instance, α-pyrrolidone polymerizes readily at 30°C to a polymer of a molecular weight of 15,000, while ε-caprolactam requires 178°C to form polymers of that size or larger [137]. A third lactam, α-piperidone is hard to polymerize to a high molecular weight polymer in good yields [137]. The regular molecules that form in activated anionic polymerizations, as already shown, are [139]:



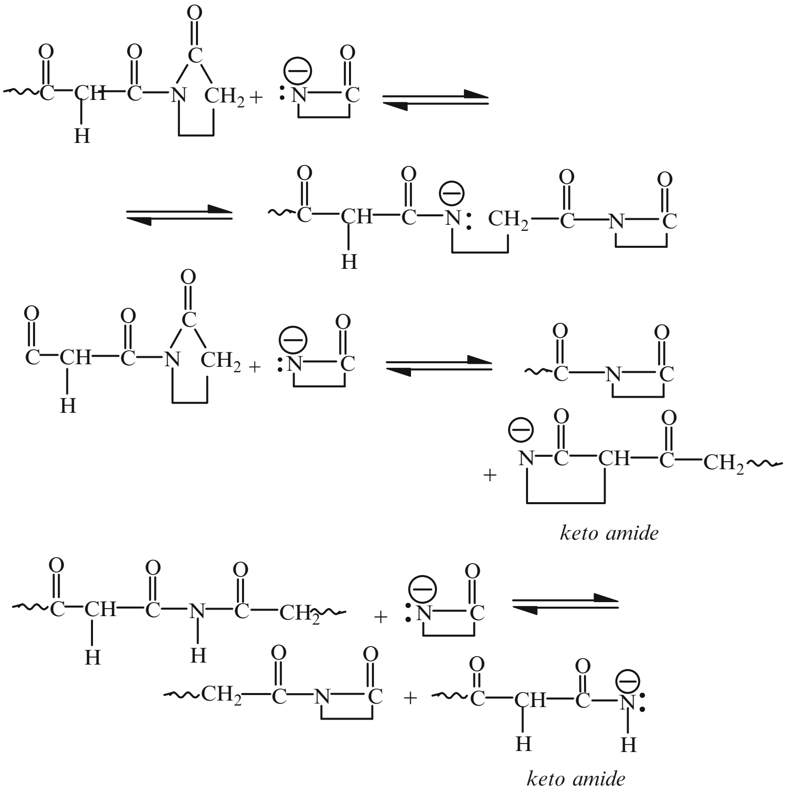
while those activated by lactam anions, are:



At higher polymerization temperatures, however, side reactions occur. Among them are Claisen type condensations. They lead to two type of N-acylated β-keto imide structures and take place readily above 200°C. Formation of these imides decreases the concentration of lactam anions:



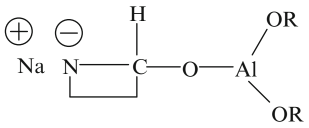
Cyclic keto imides as well as linear ones can yield active species through acylation of lactam anions. This results in formations of growth centers and keto amides:



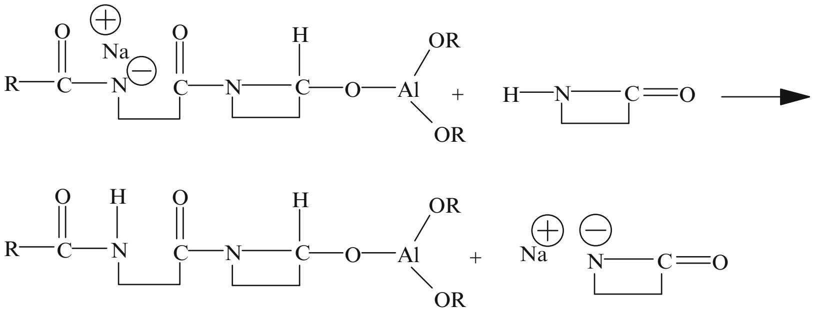
The acidity of keto amides with α-hydrogen atoms is much greater than that of the monomers or of polymer amide groups. Any formation of such structures, therefore, decreases the concentration of lactam anions.

Side reactions give rise to a variety of irregular structures that may be present either in the backbones, or at the ends of the polymer molecules, or both. Formation of branches in anionic polymerizations occurs in polymerizations of ε-caprolactam [140, 141]. This lactam and higher ones polymerize at temperatures greater than 120°C. Above 120°C the β-keto-amide units and possibly the *n*-acyl-keto-amide structures are preserved. They may, however, be potential sites for chain splitting later during polymer processing that takes place at much higher temperatures [142].

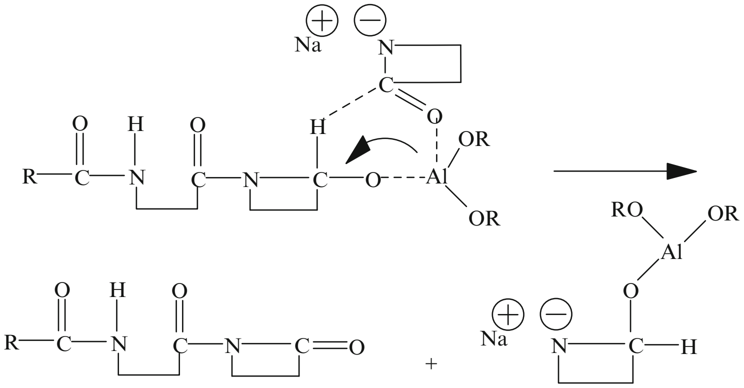
A new group of catalysts, metal dialkoxyaluminum hydrides, for anionic polymerizations of lactams, were reported recently [143]. A different anionic mechanism of polymerization apparently takes place. When ε-caprolactam is treated with sodium dialkoxyaluminum hydride, a sodium salt of 2(dialkoxyaluminoxy)-1-azacycloheptane forms:



Such compound differs in nucleophilicity from activated monomers. These salts are products of deprotonation of lactam monomers at the amides followed by reduction of the carbonyl functions. It is postulated that during lactam polymerizations, after each monomer addition, the active species form again in two steps [143]. In the first one proton exchanges take place:



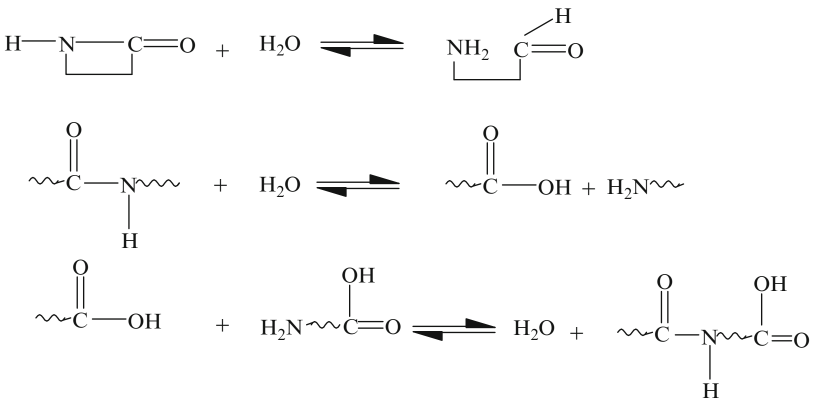
in the second step hydrogen and dialkoxyaluminum group are transferred:



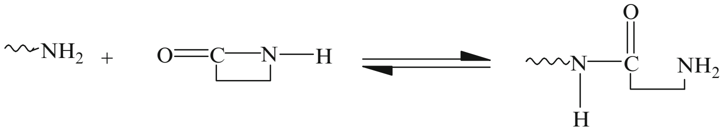
The third step is propagation. It consists of addition of a unit to the chain end and takes place upon reaction of the terminal acyl lactam with a sodium salt of 2(dialkoxyaluminoxy)-1-azacycloheptane shown above [143].

5.9.3 Hydrolytic Polymerization of Lactams

This polymerization can be looked upon as a special case of cationic polymerization. It is particularly true when weak acids are added to the reaction mixture, as is often the case in industrial practice. In hydrolytic polymerizations of lactams initiated by water, the hydrolysis–condensation equilibria determine the concentrations of the amine and the carboxylic acid groups. Both functional groups participate in the propagation reactions:



The concentration of these groups also determines the molecular weights of the final products [118–128]. This type of equilibria also occurs in polymerizations initiated by amino acids or by salts of carboxylic acids formed with primary and secondary amines. In the hydrolytic polymerizations of caprolactam the above reactions involve only a few percent of the total lactam molecules present [144, 145]. The predominant propagation reaction is a step-growth addition of lactam molecules to the end groups. It is acid catalyzed [144, 145]:



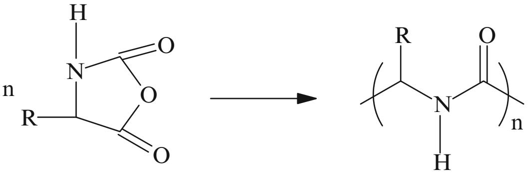
The exact mechanism of this addition is uncertain. It was postulated that the addition steps are through reactions of neutral lactam molecules with ammonium cations [146–148]. Others felt, however, that the lactam molecules add to the undissociated salts [149].

Hydrolytic polymerizations are the smoothest of all three types of polymerization reactions because the growing species are less activated than in either cationic or anionic polymerizations. Many commercial processes utilize it in ε-caprolactam polymerizations. Formation of irregular structures, however, and even crosslinked material was detected. In addition, at elevated temperatures deamination and decarboxylation of polycaprolactam can take place [150] Such reactions can result in formations of ketones and secondary amine groups. The ketones, in turn, can react with amines and form Schiff bases. This leads to branching and crosslinking.

In industrial preparations most of the water used to initiate the polymerizations is removed after conversions reach 80–90% in order to attain high molecular weights. The final products contain about 8% of caprolactam and about 2% of a cyclic oligomer [150]. These are removed by vacuum or hot water extraction. The material is then dried under vacuum at 100–200°C to reduce moisture to about 0.1%.

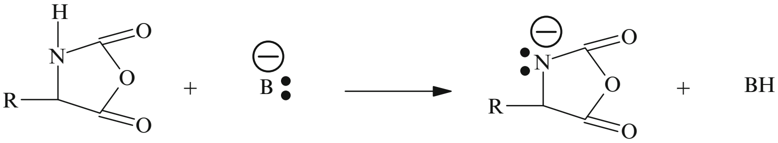
5.10 Polymerization of *N*-Carboxy-α-Amino Acid Anhydrides

The polymerizations of these anhydrides (or substituted oxazolidine-2,5-diones) can be carried out with basic catalysts to yield polyamides:

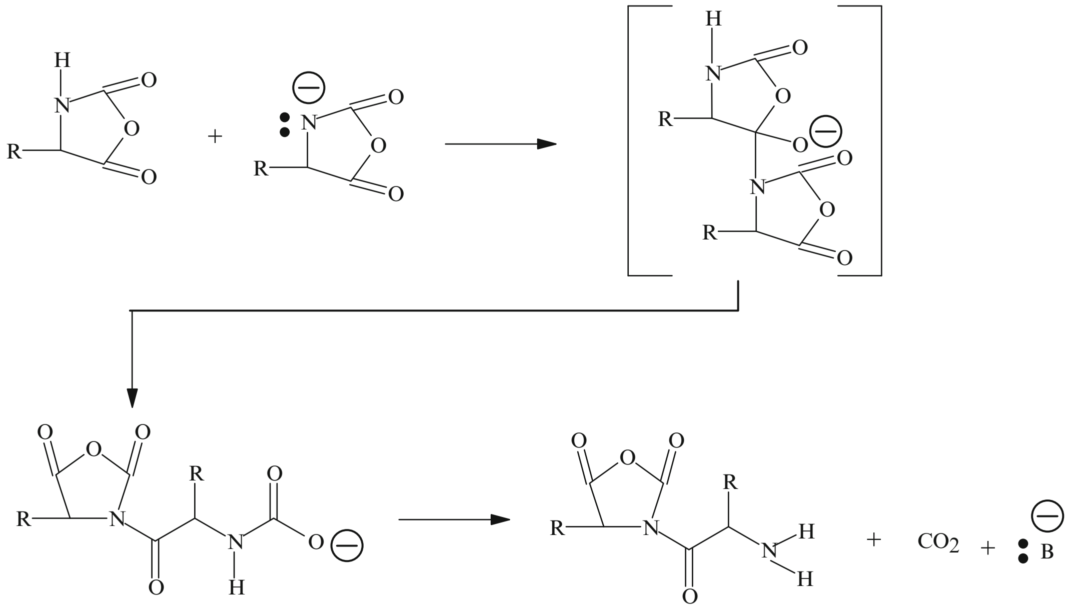


These polymerization reactions are important to biochemists because the products are poly(α-amino acid)s and resemble the building blocks of naturally occurring polyamides.

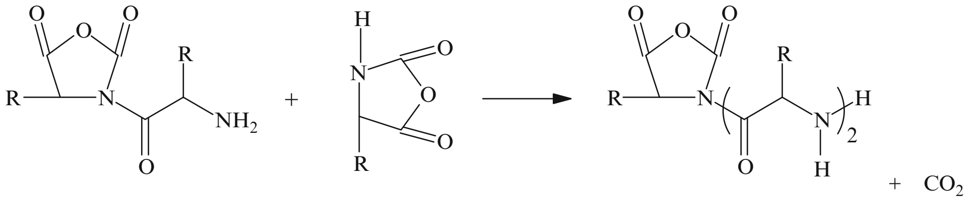
When the polymerization is initiated with strong bases, the initiating step is hydrogen abstraction from the anhydride by the base. This results in formation of *activated* species:



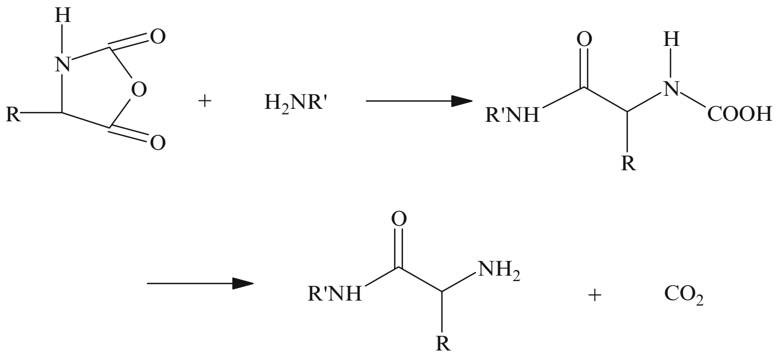
The reaction then proceeds by the *activated mechanism*. The initiation reaction was pictured by Ballard and Bamford [151] as follows:



Each propagation step consists of an addition of one unit of the anhydride and an accompanying loss of carbon dioxide:

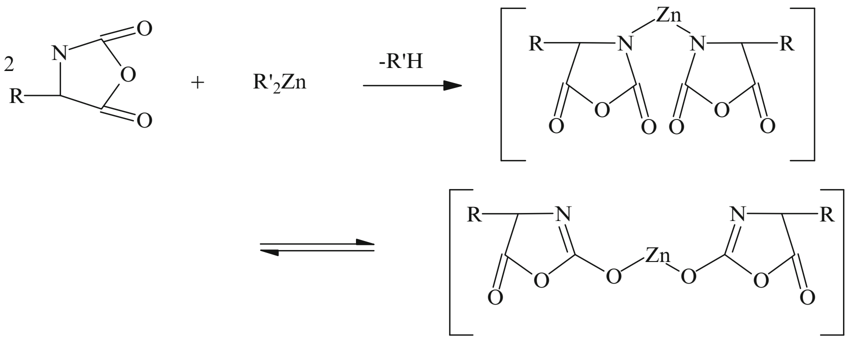


When the reaction is initiated by primary amines, the first step is a nucleophilic attack by the amine on the C_3 of the anhydride [151–153]. The carbon dioxide that is released comes from the C_2 carbonyl group. The propagation proceeds by addition of terminal amine groups to the C_3 carbonyl groups of the monomers [151–153]:

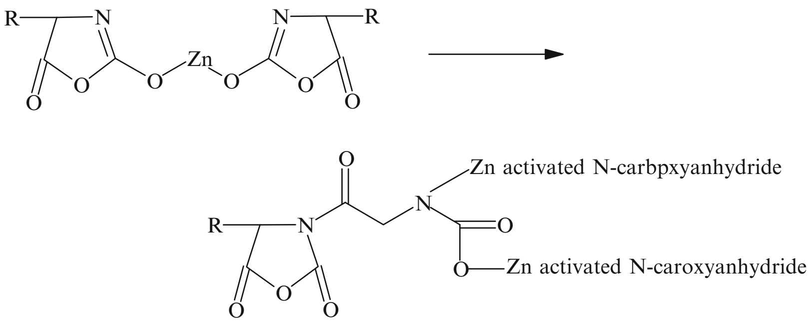


The polymerization rate depends upon the concentration of the amine and the monomer. The degree of polymerization is often but not always equal to the ratio of the monomer to the amine [154]. It means that the reaction may be similar to but not identical to a living type polymerization. In addition, the molecular weight distribution curve may be broadened or bimodal. This may be due to some chemical termination reactions. These can be intramolecular reactions of the terminal amine group with some functional group in the side chain and lead to formation of hydantoic acid end groups [154]. It may also be due to physical termination from precipitation of the product.

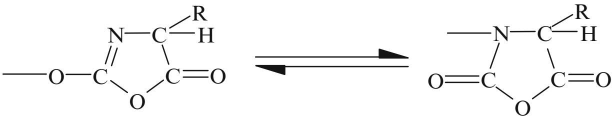
Dialkylzinc initiated polymerizations apparently take place by a different mechanism. The first step is pictured by Makino, Inoue, and Tsuruta as a hydrogen abstraction by dialkylzinc from NH [155]. This is similar to the reaction with a base shown earlier. The second stage of initiation, however, is a reaction between two molecules of the activated carboxyanhydrides, and formation of zinc carbamate [155]:



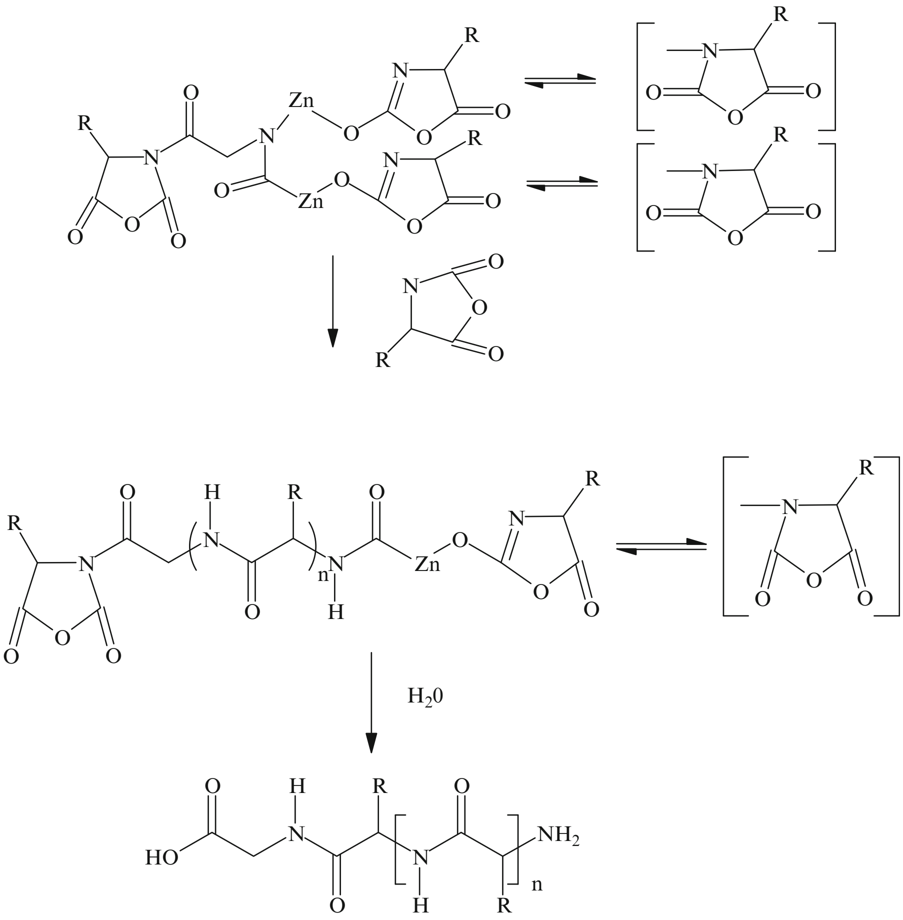
The propagation is a carbonyl addition of the zinc carbamate to the activated *N*-carboxyanhydride to form a mixed anhydride. The mixed anhydride then changes into an amide group with elimination of carbon dioxide [155]:



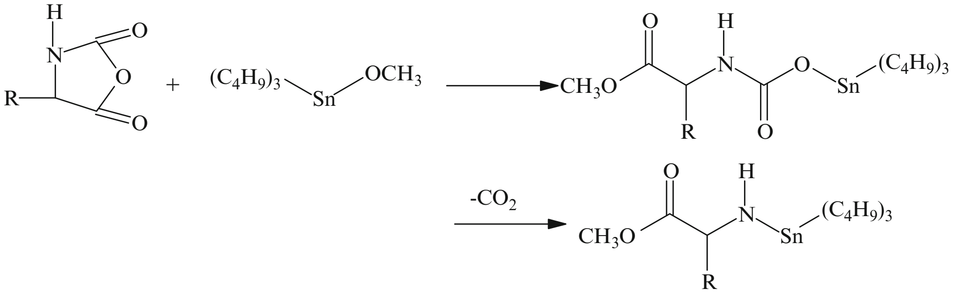
where, the activated *N*-carboxyanhydride portion is [155]:



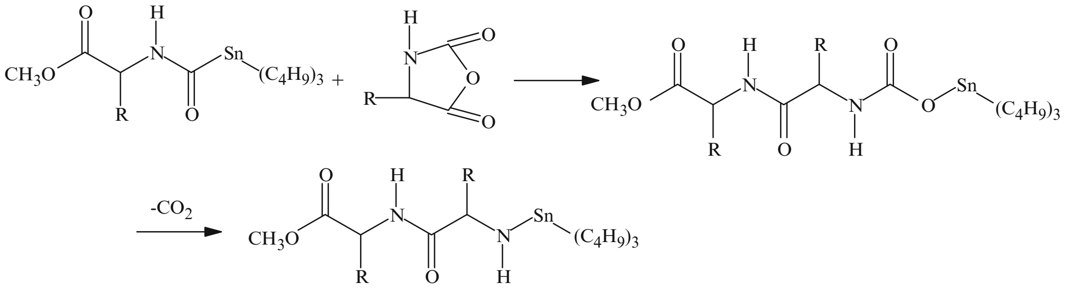
The complete reaction can be illustrated as follows:



Organotin compounds are also active as catalysts in the polymerizations of *N*-carboxyanhydrides [156]. The mechanism of the reaction was postulated by Freireich, Gertner and Zilkha [156] to consist of addition of the organotin compound to the anhydride and formation of organotin carbamate. It subsequently decarboxylates and leaves an active –N–Sn– group that adds to another molecule of *N*-carboxyanhydride. This process is repeated in every step of the propagation [156]:



Propagation



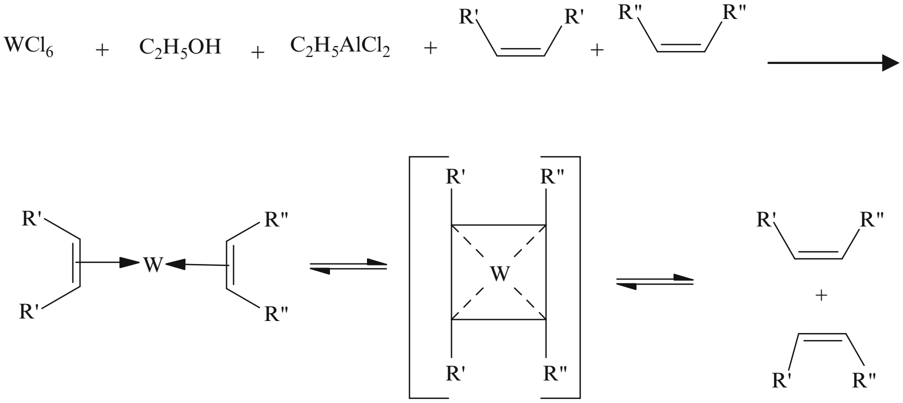
When *N*-carboxyanhydride polymerizations are initiated by secondary amines with small substituents, the amines act as nucleophiles, similarly to primary amines [157]. Secondary amines with bulky substituents, however, produce only *N*-carboxyanhydride anions. The same is true of tertiary amines. These anions in turn initiate polymerizations that proceed by the "active monomer mechanism."

Messman and coworkers did a mechanistic study of α-amino acid carboxy anhydride polymerization [158] They polymerization in high vacuum with polymerization at atmospheric The conclusion of their work was that poly(*O*-benzyl-L-tyrosine) prepared in vacuum yields a polymer by normal amine mechanism with minimum termination. By contrast when the reaction was not carried out at high vacuum, there were several termination products.

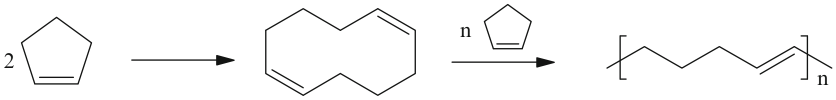
5.11 Metathesis Polymerization of Alicyclics

Ring-opening polymerizations of alicyclics by Ziegler–Natta type catalysts resulted from general studies of olefin metathesis [158–160]. These interesting reactions can be accomplished with the aid of many catalysts. The best results, however, are obtained with complex catalysts based on tungsten or molybdenum halides. One such very good catalyst forms when tungsten hexachloride is combined in right proportions with ethylaluminum dichloride and ethanol.

Several reaction mechanisms were proposed to explain the course of olefin metathesis. Most of the evidence supports a carbene mechanism involving metal complexes, originally suggested by Harrison and Chauvin [160–163]. A typical metathesis reaction of olefins can be illustrated as follows:

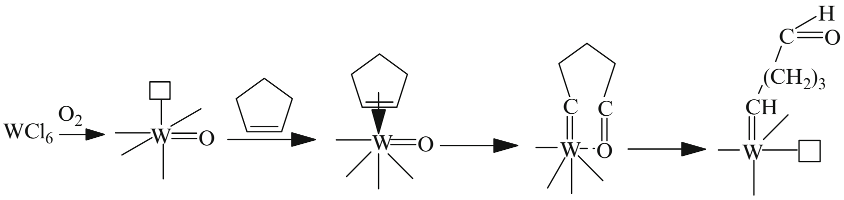


When this reaction is applied to cyclopentene, a high molecular weight polymer forms [164]:

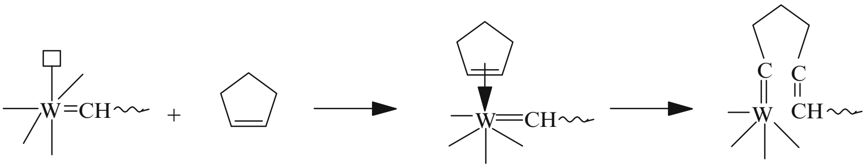


Tungsten hexachloride can apparently also act as a catalyst without the aluminum alkyl. In that case it is believed to be activated by oxygen [166].The propagation reaction based on the tungsten carbene mechanism can be shown as follows [162]:

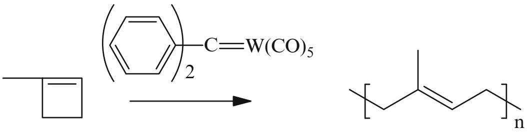
Initiation



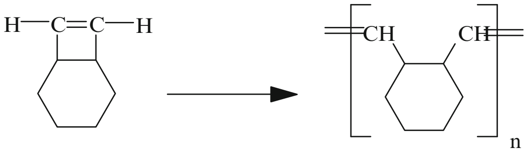
Propagation



It is significant that metal carbenes can act as catalysts for this reaction. Thus, a carbene $(C_6H_5)_2$–C=W(CO)$_5$ will polymerize 1-methylcyclobutene to yield a polymer that is very similar in structure to *cis*-polyisoprene [162]:

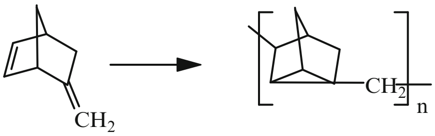


This carbene also yields high molecular weight linear polymers from bicyclo[4.2.0]octa-7-ene monomer [167]:

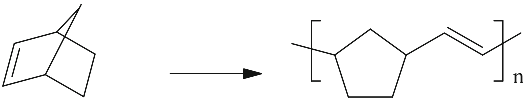


The same product can also be obtained with $WCl_6/Sn(CH_3)_4$ catalyst. The molecular weight of the product, however, is lower [167].

Some cycloolefins can undergo either a regular cationic polymerization or a metathesis one, depending upon the catalyst. One of them is norbornene and its derivatives. For instance, 5-methylene-2-norbornene polymerizes by a cationic mechanism with a 1:1 combination of tungsten hexachloride with tetraalkyltin. A 1:4 combination of a tungsten halide with either $C_2H_5AlCl_2$, or $MoCl_5$, or $TiCl_4$, or other acidic catalysts [166] yields the same product. The polymer that forms has the repeat units:



On the other hand, metathesis type polymerizations of norbornene takes place with WCL$_6$–[(C$_2$H$_5$)$_3$Al]$_{1.5}$ or WCl$_6$–(CH$_3$)$_4$Sn to yield [166]:



The product, poly[1,3-cyclopentylenevinylene], is a commercial synthetic specialty rubber, with a trade name of *Norsorex*. Reports in the literature show that there may be more than one mechanism of termination [160, 165]. One may be by formation of cyclopropane rings. This is a typical reaction of carbenes [160]. Another one, by a reduction of the transition metal and formation of free radicals [160]:

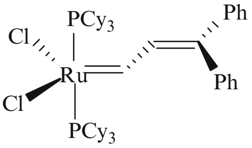
$$\sim\!\sim CH{=}WCl_x \longrightarrow \sim\!\sim CHCl^{\bullet} + WCl_{x-1}$$

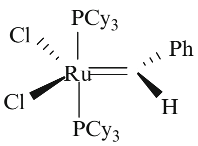
Still another way may be by hydrogen migration in the carbene complex [151]:

$$\sim\!\sim CH_2{-}CH{=}WCl_x \longrightarrow \sim\!\sim CH{=}CH_2 + WCl_x$$

The chemistry of metathesis polymerization has been applied to preparation of unsaturated polycarbonates [168].This is a case of an acyclic diene metathesis. It takes place when Lewis acid free-catalysts are employed [169]. An example of one such catalyst is Mo[CHC(CH$_3$)$_2$Ph](*N*-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCCH$_3$(CF$_3$)$_2$]$_2$. One interesting point about this process is that unconjugated dienes are polymerized to high molecular weight linear polymers without formations of any cyclic structures.

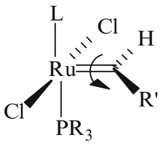
The ring-opening catalysts described above show sensitivity towards oxygen and moisture. Catalysts, however, that are based on ruthenium and osmium, often referred to as ***Grubbs catalysts***, exhibit good stability towards oxygen and moisture [170]. Examples of such catalysts are RuCl$_3$(hydrate), OsCl$_3$(hydrate), and ruthenium benzylidine catalyst, like (Cyclohexyl$_3$P)$_2$Cl$_2$ Ru=CH–CH=CPh and (Cyclohexyl$_3$P)$_2$Ru=CHPh [170]. They can be illustrated as follows:





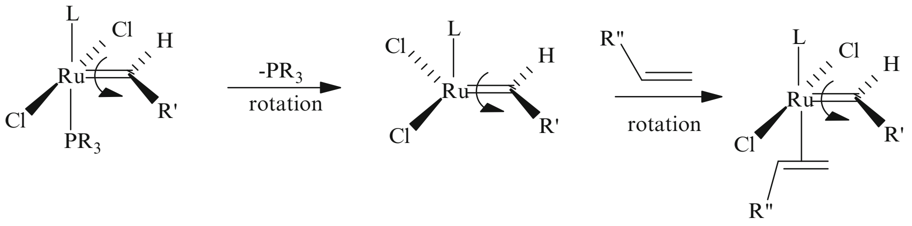
These materials require a small amount of solvent for activation.

A second generation of the Grubbs catalyst has a higher metathesis activity. It can be illustrated as follows:



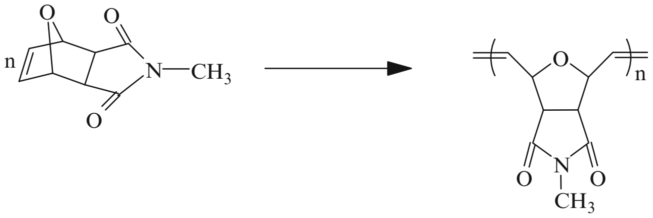
In the first generation, L is PR$_3$, as shown above, but in the second generation L is N-heterocyclic carbene, R is a cyclohexyl group, and R′ is a phenyl group.

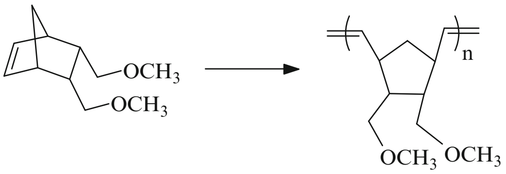
The discrepancy between the two catalysts was elucidated by Truhlar et al. [170] with aid of a computational density functional method named Mo6-L. They found that the benzylidine ligand in both catalysts rotates and serves as a toggle switch to trigger the metathesis reaction. The rotation precedes dissociation in the Grubbs 1 catalyst but occurs in synchronization with the dissociation in the Grubbs 2 catalyst [170].



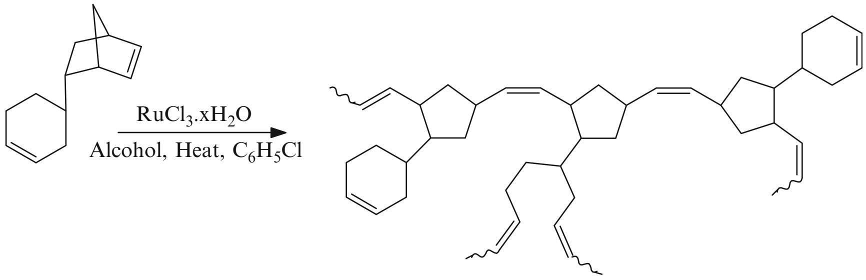
When the olefin substrate coordinates to ruthenium in the Grubbs 1, the catalyst must overcome electronic effects stemming from the rotation, a barrier that is lower in Grubbs 2.

Following are examples of polymerization reactions that were carried out with Grubbs catalysts [170]:



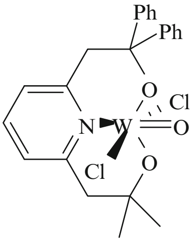


Another example, using a different ruthenium catalyst is polymerization of cyclohexenyl norbornene to form high molecular weight products [171]:



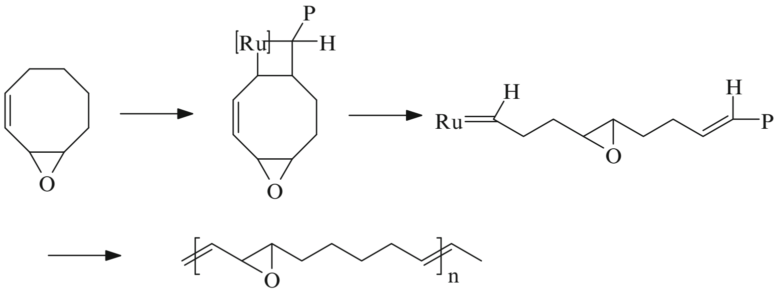
The versatility of these catalysts was further illustrated, when ring-opening metathesis polymerizations of norbornene were carried out in liquid carbon dioxide at high pressure, using Ru $(H_2O)_6$–$(Tos)_2$. The product was reported to be *cis*-ditactic polynorbornene [172]. It should be noted, however, that stereoselective polymerizations of norbornene are not confined to these catalysts only.

For instance, polymerization of norbornene with a tungsten based catalyst, combined with $(C_2H_5)_3Al$ as the co-catalyst,



was reported to have yielded at −78°C, 92% *cis* polymer [173].

Nevertheless, the Grubbs catalysts are very versatile and have made a great impact on polymer chemistry. Following are additional examples of use of Grubbs catalysts. One of them is ruthenium catalysts based on $[RuCl_2(arene)]$ dimers, with ligands of durene or *p*-cymene. They were formed by addition of tricyclohexylphosphine and activated with (trimethylsilyl)diazomethane [174]. These catalysts show good functional compatibility in preparation of a variety of polyoctenamers with epoxide, acid, ether, ester, acetal and bromine functionalities.^{236} The following illustration serves as an example [174]:

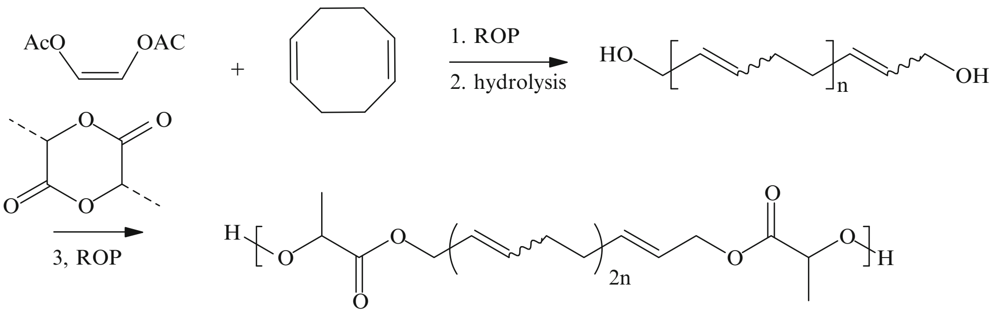


In addition, it was shown that some ring-opening metathesis polymerizations exhibit the characteristics of living polymerizations. Thus, the polymerization of cyclobutene with a tungsten catalyst $[W(CH\text{-}t\text{-}C_4H_9)(NAr)(O\text{-}t\text{-}C_4H_9)_2]$ (Ar = 2,6-diisopropyllphenyl), was shown to fit the category of living polymerization and was used to form block copolymers [175, 176]. Similarly, some substituted cyclobutanes were polymerized in a living manner using a molybdenum catalyst, $Mo(CHC(CH_3)_2Ph)(NAr)(OC(CH_3)_2CF_3)_2$ [Ar = 2,6-diisopropylphenyl] in combination with $PPhMe_2$ [177]. Also, bicyclo[3.4.0]heptene polymerization was found to be a living one when a ruthenium catalyst, $(PPh_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ was used [178].

Polymers that contain pendant carbazole groups can exhibit photoconductivity (see Chap. 10). Formation of block copolymers with pendant carbazole groups was reported via a living ring-opening metathesis polymerization using a ruthenium catalyst [179]. In addition, what appears to be a first example of a homogeneous living polymerization in water was reported recently [180]. The reaction was carried out in the presence of a Bronsted acid using alkylidine ruthenium complexes. Water-soluble monomers polymerized quickly and quantitatively in the absence of surfactants or organic solvents. These polymerizations were found not to be living, however, when the Bronsted acid was absent [180]. It was suggested that the function of the acid is to eliminate hydroxide ions and to enhance the catalyst activity by protonating the phosphine ligands [2180].

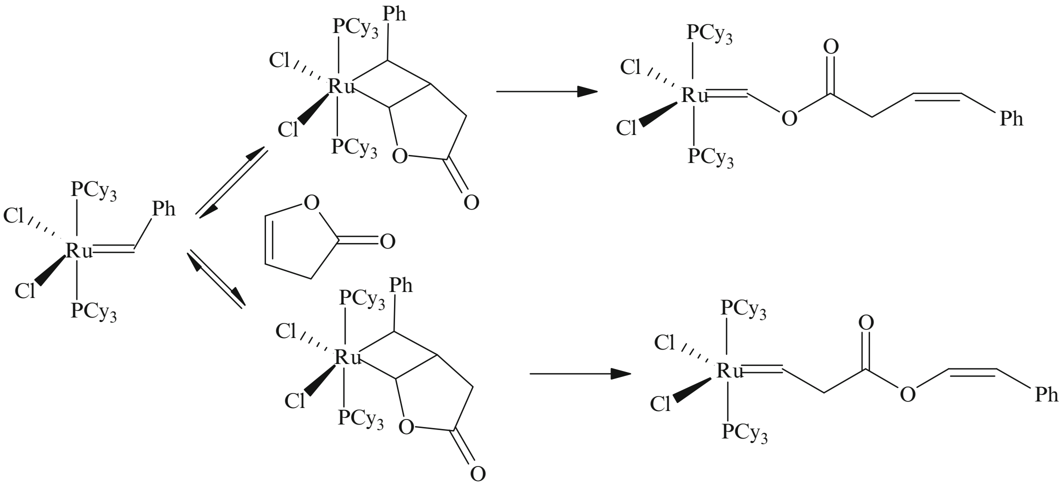
Yong and Swager [181] reported ring-opening metathesis copolymerizations of calixarene containing monomers with cyclooctene and norbornene to yield high molecular weight transparent elastic polymers.

Pitet and Hillmyer [182] combined metathesis ring-opening polymerization with cyclic ester ring-opening metathesis polymerization to form triblock AABA copolymers of cycloocatadiene and D,L-lactide.



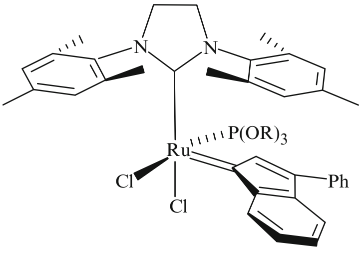
The product is a terpolymer with a soft midblock component with hard blocks at the end. As a result the polymer is a strong and tough material.

Ruthenium catalysts are reactive only towards olefins. As a result, it is possible to introduce functional groups into the monomer prior to polymerizations. This was demonstrated by Hilf and Kilbinger [183] They demonstrated that small ring vinyl lactones and carbonates are efficient quenchers for the olefin metathesis polymerization. The slow kinetics of the reaction can be overcome by an excess of the reagent. The rapid termination of the polymerization reaction yields highly functionalized polymers with narrow molecular weight distribution:



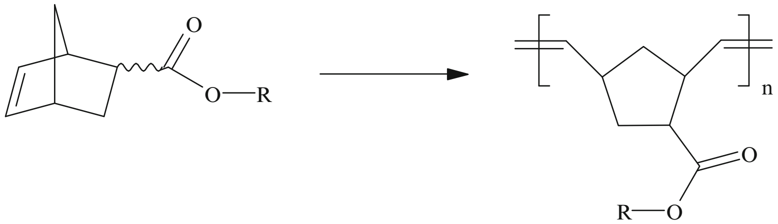
Metathesis type catalysts can also polymerize substituted acetylenes. This is discussed in Chap. 10.

A class of olefin metathesis catalysts that contains phosphite ligands has advantages over current catalysts for some challenging reactions, such as ring-closing metatheses of hindered dienes. Cazin et al. [184] modified an existing ruthenium indenylidene metathesis catalyst with triisopropyl phosphite groups to form *cis* and *trans* phosphite complexes.



The catalysts, that they call *cis*- and *trans*-Caz-1, promote a difficult tosylamine ring-closing with 100% conversion, compared with about 60% achieved by existing catalysts. And a considerably smaller amount of Caz-1 is needed to promote ring-closing metathesis of hindered dienes than is required for current catalysts. The Caz-1 catalysts also show unusually good stability and longevity in reactions [184].

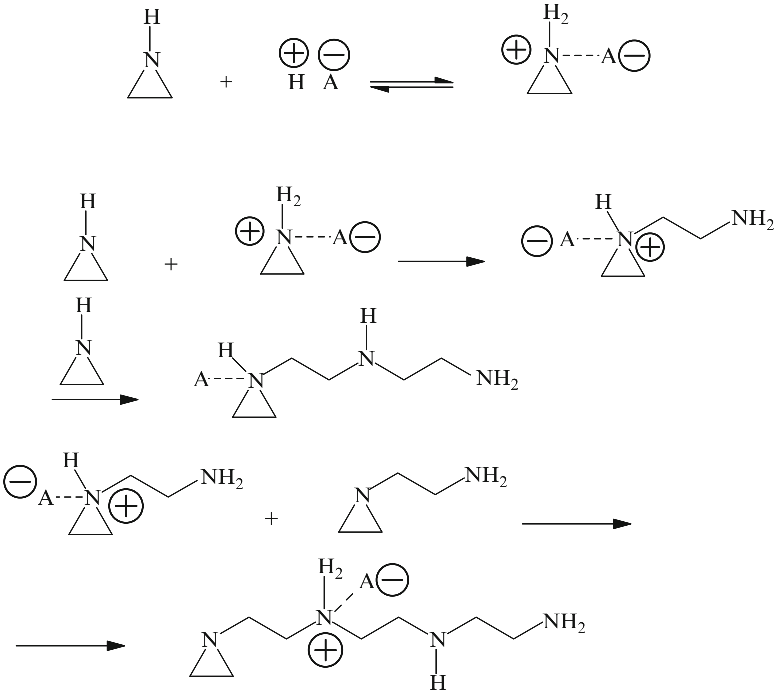
Wathier, Stoddart, and Grinstaff reported using the Grubs catalyst to form high molecular weight polymers, poly(ethyl-5-norbomene-2-carboxylate) and poly(methyl-5-oxanorbomene-2-carboxylate) carrying ester functions. The preparations were illustrated as follows [185]:

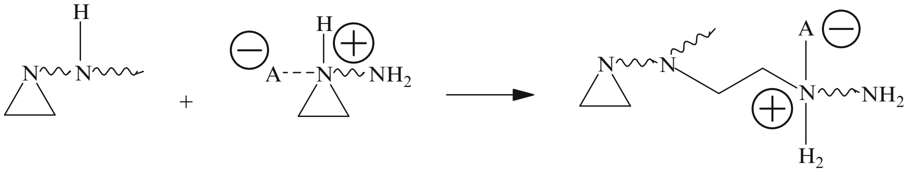


The authors point out that synthesizing high molecular weigh polymers with the aid of the Grubbs' catalyst can be difficult. Small changes in the structure of the monomer (i.e., oxa-norbornene vs. norbornene) can lead to drastic change in polymerization outcomes. On the other hand, the polymerization of norbornene with Grubbs' catalyst can lead to high molecular weight polymers with relatively narrow molecular weight distribution [185].

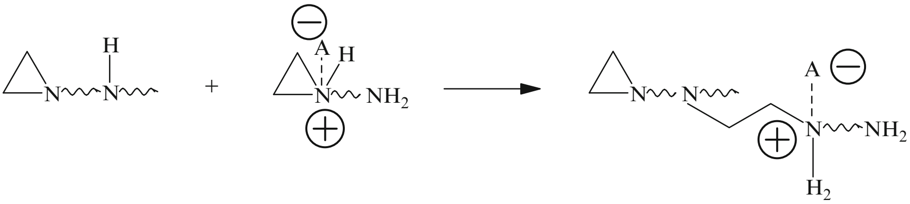
5.12 Polymerization of Cyclic Amines

The cyclic amines or imines (aziridines) polymerize only with acidic catalysts [186]. This reaction can be illustrated as follows:



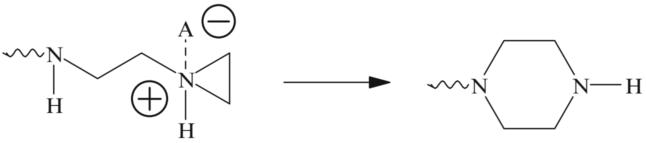


The high degree of strain in the three-membered rings causes very rapid polymerizations. A variety of cationic species act as efficient catalysts for such reactions. The propagating species are iminium ions and the propagation steps result from nucleophilic attacks by the monomers on the ions, as shown above. Branches form due to reactions of secondary amine groups with the iminium centers. They can also result from attacks by the imine end groups of inactive polymer chains on the iminium centers of the propagating species. As the reaction progresses, it slows down



because the protons become equilibrated with various amines [185]. The polymer is also extensively cyclized due to intramolecular nucleophilic attacks of primary and secondary amines on the iminium group. The product contains cyclic oligomers and polymer molecules with large size rings.

The termination mechanism is still not fully explained. It is believed that it may take place by proton abstractions from the iminium ions by the counterions, or by any nitrogen in the polymer chains, or by the nitrogens of the monomer units. It was also suggested [185, 186] that backbiting and ring expansion terminate the reactions. Such ring expansions result in formations of relatively unreactive piperazine end groups:



Substitution on the ethylene imine ring hinders polymerization [185]. The 2,3 and 1,2 substituted aziridines fail to polymerize. Only low molecular weight linear and cyclic oligomers form from 1 and 2 substituted ethylene imines.

In polymerization of secondary cyclic amines, formation of the nonstrained ammonium salt is actually a termination reaction. If the rate, therefore, of propagation, is not considerably higher than the rate of termination, the formation of high molecular weight material will not be possible. Thus ratio of k_p/k_t should, therefore be high. The rate of polymerization can be written as:

$$R_p = -\mathrm{d}m/\mathrm{d}t = k_p m[P_n{}^+]$$

where, m is the concentration of the monomer and $[P_n{}^+]$ is the concentration of the growing chains. Assuming that the termination is a first-order reaction, then, the rate of termination can be expressed as:

$$R_t = -\mathrm{d}[P_n{}^+]/\mathrm{d}t = k_t[P_n{}^+]$$

If, on the other hand, termination is a result of reactions of the growing chains with any of the amino functions of the polymer and is a second-order reaction then:

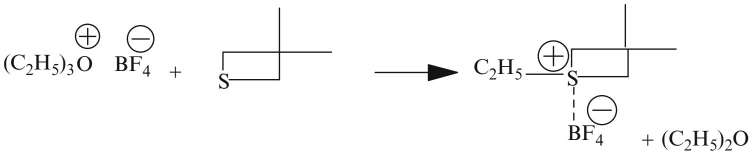
$$R_t = -d[P_n^+]/dt = k_t[P_n^+](m_0 - m)$$

where m_0 is the original monomer concentration

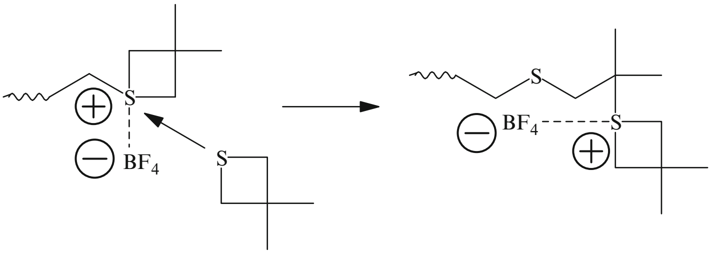
5.13 Ring-Opening Polymerizations of Cyclic Sulfides

Ring-opening polymerizations of cyclic sulfides can be carried out by anionic, cationic, and coordinated mechanisms [187–189]. These polymerizations are easier to carry out then those of the oxygen analogs, because the sulfur–carbon bond is more polarizable. On the other hand, due to the larger size of the sulfur atoms the rings are less strained than in the oxygen compounds. As a result, the sulfur analog of tetrahydrofuran fails to polymerize. In cationic polymerizations, the propagating species are sulfonium ions [189, 190] and in anionic ones the sulfide anions. Goethals and Drigvers proposed the following cationic mechanism for the polymerization of dimethyl thiethane [189]:

1. The initiation mechanism with triethyl fluoroborate consists of alkylation of the monomer molecule and formations of cyclic sulfonium ions. The reaction occurs instantaneously and quantitatively:



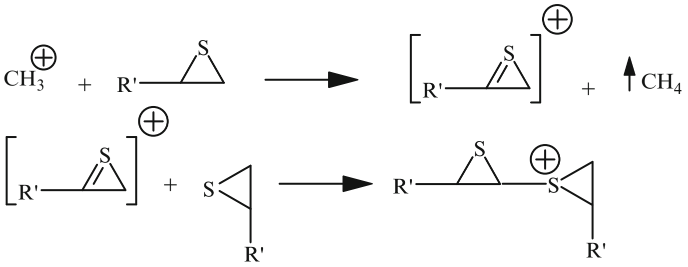
2. The propagation reaction probably involves nucleophilic attacks at the α-carbon atom of the cyclic sulfonium ions by the sulfur atoms from other monomer molecules:



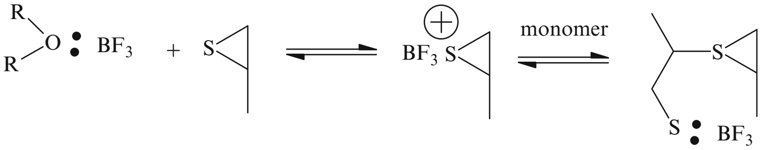
The existence of the sulfonium ions among the propagating species was confirmed with NMR studies [191].

3. Termination is presumed to occur through formations of unreactive sulfonium ions.

Two mechanisms of formation of sulfonium ions are possible: (1) by approaches to the catalyst's electron accepting sites, (2) by abstraction of hydrides by methyl cations [190]:

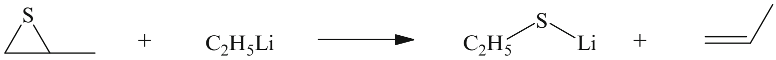


There are indications of a “living” chain-growth mechanism in boron trifluoride diethyl etherate initiated polymerizations of propylene sulfide [192] at conversions of 5–20%. In these early stages of polymerization the molecular weight corresponds to that calculated for typical “living” polymers. This is believed to take place through formations of stable sulfonium ions:

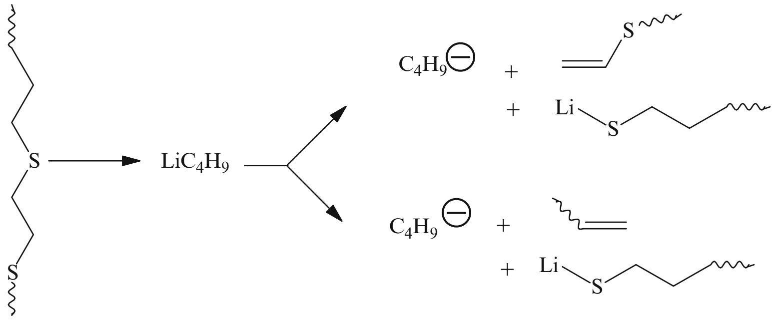


Higher conversions in thiirane polymerizations, however, proceed with chain scission transfer mechanism under the influence of $BF_3 \bullet (C_2H_5)_2O$ [192]. This is indicated by a change in the molecular weight distribution, a bimodal character. When the reaction is complete there is a marked decrease in the average molecular weight of the polymer. When thietane polymerizes with triethyl-oxonium tetrafluoroborate initiation in methylene chloride, the reaction terminates after only limited conversion [193]. This results from reactions between the reactive chain ends (cyclic sulfonium salts) and the sulfur atoms on the polymer backbone. In propylene sulfide polymerization, however, terminations are mainly due to formations of 12-membered ring sulfonium salts from intramolecular reactions [193].

When the polymerizations of cyclic sulfides are carried out with anionic initiators, many side reactions can occur. On the other hand, common anionic initiators, like KOH yield optically active polymers from optically active propylene sulfide [194]. An example of a side reaction is formation [192] of propylene and sodium sulfide in sodium naphthalene initiated polymerizations. Such reactions are very rapid even at −78°C. A similar reaction was shown to take place with ethyllithium [195]:



Other side reactions that occur in butyllithium-initiated polymerizations are cleavages of the polysulfides [192]:



High molecular weight polymers can be prepared from ethylene sulfide with a diethylzinc–water catalyst [196]. The polymers form in two steps. Initially insoluble crystalline polymers form at room temperature with a high catalyst to monomer ratio. These product polymers, that contain all of the catalyst act as seeds for further polymerizations. Though the final polymers are insoluble, the molecular weights are estimated to be high. At a conversion of 20% the molecular weights are believed to be about 900,000 [196]. When diethylzinc is prereacted with optically active alcohols, optically active poly(propylene sulfide)s form [197–199]. Cadmium salts are also very effective catalysts for polymerization of thiiranes. The polymers of substituted thiiranes have high stereoregularity.

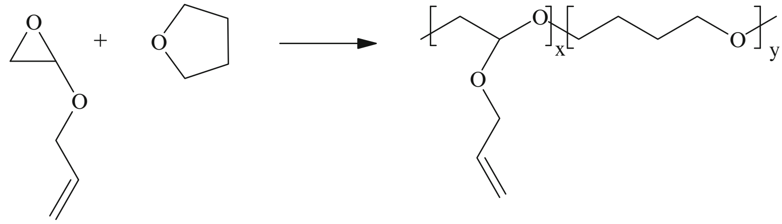
5.14 Copolymerization of Cyclic Monomers

Many copolymers have been prepared from cyclic monomers. These can form through ring-opening copolymerizations of monomers with similar functional groups as well as with different ones. Some cyclic monomers can also copolymerize with some linear monomers. Only a few copolymers of cyclic monomers, however, are currently used industrially.

The composition of the copolymers depends upon the reaction conditions, the counter ions, the solvents, and the reaction temperatures. The initiator system can be very important when cyclic monomers with different functional groups are copolymerized. Also, if different propagating centers are involved in the propagation process, copolymerizations can be very difficult to achieve.

Prominent among copolymers of cyclic ethers are interpolymers of oxiranes with tetrahydrofuran. Thus, ethylene oxide copolymerizes with tetrahydrofuran with the aid of boron trifluoride–ethylene glycol catalytic system [200]. The resultant copolyether diol contains virtually no unsaturation.

Another example is a copolymer of allyl glycidyl ether with tetrahydrofuran formed with antimony pentachloride catalyst [201]:

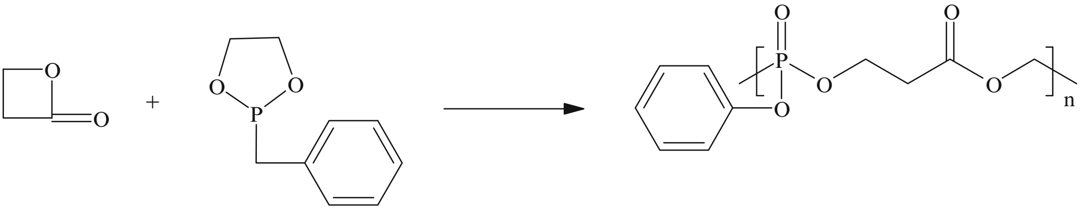


In addition to the above, liquid copolymers form from 1,3-dioxolane with ethylene oxide, when boron trifluoride is used as the catalyst [1]. Also, a rubbery copolymer forms from tetrahydrofuran and 3,3-diethoxycyclobutane with phosphorus pentafluoride catalyst [202]. A 3,3-bis(chloromethyl) oxacyclobutane copolymerizes with tetrahydrofuran with boron fluoride or with ferric chloride catalysis. The product is also a rubbery material [1].

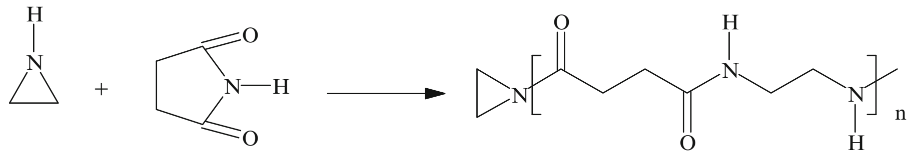
Various copolymers were reported from trioxane with dioxolane or with glycidyl ethers [2, 3]. For instance, a copolymer of trioxane and dioxolane forms with $SnCl_4$, BF_3, or $HClO_4$ catalysts. The products from each reaction differ in molecular weights and in molecular weight distributions. Copolymerizations of trioxane with phenylglycidyl ether yield random copolymers [203].

Different lactones can be made to interpolymerize [204]. The same is true of different lactams [205–207]. The products are copolyesters and copolyamides, respectively.

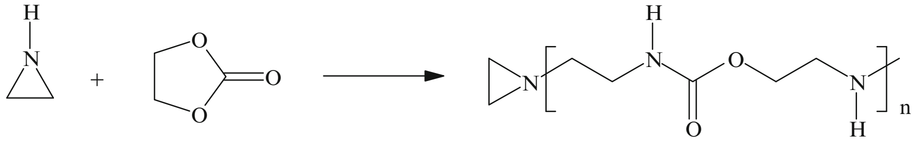
More interesting are copolymers from cyclic monomers of different chemical types. For instance, cyclic phosphite will copolymerize with lactone at 150°C or above in the presence of basic catalysts [208]:



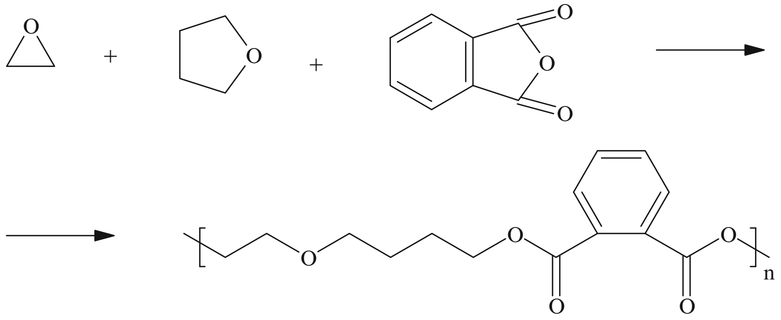
Aziridine copolymerizes with succinimide to form a crystalline polyamide that melts at 300°C [209]:



When in place of succinimide a cyclic carbonate is used, a high molecular weight polyurethane forms [210]:



Terpolymers form from epoxides, anhydrides, and tetrahydrofuran or oxetane with a trialkylaluminum catalyst [211]:

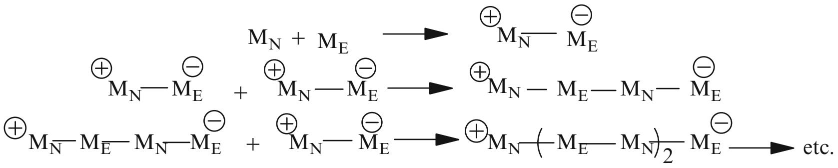


Copolymerizations of caprolactone with caprolactam in various ratios take place with lithium tetraalkylaluminate as the catalyst [212]. The products are mainly random copolymers with some block homopolymers.

When lactones copolymerize with cyclic ethers, such as β-propiolactone with tetrahydrofuran, in the early steps of the reaction the cyclic ethers polymerize almost exclusively [213]. This is due to the greater basicity of the ethers. When the concentration of the cyclic ethers is depleted to equilibrium value, their consumption decreases markedly. Polymerizations of the lactams commence. The products are block copolymer [213].

5.15 Spontaneous Alternating Zwitterion Copolymerizations

This type of copolymerization results from spontaneous interactions of nucleophilic and electrophilic monomers (M_N and M_E, respectively) without any additions of catalysts. Zwitterions form in the process that subsequently leads to formation of polymers [214–226]. The mechanism is a step-growth polymerization. It can be illustrated as follows:

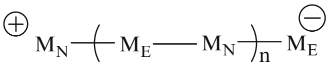


$$M_N + M_E \longrightarrow \overset{\oplus}{M_N}-\overset{\ominus}{M_E}$$

$$\overset{\oplus}{M_N}-\overset{\ominus}{M_E} + \overset{\oplus}{M_N}-\overset{\ominus}{M_E} \longrightarrow \overset{\oplus}{M_N}-M_E-M_N-\overset{\ominus}{M_E}$$

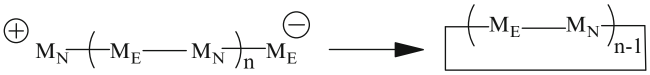
$$\overset{\oplus}{M_N}-M_E-M_N-\overset{\ominus}{M_E} + \overset{\oplus}{M_N}-\overset{\ominus}{M_E} \longrightarrow \overset{\oplus}{M_N}\left(M_E-M_N\right)_2 \overset{\ominus}{M_E} \longrightarrow \text{etc.}$$

Repeated additions of the charged species and the resulting zwitterionic products lead to high polymers:

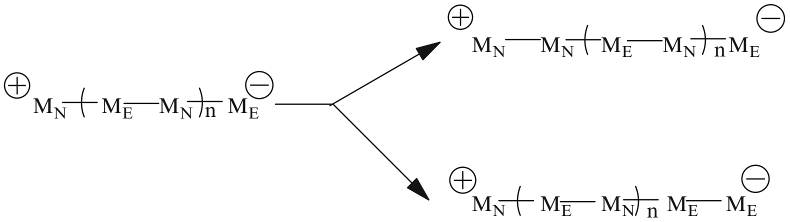


$$\overset{\oplus}{M_N}\!-\!\left(M_E\!-\!M_N\right)_n\!-\!\overset{\ominus}{M_E}$$

The initial zwitterion that forms upon combination of a nucleophilic with an electrophilic monomer is called a *genetic zwitterion* [214]. Intramolecular reactions can produce “macrocycles”:

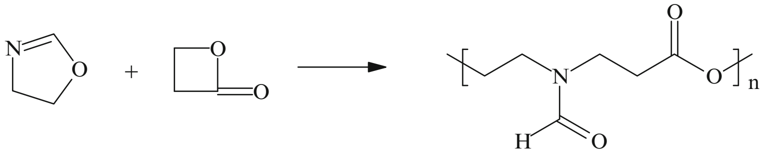


The contribution of the cyclization reaction, however, is, apparently, small [214]. A reaction can also take place between a free monomer and any zwitterion at one of the ionic sites:

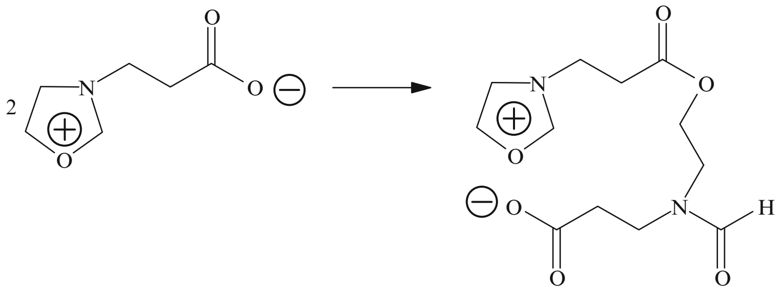


Such reactions disturb the alternating arrangements of the units –M_N–M_E– in the products. The reactivity of the monomers determines whether homopropagations occur as well. Alternating propagation depends upon dipole–dipole interactions between M_N and M_E monomers in preference to ion–dipole reactions between ion centers of zwitterions and monomers in homopropagations [214].

An example of an alternating copolymerization via zwitterion intermediates is a copolymerization of 2-oxazoline with β-propiolactone. It takes place in a solution in a polar solvent like dimethylformamide at room temperature over a period of a day to yield quantitative conversions [215]:

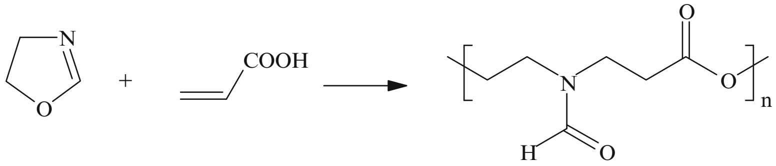


A zwitterion that forms first is the key intermediate for the polymerization. The onium ring from 2-oxazoline is opened by a nucleophilic attack of the carboxylate anion at carbon [214]:



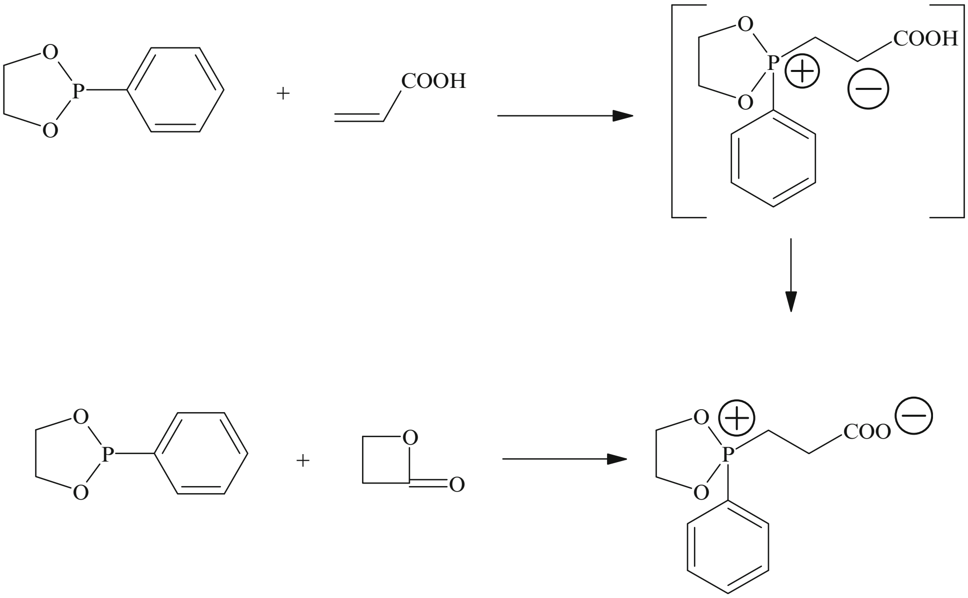
In this reaction the number of copolymer molecules increases at first, then reaches a maximum and finally decreases as the conversion becomes high [214–226]. When the concentration of both monomers is high then the formation of "genetic" zwitterions is favored. As the concentration of macro-zwitterions becomes high and the monomer concentration decreases, the macro zwitterions react preferentially with each other. When stoichiometry is not observed and β-propiolactone molecules predominate in the reactions mixture, the carboxylate end groups can react in various ways. They can react not only with the cyclic onium sites of the zwitterions, but also with free β-propiolactones and incorporate more than 50% of the propiolactone units [214].

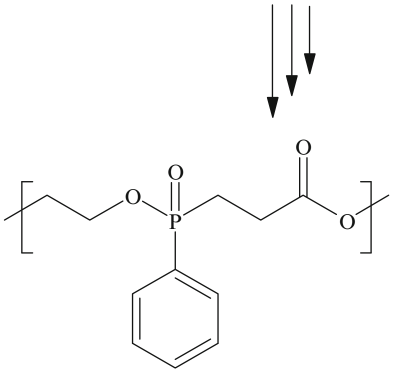
Another example of such copolymerization is that of 2-oxazoline with acrylic acid. The reaction can be carried out by combining the two in equimolar quantities and then heating the reaction mixture to 60°C in the presence of a free radical inhibitor. Such an inhibitor can be *p*-methoxy phenol. The reaction mixture becomes viscous as an alternating copolymer forms [218]:



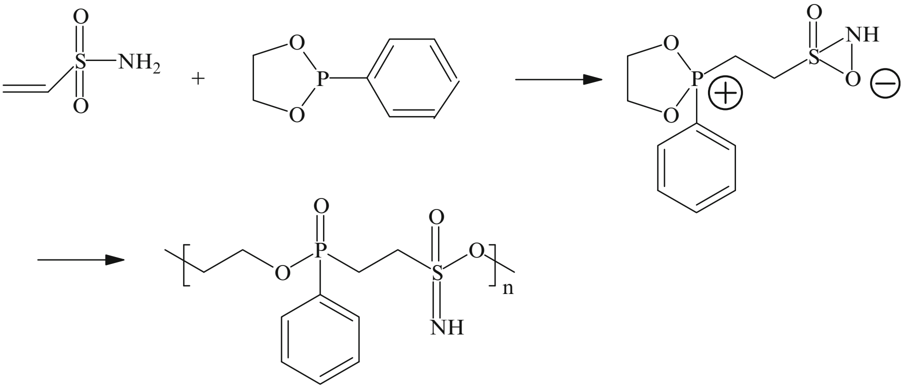
This copolymer is identical to the one obtained from reacting 2-oxazolone with β-propiolactone. The acrylic acid is converted into the same repeat unit as the one that forms from ring-opening of β-propiolactone shown in the previous example. The suggested reaction mechanism involves a nucleophilic attack by oxazolone on acrylic acid and is followed by proton migration [214]:

A similar proton migration takes place in copolymerizations of acrylamide with cyclic imino ethers. The proton migration is part of the propagation process [219]. Other examples are copolymerizations of a nucleophilic monomer, 2-phenyl-1,2,3-dioxaphospholane with electrophilic monomers [224, 225]. Here too the electrophilic monomers can be either acrylic acid or propiolactone. Identical products are obtained from both reactions [223]:

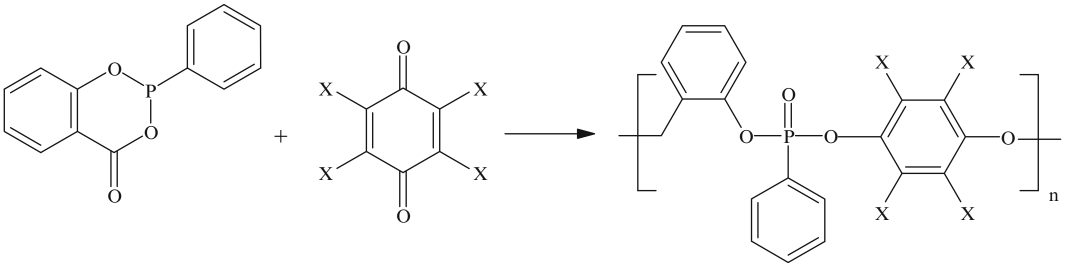




The opening of the phosphonium ring requires higher temperatures (above 120°C) and follows the pattern of the Arbusov reaction [224, 226]. Examples of some other monomers that can also act as nucleophiles in the above reaction are *p*-formyl benzoic acid [214], acrylamide [224], and ethylene sulfonamide. All three react in the same manner [224]:

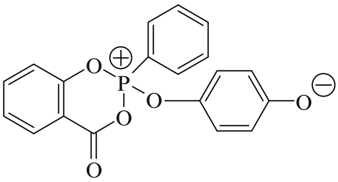


It is reasonable to expect that some compounds can act at one time as M_N monomers and at other times as M_E, depending upon the comonomer. This is the case with salicylyl phenyl phosphonite [224]. In the presence of bezoquinone it behaves as an M_N monomer and produces a 1:1 alternating copolymer at room temperature [224]:



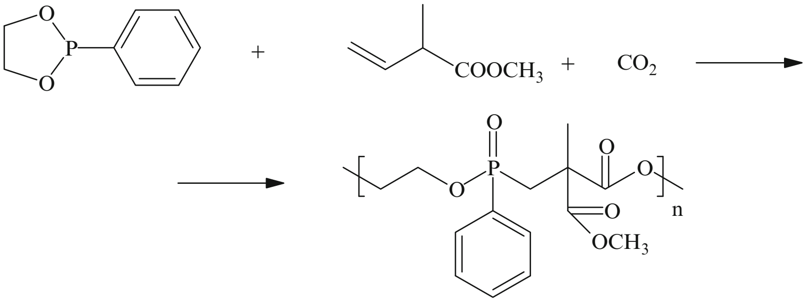
where, X = Y = H; X = Y = Cl; X = Y = CH_3; X = Cl; and Y = CN.

The above reaction is called a ***redox copolymerization*** reaction [224]. The trivalent phosphorus in the monomer is oxidized to the pentavalent state in the process of polymerization and the quinone structure is reduced to hydroquinone. The phosphonium-phenolate zwitterion is the key intermediate:

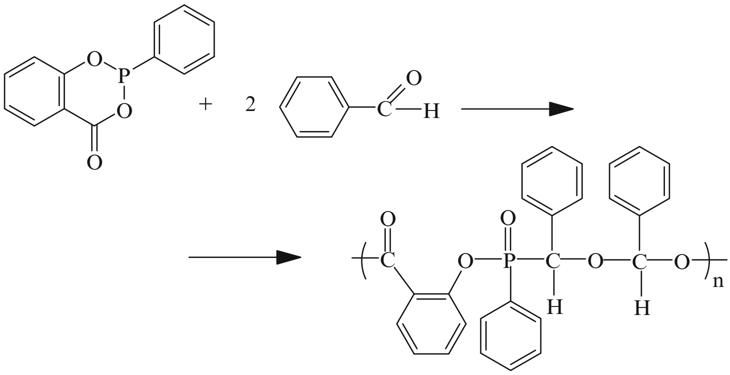


Nucleophilic attack of the phenoxide anion opens the phosphonium ring due to enhanced electrophilic reactivity of the mixed anhydride and acid structures [224]. Salicylyl phenylphosphonite, however, in combination with 2-methyl-2-oxazoline behaves as an M_E monomer [224].

Terpolymerizations by this mechanism of sequence ordered 1:1:1 components can also take place. The following is an example [224]:

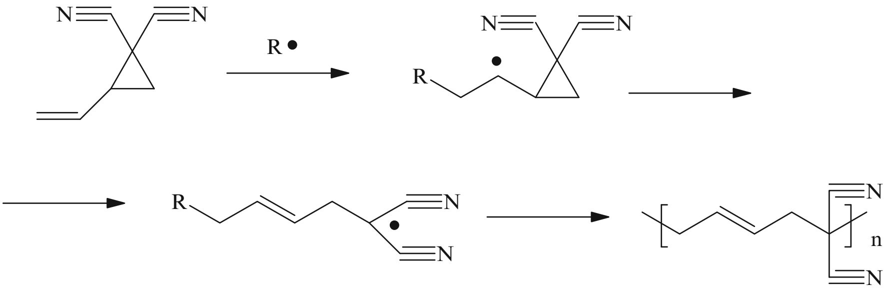


In addition 2:1 binary copolymerizations were also observed. Following is an example of a binary copolymerization [226]:



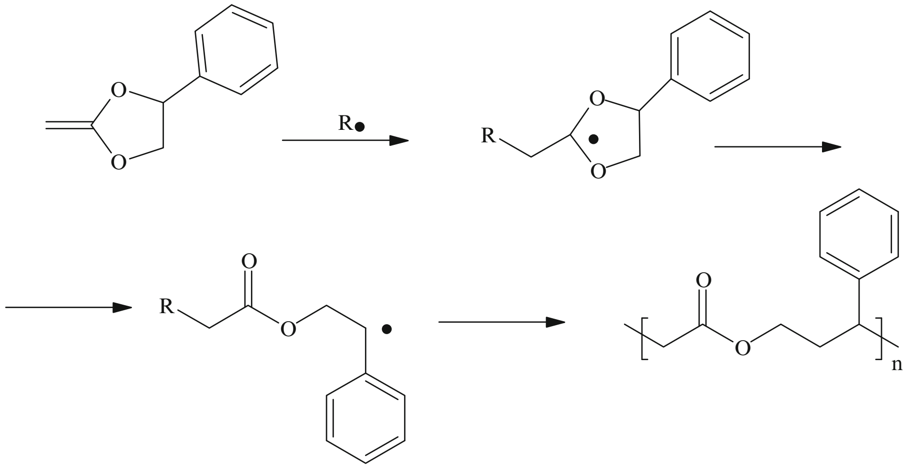
5.16 Ring-Opening Polymerizations by a Free Radical Mechanism

There are some reports in the literature of ring-opening polymerizations by free radical mechanism. One is a polymerization of substituted vinyl cyclopropanes [227]. The substituents are radical stabilizing structures that help free radical ring-opening polymerizations of the cyclopropane rings. This can be illustrated as follows:

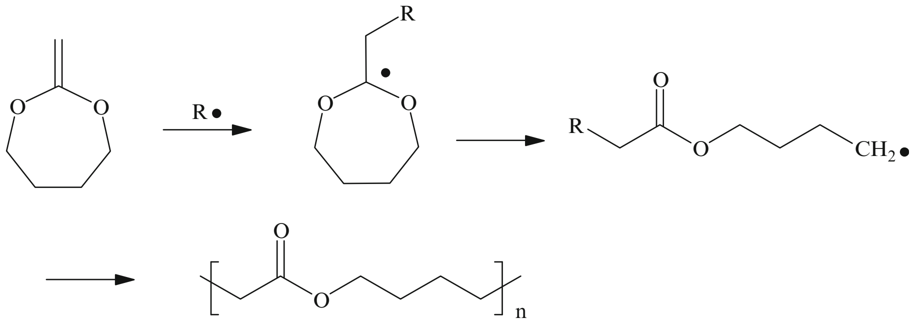


A high molecular weight polymer forms. In place of nitrile groups ester groups can be utilized as well. The polymerizations of vinyl cylopropanes proceed by cationic and coordination mechanisms exclusively through the double bonds. Free radical polymerizations of these substituted vinyl cyclopropanes, however, take place only through ring-opening polymerizations of the propane rings.

In a similar manner, ring-opening polymerizations of five-membered acetals are helped by free-radical stabilizing substituents [228]. Complete ring-opening polymerizations take place with phenyl substituted compounds:

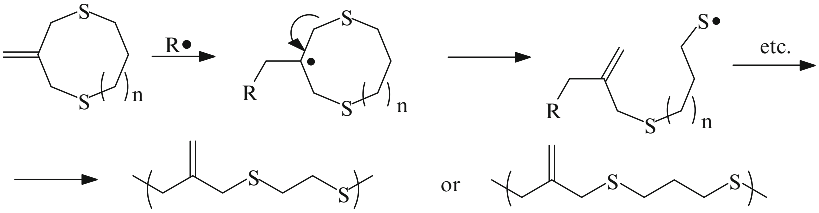


Some other heterocyclic monomers, like acetals, also polymerize by free-radical mechanism [229]. Particularly interesting is an almost quantitative ring-opening polymerization of a seven-membered acetal, 2-methylene-1,3-dioxepane [230]:



The product is an almost pure poly(ε-caprolactone).

Cyclic allylic sulfides were shown to polymerize by a free-radical ring-opening mechanism [231]. The key structural unit that appears to be responsible for the facile ring-opening is the allylic sulfide fragment. In it the carbon–sulfur bond is cleaved [231]:



It was also reported recently that a controlled free-radical ring-opening polymerization and chain extension of the "living" polymer was achieved in a polymerization of 2-methylene-1,3-dioxepane in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) [232] The reaction was initiated with di-*tert*-butyl peroxide at 125°C

At high concentrations of the piperidinyloxy radical, the polydispersity of the product was 1.2 [232]

5.17 Thermodynamics of Ring-Opening Polymerization

The stability of the ring structure as well as the stability of the resultant linear polymer determines the polymerizability of cyclic monomers. Thermodynamic factors, therefore, are of paramount importance in ring-opening polymerizations [233]. Actually, the polymerization of many bond-strained ring monomers is favored thermodynamically. Thus, for instance, ΔH, for three-membered cycloalkanes is -113.0 kJ/mole and ΔS is -69.1 J/mole °C. It was shown (Sawada) that in three- and four-membered ring structures, the change in enthalpy is a major factor in determining ΔF, the change in free energy. For three-membered cycloalkanes ΔF is -92.0 kJ/mole, while for four-membered ones it is -90.0 kJ/mole. The entropy change, ΔS is a major factor in polymerization of five-membered cyclic monomers. The six-membered ring monomers that are relatively strain free are very hard to polymerize. An exception is trioxane, whose ΔH is close to zero. On the other hand, the enthalpy and entropy factors contribute about equally to the free energy change of larger rings. This means that with increases in temperature ΔF becomes less and less negative and above certain temperatures some large cyclic monomers will not polymerize. The transanular strain in seven- and eight-membered rings contributes to their polymerizability. Presence of substituents in cyclic monomers has a negative effect on the thermodynamic feasibility to polymerize. On the other hand, thermodynamic feasibility alone does not determine whether a cyclic monomer will polymerize.

The entropy changes do not show much dependence of on angle strain. They are susceptible, however, to configurational influences. Sawaada [233] writes the entropy change of polymerization as a function of the probability of ring closure:

$$\Delta S_{\mathrm{p}} = -b \ln P - a$$

where P is the probability of ring closure and a and b are constants. The probability of ring closure for a chain with n repeating units can be taken as a function of the probability that the chain ends will come together. This probability is usually expressed as a radius of gyrations, (r^2), the root square distance of end to end. The entropy change for three-membered rings would have a large negative value. For larger rings the negative value would be less, because the end to ends would be further apart. Statistical mechanics treatment has shown that the entropy change of ring closure is [223]:

$$\Delta S_{\mathrm{r}} = R \ln\{PV/2xV_{\mathrm{s}}N\}$$

where P is the probability of ring closure or the fraction of chain ends that will come together and close to form ring structures, V is the total volume of the system, V_{s} is the volume of a constrained skeletal atom prior to bond breaking, x is the number of monomer units in the ring, and N is the Avogadro's number.

Review Questions

Section 5.1

1. Are the mechanisms of ring-opening polymerizations of cyclic monomers chain-growth of step-growth reactions? Explain

Section 5.2

1. Write the rate expression for propagation in ring-opening polymerizations where there is an equilibrium between propagation and depropagation.
2. Write the kinetic expression for the total concentration of monomer segments that are incorporated into the polymer.

Section 5.3

1. Oxiranes can be polymerized by three different mechanisms. What are they? Explain.
2. Write the chemical reactions for the mechanism of polymerization of ethylene oxide with the aid of stannic chloride. Does a high molecular weight polymer form? If not, explain why.
3. Write the chemical reactions for the mechanism of polymerization of propylene oxide with boron trifluoride–water.
4. Describe the mechanism and write the chemical reactions of ring-opening polymerizations of oxiranes with potassium hydroxide. In polymerization of propylene oxide with KOH what type of tacticity polymer forms. Explain.
5. Describe the mechanism and write the chemical equations for coordinated anionic polymerizations of propylene oxide by ferric chloride and by diethylzinc–water. Show reaction mechanism.
6. Discuss the general characteristics of steric control in the polymerizations of oxiranes.
7. Explain the mechanism postulated by Tsuruta of steric control in polymerizations of oxiranes with the aid of organozinc compounds, giving the structure of the catalyst and the mode of monomer insertion and the mode or ring opening.

Section 5.4

1. Describe the initiation process in polymerizations of oxetanes, including initiators and reaction mechanism
2. Describe the mechanism of propagation in polymerizations of oxetanes.

Section 5.5

1. Discuss, including chemical equations, the initiation reactions in tetrahydrofuran polymerization, including the mechanism and various initiators
2. Discuss the propagation reaction in polymerization of tetrahydrofuran.
3. When are both ionic and covalent species present during the polymerization of tetrahydrofuran. Explain conditions that cause formation of both species and draw structures of both.
4. Describe the termination reaction in tetrahydrofuran polymerization, including living polymerization.

Section 5.6

1. How do the rates of oxepane polymerization compare with those of oxetane and tetrahydrofuran? What affects these rates.

Section 5.7

1. How and why do the cationic polymerizations of cyclic acetals differ from those of other cyclic ethers?
2. What initiators are effective in polymerizations of trioxane? Discuss polymerizations with different initiators.
3. Describe typical polymerization conditions of trioxane.
4. Explain the proposed reaction mechanisms for polymerization of trioxane including the coordinated mechanism in polymerizations with molybdenum acetylacetonate. Illustrate all with chemical structures.
5. Discuss the polymerization of dioxalane, showing mechanism of initiation, propagation, and terminations with different initiators.
6. How does a polymer and a copolymer form side by side in boron trifluoride initiated polymerizations of dioxepane?
7. What type of structures are obtained from ring-opening polymerizations of trioxocane? Show and explain.

Section 5.8

1. Describe cationic polymerization of lactones, showing the initiation and propagation processes.
2. Repeat question one for anionic polymerization.

3. Describe the coordination polymerization of lactones.
4. What are the instances of “living” polymerizations of cyclic lactones and what type of catalysts yield this type of polymerization? Describe and give examples.

Section 5.9

1. What are the three mechanisms of polymerization of lactams?
2. Describe the catalysts that are useful in cationic polymerizations of lactams and the mechanism of polymerization.
3. Show how amidine salts form in cationic polymerizations of lactams and explain how that influences the reaction.
4. Discuss the anionic polymerization of lactams and compare that with the cationic one.
5. What is meant by lactomolytic propagation? Explain.
6. Describe the proposed mechanism for polymerizations of lactams with dialkoxyaluminum hydrides.
7. Describe hydrolytic polymerization of lactams.
8. Compare cationic, anionic, and hydrolytic polymerizations of lactams by writing out all three modes of polymerization side by side and discuss and show the side reactions that take place in each one of them.

Section 5.10

1. Discuss the polymerization of *N*-carboxy-α-amino acid anhydrides

Section 5.11

1. What is metathesis polymerization? Explain the mechanism and show the reaction on a disubstitued olefin.
2. Describe metathesis polymerization of methyl cyclobutene showing the mechanisms of initiation and propagation.
3. Describe “living” metathesis polymerization. What types of catalysts are useful in such polymerizations?

Section 5.12

1. Describe the polymerization of aziridines, showing the initiation and propagation processes.

Section 5.13

1. Explain the three mechanisms by which cyclic sulfides can be polymerized. Describe each.
2. Describe the initiation and propagation reactions in cationic polymerizations of cyclic sulfides.

3. Describe the termination reaction in cyclic sulfides cationic polymerizations.
4. What type of side reactions can occur in anionic polymerizations of cyclic sulfides?

Section 5.14

1. Discuss copolymerizations of cyclic monomers giving several examples.

Section 5.15

1. How does a spontaneous zwitterion copolymerization occur. Explain.
2. What is meant by a genetic zwitterion?
3. Give several examples of zwitterion copolymerization.

Section 5.16

1. Explain ring-opening polymerizations by free-radical mechanism, giving two examples.

Recommended Reading

K.J. Ivin and J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997

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Chapter 6
Common Chain-Growth Polymers

6.1 Polyethylene and Related Polymers

Polyethylene is produced commercially in very large quantities in many parts of the world. The monomer can be synthesized from various sources. Today, however, most of ethylene comes from petroleum by high temperature cracking of ethane or gasoline fractions. Other potential sources can probably be found, depending upon the availability of raw materials.

Two main types of polyethylene are manufactured commercially. These are low (0.92–0.93 g/cm^3) and high (0.94–0.97 g/cm^3) density polymers. The low-density material is branched while the high-density one is mostly linear and much more crystalline. The most important applications for the low-density polyethylene are in films, sheets, paper, wire and cable coatings, and injection molding. The high-density material finds use in blow molded objects and in injection molding.

6.1.1 Preparation of Polyethylene by a Free-Radical Mechanism

Up to the late 1960s, most low-density polyethylene was produced commercially by high-pressure free-radical polymerization. Much of this has now been replaced by preparation of copolymers of ethylene with α-olefins by coordination polymerization. These preparations are discussed further in this chapter. High-pressure polymerizations of ethylene, however, might still practiced in some places and it is, therefore, discussed here. The reaction requires a minimum pressure of 500 atm [1] to proceed. The branched products contain long and short branches as well as vinylidene groups. With an increase in pressure and temperature of polymerization, there is a decrease in the degree of branching and in the amount of vinylidene groups [2, 3].

Free-radical commercial polymerizations are conducted at 1,000–3,000 atm pressure and 80–300°C. The reaction has two peculiar characteristics: (1) a high exotherm and (2) a critical dependence on the monomer concentration. In addition, at these high pressures oxygen acts as an initiator. At 2,000 atm pressure and 165°C temperature, however, the maximum safe level of oxygen is 0.075% of ethylene gas in the reaction mixture. Any amount of oxygen beyond that level can cause explosive decompositions. History of polyethylene manufacture contains stories of workers being killed by explosions. Yet, the oxygen concentration in the monomer is directly proportional to the

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percent conversion of monomer to polymer, though inversely proportional to the polymer's molecular weight. This limits many industrial practices to conducting the reactions below 2,000 atm and below 200°C. These reactions were done, therefore, between 1,000 and 2,000 atm pressures. Small quantities of oxygen, limited to 0.2% of ethylene, are accurately metered in [4, 5]. The conversion per each pass in continuous reactors is usually low, about 15–20%.

There is an induction period that varies inversely with the oxygen concentration to the power of 0.23. During this period oxygen is consumed autocatalytically. This is not accompanied by any significant decrease in pressure. A high concentration of ethylene is necessary for a fast rate of chain growth, relative to the rate of termination. Also, high temperatures are required for practical rates of initiation.

If oxygen is completely excluded and the pressure is raised to between 3,500 and 7,750 atm, while using relatively low temperatures of 50–80°C, linear polyethylene forms [6]. The reactions take about 20 h. Various solvents can be used, like benzene, isooctane, methyl, or ethyl alcohols. Higher ethyl alcohol concentrations and low concentrations of the initiator result in higher molecular weights. The products range from 2,000 for wax-like polymers to 4,000,000 for nearly intractable materials. Favorite free-radical initiators for this reaction are benzoyl peroxide, azobisisobutyronitrile, di-*t*-butylperoxydicarbonate, di-*t*-butyl peroxide, and dodecanoyl peroxide. Above conditions differ, however, from typical commercial ones, because such high pressures and long reaction times are not practical.

The actual commercial conditions vary, depending upon location and individual technology of each company. Often, tubular and multiple-tray autoclaves are used [7]. Good reactor design must permit dissipation of the heat of polymerization (800–1,000 cal/g), with good control over other parameters of the reaction. Tubular reactors are judged as having an advantage over stirred autoclaves in offering greater surface-to-volume ratios and better control over residence time [7]. On the other hand, the stirred autoclaves offer a more uniform temperature distribution throughout the reactor.

The tubular reactors have been described as consisting of stainless steel tubes between 0.5 and 1 in. in internal and about 2 in. in the external diameters. The residence time in these tubes is from 3 to 5 min, and they can be equipped with pistons for pressure regulation. Pressure might also be controlled by flow pulses to the reactor [8]. For the oxygen-initiated reactions, the optimum conditions are [7] 0.03–0.1% oxygen at 190–210°C and 1,500 atm pressure. At this pressure, the density of ethylene is 0.46 g/cm^3. This compares favorably with the critical density of ethylene that is 0.22 g/cm^3. Once the polymerization is initiated, the liquid monomer acts as a solvent for the polymer. Impurities, such as acetylene or hydrogen cause chain transferring and must be carefully removed. In some processes, hindered phenols are added in small quantities (between 10 and 1,000 ppm). This has the effect of reducing long-chain branching and yields film grade resins with better clarity, lower haze, and a reduced amount of microgels. Also, diluents are used in some practices. Their main purpose is to act as heat-exchanging mediums, but they can also help remove the polymer from the reactor. Such diluents are water, benzene, and ethyl or methyl alcohols. Sometimes, chain transferring agents like carbon tetrachloride, ketones, aldehydes, or cyclohexane might also be added to control molecular weight. The finished product (polymer–monomer mixture) is conveyed to a separator where almost all of the unreacted ethylene is removed under high pressure (3,500–5,000 psi) and recycled. The polymer is extruded and palletized. Ethylene conversion per pass is a limiting factor on the economics. A tubular reactor is illustrated in Fig. 6.1.

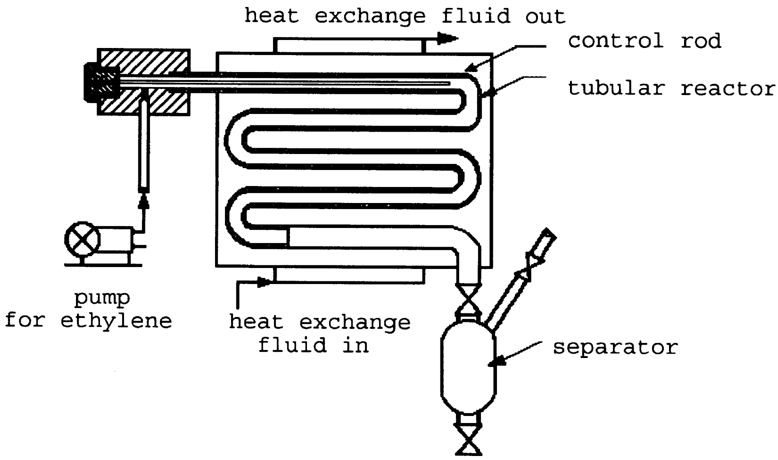
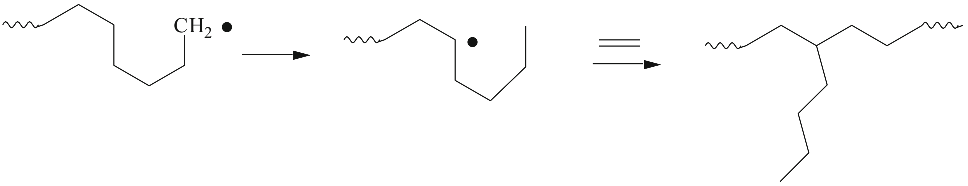
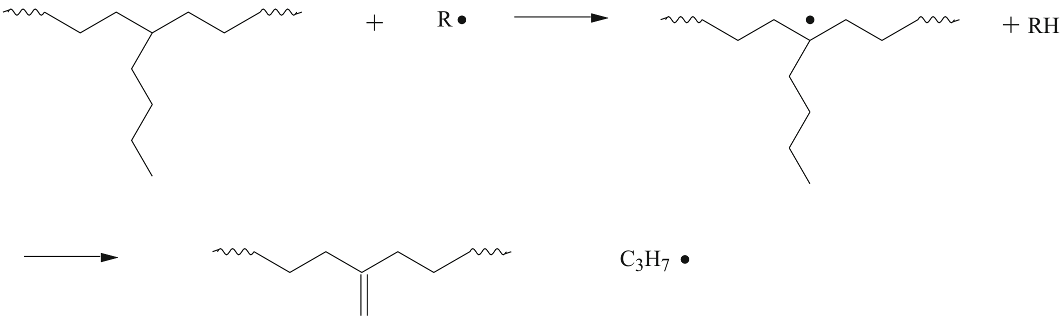


Fig. 6.1 Illustration of a tubular reactor

Polyethylene prepared in this way may have as many as 20–30 short branches per 10,000 carbon atoms in the chain [9] and one or two long-chain branches per molecule, due to "backbiting" [10] (explained in Chap. 3):



The reaction results in predominantly ethyl and butyl branches. The ratio of ethyl to butyl groups is roughly 2:1 [11, 12]. Chain transferring to the tertiary hydrogens at the location of the short branches causes elimination reactions and formation of vinylidene groups [13, 14]. This mechanism also accounts for formation of low molecular weight species.

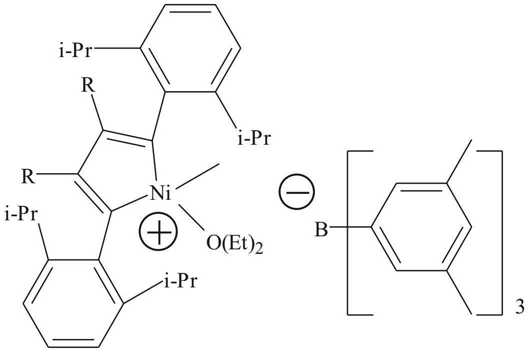


Commercial grades of low-density polyethylene vary widely in the number of short and long branches, average molecular weights, and molecular weight distributions. M_w/M_n is between 20 and 50 for commercial low-density materials. The short branches control the degree of crystallinity, stiffness, and polymer density. They also influence the flow properties of the molten material.

6.1.2 Preparation of Polyethylene by Coordination Mechanism

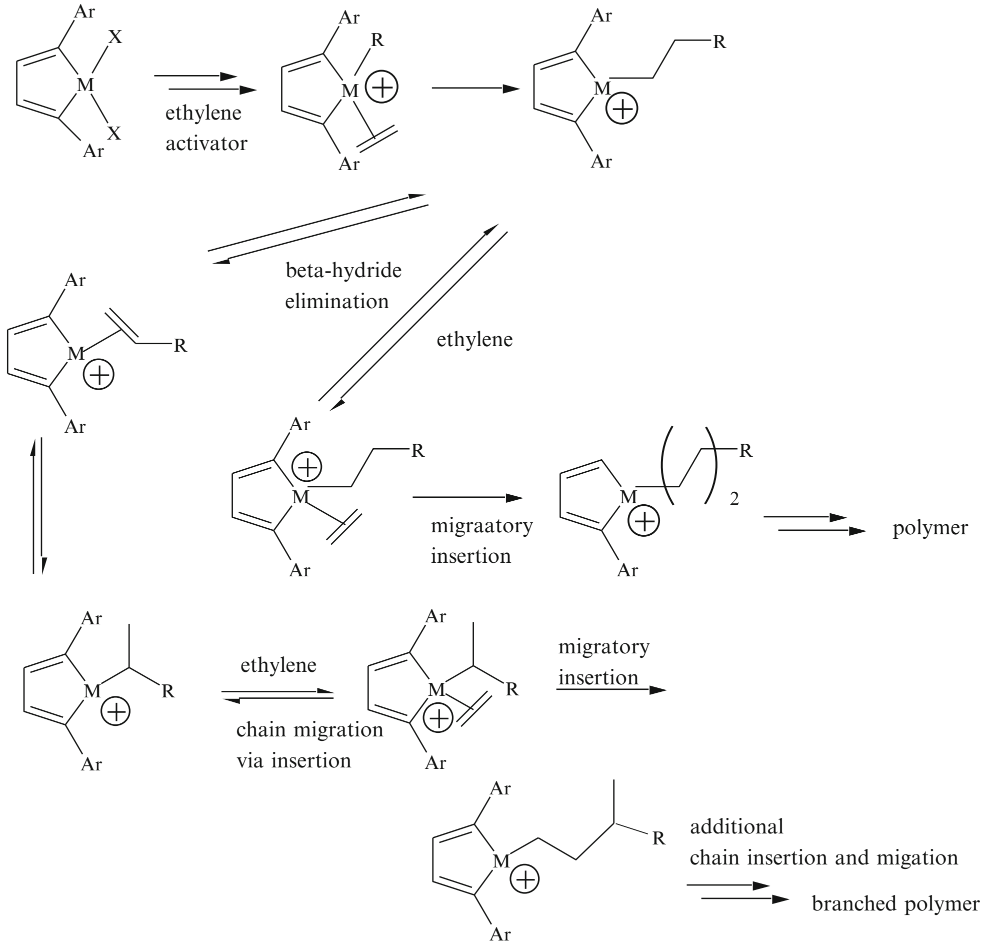
Low-density polyethylene can be prepared by coordination polymerization through copolymerization of ethylene with α-olefins. This is discussed in the section on copolymers of ethylene. Finding catalytic systems that would allow formation of amorphous, low-density polyethylene from the monomer alone by low-pressure polymerization, however, is an economically worthwhile goal. To this end, considerable research is being carried out to develop such catalytic systems. Particular attention is given to metallocenes and other single-site catalysts for olefin polymerization. Originally, the metallocene catalysts were typical metal complexes with two cyclopentadienyl or substituted cyclopentadienyl groups. Many variations were developed since. These materials are used in combination with methyl aluminoxane and have the potential of forming the polymers with high precision. Nevertheless, at this time it is probably still safe to say that low-density polyethylene is prepared by many but perhaps not by all of the processes and catalytic systems mentioned in this book. This is because the material is manufactured all over the world and different considerations govern the decisions on the processes and catalytic systems. The same is probably true of high-density polyethylene.

New catalysts based on palladium and nickel complexes with bulky α-diimine ligands were developed [17–19]. They can yield highly branched or moderately branched polymers of ethylene, as well as propylene and 1-hexene. The polyolefins produced by such catalysts can contain a considerable amount of branches along the backbone that are randomly distributed throughout the molecules. In these catalysts, the molecular weight-limiting β-hydrogen elimination process that is common to palladium and nickel catalysts has been suppressed through use of bulky α-diamine ligands [19]. This allows formation of high molecular weight polymers from ethylene and α-olefins. A nickel-based catalyst can be illustrated as follows:



It is claimed that the branching of polyethylene can be controlled to the extent that the product can even be more branched than conventional low-density polyethylene (1,2—300 branches/1,000 atoms) [18, 19]. The cationic Ni-diimine catalyst shown above (R = H, CH_3), with the methylaluminoxane analog, has been found to polymerize ethylene in toluene at room temperature at the rate of 110,000 kg/Ni/h. This is comparable to the metallocene rates. The Pd-based catalysts are less active than their Ni analogs [19].

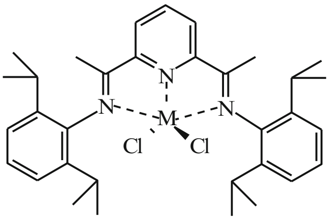
When nickel catalysts are used, the extent of branching is a function of the temperature, ethylene pressure, and catalyst structure. Branching increases as the temperature rises. At higher ethylene pressure less branching occurs. Brookhart et al. illustrate the mechanism of polymerization as follows [18]:



where X = CH_3, Br; M = Pd, Ni; R = $(CH_2CH_2)_nCH_3$; Ar = 2,6-dialkylphenyl.

A patent for the polymerization process of olefins (especially ethylene, α-olefins, cyclopentene, and some fluorinated olefins) describes the above catalytic systems [20]. The hindered diimines stabilize alkyl Ni(II) or Pd(II) with cationic complexes. After preparation, the complexes are reduced with methylaluminoxane and then activated with Lewis acids capable of forming non-coordinating counterions [20].

In addition, preparation of catalysts based on iron and cobalt [21] was also reported. These are complexes of bulky pyridine bis-imine ligands with iron or cobalt that are also activated by methylaluminoxane:

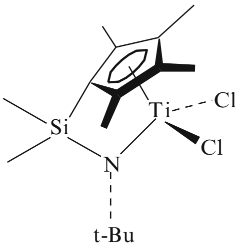


The iron-based catalysts are reported to be considerably more active than the cobalt analogs [21]. The yield of linear, narrow molecular weight distribution polyethylene per gram is reported to be very high [21].

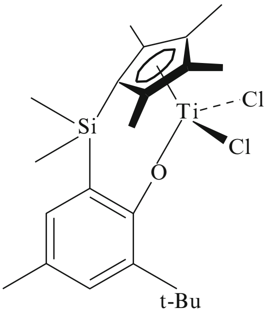
Baugh et al. [22] synthesized and characterized a series of nickel(II) and iron(II) complexes of the general formula [LMX_2] containing bidentate (for M = Ni) and tridentate (for M = Fe) heterocycle-imine ligands. Activation of these pre-catalysts with methyl aluminoxane yields active catalyst systems for the oligomerization/polymerization of ethylene. Compared to α-diimine nickel and bis (imino)pyridine iron catalysts, both metal systems provide only half of the steric protection and consequently the catalytic activities are significantly lower.

Lower activities were attributed to reduced stability of the active species under polymerization conditions. The lower molecular weights of their products were explained to be the result of increased hydrogen transfer rates. Variations within the heterocyclic components of the ligand showed that both steric and electronic factors influence polymerization behavior of such catalysts.

Hanaoka, Oda, and coworkers report [23] that single-site polymerization catalysts are of considerable interest industrially today, because they afford highly controllable polymerization performances based on precise design of catalyst architecture and their industrial applications. Among them, they point to constrained geometry catalyst and phenoxy-induced complex, they call phenics–Ti, that are used together with methyl aluminoxane



concentrated geometry catalyst-Ti



phenics-Ti

These are half-metallocene catalysts with an anionic armed-pendant that have now been well developed for industrial production of copolymers of ethylene with 1-olefins. Modification at the cyclopentadienyl ring system has been mainly tuned to finely control polymerization behaviors such as activity, molecular weight, and regiochemistry. In general, minimizing 2,1-insertion is essential to obtain high molecular weight polyolefins; otherwise, facile 6-elimination occurs, leading to termination of chain growth. Thus, the largely open coordination sites of half-metallocene catalyst systems possess an indispensable problem of irregularity in propagation. Through tuning bulkiness of substituents on the bridged-silicon unit of phenics–Ti, is claimed to have demonstrated that 2,1-insertion of propylene can also controlled by the bridging substituents to produce high molecular weight polypropylene [23].

Hong and coworkers [24] concluded that it is generally desirable to immobilize the single-site metallocene catalysts on a suitable carrier to obtain ideal product morphology. Ultrahigh molecular weight polyethylenes were successfully prepared by them through titanium complexes bearing phenoxy-imine chelate ligands

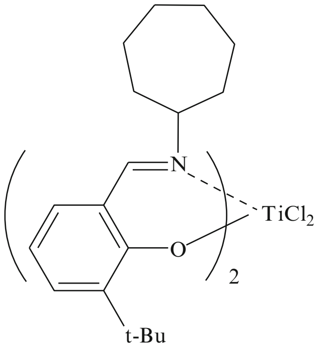


Table 6.1 Typical conditions for some preparation of high-density polyethylene

	Ziegler–Natta process	Cr_2O_3/support	MoO_3/support
Approx. temperature	75°C	140°C	234°C
Approx. pressure	60 psi	420 psi	1,000 psi
Usual state of the polymer in reaction mixture	Suspension	Suspension	Suspension

They demonstrated that the catalyst can be immobilized on silica. The product yields ultrahigh molecular weight polyethylene. Increased polymerization temperature resulted in higher activity, but lower molecular weight of polyethylene.

6.1.3 Commercial High-Density Polyethylene, Properties, and Manufacture

High-density polyethylene (0.94–0.97 g/cm^3) is produced commercially with two types of catalysts:

1. Ziegler–Natta type catalysts
2. Transition metal oxides on various supports

The two catalytic systems are used at different conditions. Both types have undergone evolution from earlier development. The original practices are summarized in Table 6.1.

The Ziegler process yields polyethylene as low as 0.94/cm^3 in density, but process modifications can result in products with a density of 0.965 g/cm^3. The transition metal oxide catalysts on support, on the other hand, yield products in the density range of 0.960–0.970 g/cm^3.

The original development by Ziegler led to what appears to be an almost endless number of patents for various coordination-type catalysts and processes. As described in Chap. 4, such catalysts have been vastly improved. Progress was made toward enhanced efficiency and selectivity. The amount of polymer produced per gram of the transition metal has been increased manyfold. In addition, new catalysts, based on zirconium compounds complexed with methyl aluminoxane oligomers (sometimes called Kominsky catalysts), were developed. They yield very high quantities of polyethylene per gram of the catalyst. For instance, a catalyst, bis(cyclopentadienyl)-zirconium dichloride combined with methylaluminoxane, is claimed to yield 5,000 kg of linear polyethylene per gram of zirconium per hour [14].

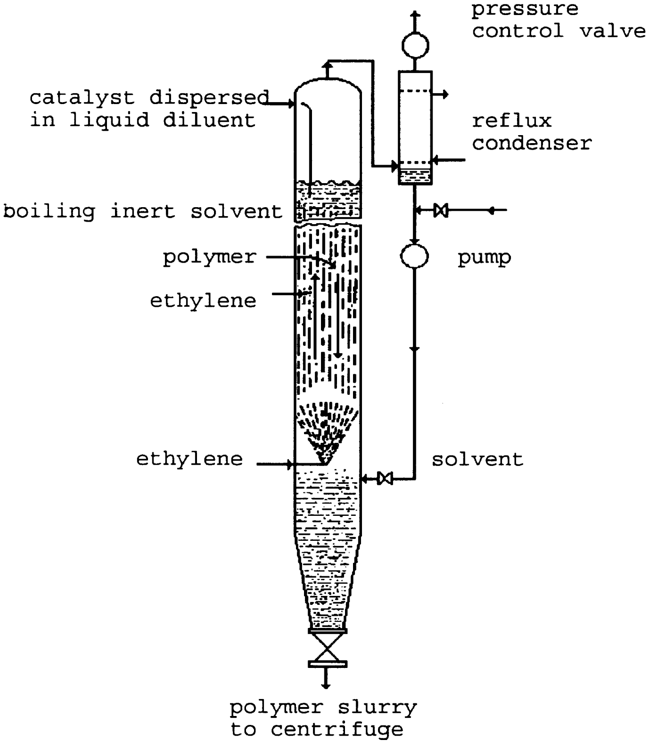
An important factor in the catalysts activity is the degree of oligomerization of the aluminoxane moiety. The catalytic effect is enhanced by increase in the number of alternating aluminum and oxygen atoms. These catalysts have long storage life and offer such high activity that they need not be removed from the product, because the amount present is negligible [14, 15]. This makes the work-up of the product simple.

The continuous solution processes are usually carried out between 120 and 160°C at 400–500 lb/in.^{2} pressure. The diluents may be cyclohexane or isooctane. In one zone reactors, the solid catalyst is evenly dispersed throughout the reactor. In the two zone reactors (specially constructed), the polymerizations are conducted with stirring in the lower zone where the catalysts are present in concentrations of 0.2–0.6% of the diluent. Purified ethylene is fed into the bottom portions of the reactors. The polymers that form are carried with small portions of the catalyst to the top and removed. To compensate for the loss, additional catalysts are added intermittently to the upper "quiescent" zones.

In suspension or slurry polymerizations, various suspending agents, like diesel oil, lower petroleum fractions, heptane, toluene, mineral oil, chlorobenzene, or others, are used. The polymerization temperatures are kept between 50 and 75°C at only slightly elevated pressures, like 25 lb/in.^{2}. If these are batch reactions, they last between 1 and 4 h. The slurry reactor is illustrated in Fig. 6.2.

Polymerizations catalyzed by transition metal oxides on support were described variously as employing solid/liquid suspensions, fixed beds, and solid/gas-phase operations. It appears, however, that the industrial practices are mainly confined to use of solid/liquid suspension processes. The polymerization is carried out at the surface of the catalyst suspended in a hydrocarbon diluent.

Fig. 6.2 Commercial flow reactor for slurry polymerization of ethylene with Ziegler–Natta catalysts as illustrated in a British patent # 826 523



In continuous slurry processes, the temperatures are kept between 90 and 100°C and pressures between 400 and 450 lb/in.^{2}. The catalyst concentrations range between 0.004 and 0.03% and typical diluents are *n*-pentane and *n*-hexane. Individual catalyst particles become imbedded in polymer granules as the reaction proceeds. The granules are removed as slurry containing 20–40% solids.

There are variations in the individual processes. In some procedures, the temperature is kept high enough to keep the polymer in solution. In others, it is kept deliberately low to maintain the polymer in slurry. The products are separated from the monomer that is recycled. They are cooled, precipitated (if in solution), and collected by filtration or centrifugation.

Various reactors were developed to handle different slurry polymerization processes. The slurry is maintained in suspension by ethylene gas. The gas rises to the top and maintains agitation while the polymer particles settle to the bottom where they are collected.

Several companies adopted loop reactors. These are arranged so that the flowing reactants and diluents continuously pass the entrance to a receiving zone. The heavier particles gravitate from the flowing into the receiving zone while the lighter diluents and reactants are recycled. To accommodate that, the settling area must be large enough for the heavy polymer particles to be collected and separated.

In addition to suspension, a gas-phase process was developed. No diluent is used in the polymerization step. Highly purified ethylene gas is combined continuously with a dry-powdery catalyst and then fed into a vertical fluidized bed reactor. The reaction is carried out at 270 psi and 85–100°C. The circulating ethylene gas fluidizes the bed of growing granular polymer and serves to remove the heat [15]. Formed polymer particles are removed intermittently from the lower sections of the vertical reactor. The product contains 5% monomer that is recovered and recycled. Control of polymer density is achieved by copolymerization with α-olefins. Molecular weights and molecular weight distributions are controlled by catalyst modifications, by varying operating conditions, and/or use of chain transferring agents [15], such as hydrogen [16]. This is illustrated in Fig. 6.3.

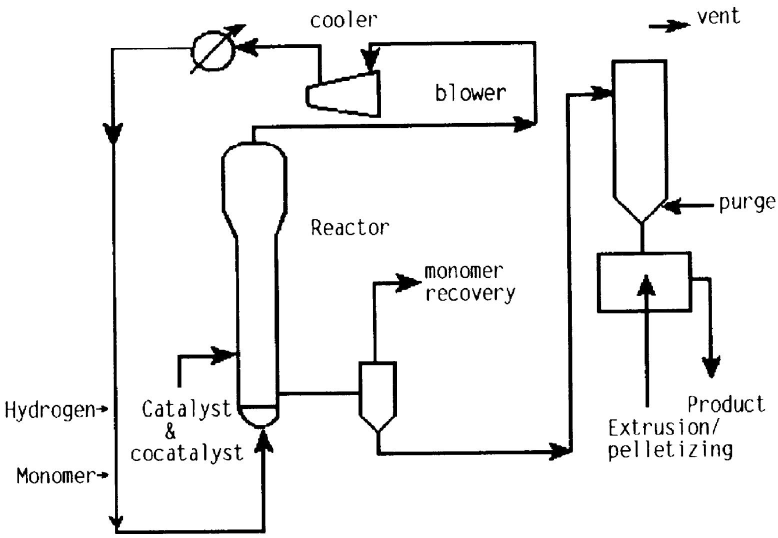


Fig. 6.3 Illustration of a gas-phase process (from Burdett, by permission of the American Chemical Society)

The reactors for the fluidized gas-phase process are simple in design. There are no mechanical agitators and they rely upon blowers to keep the bed fluidized and well mixed. Catalysts and cocatalysts are fed directly to the reactor [25].

Rieger and coworkers [26] investigated gas-phase polymerization of ethylene with supported α-diimine nickel catalysts. The reaction of 2,5 and 2,6 and 1,4 dithiane ligands with $Ni(acac)_2$ and trityl tetrakis(pentafluorophenyl)borate gave the corresponding Ni(II) complexes in high yields. These complexes were supported on silica without a chemical tether and were used as catalysts for ethylene polymerization reactions in the gas phase. Furthermore, ethylene was polymerized with the unsupported 2,5-complexes in homogeneous solution for comparison. The influence of the ligand structure, hydrogen, and temperature on the polymerization performance was investigated. The supported catalysts showed moderate to high activities and produced polyethylenes ranging from high-density polyethylene to linear low-density polyethylene, without further addition of a α-olefin comonomer.

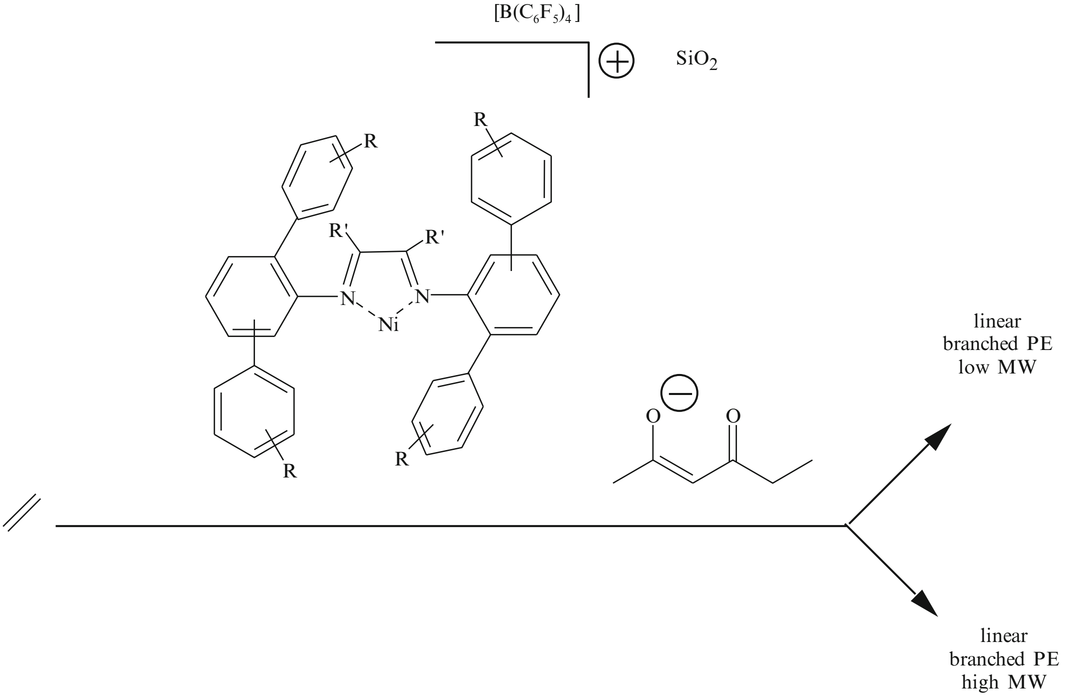


Table 6.2 Properties of commercial polyethylene

Properties	Free-radical polymerization	Ziegler–Natta type catalysts	Metal oxides on support
Density	0.92–0.93 g/cm^3	0.94 g/cm^3	0.95–0.96 g/cm^3
Melting point	108–110.7°C	129–131°C	136°C
% Amorphous	43.1	25.8	25.8
Structure	20–30 ethyl and butyl branches/1,000 carbons, a few long branches	Mainly linear 7 ethyl branches/ 1,000 carbons	Almost linear
Double bonds	0.6–2/1,000 carbons	0.1–1/1,000 carbons	Up to 3/1,000 carbons
Types of bonds	15% terminal vinyl 68% vinylidene 17% internal *trans* olefin	43% terminal 32% vinylidene 25% internal *trans* olefins	94% terminal 1% vinylidene 5% internal *trans* olefins

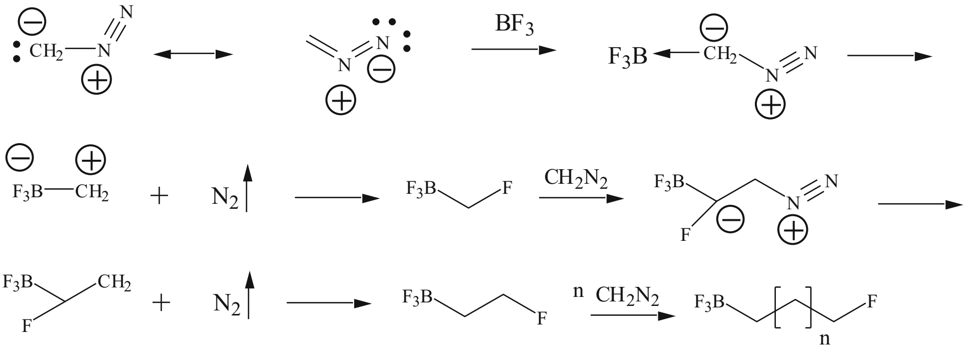
[a] From various sources in the literature

The weight average molecular weights of most commercial low- and high-density polyethylenes range between 5,000 and 300,000. Very low molecular weight polyethylene waxes and very high molecular weight materials are also available. The molecular weight distributions for high-density polyethylene vary between 4 and 15. The product generally has fewer than three branches per thousand carbon atoms [9].

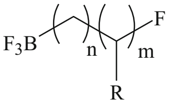
Table 6.2 summarizes the properties of various polyethylenes.

6.1.4 Materials Similar to Polyethylene

Materials that are quite similar to polyethylene can be obtained from other starting materials. The most prominent is formation of polymethylene and similar high molecular weight paraffin hydrocarbons from diazoalkanes. The reaction was originally carried out by Pechmann [27] when small quantities of a white flocculent powder formed in an ether solution of diazomethane. Bamberger and Tschirner [28] showed that this white powder is polymethylene –(–CH$_2$–)$_n$– that melts at 128°C. The synthesis was improved since by introduction of various catalysts. The reaction can yield highly crystalline polymers that melt at 136.5°C [29] with the molecular weight in millions [30]. Among the catalysts, boron compounds are very efficient [30]. Bawn et al. [31] postulated the mechanism of catalytic action. It consists of initial coordination of a monomer with the initiator, BF$_3$. This is followed by a loss of nitrogen and a shift of a fluorine atom from boron to carbon. The successive additions of molecules of diazoalkane follow a similar path with a shift of the chain fragment to the electron-deficient carbon:



The resulting macromolecules are still reactive toward additional diazoalkanes. The above step-growth polymerization reactions can also yield block copolymers:



Formation of polymethylene by this reaction is not practical for commercial utilization.

Colloidal gold and fine copper powder also catalyze diazoalkane polymerizations. The reaction appears to precede by formation of alkylidine or carbene species that are bound to the surfaces of metals [31–33]. The initiations are completed by additions of diazoalkanes to the bound carbenes followed by liberation of nitrogen. Termination may take place by chain transfer, perhaps to a monomer, or to the solvent [31–33].

Many different diazoalkanes lend themselves to these polymerization reactions. Polypentylidine, polyhexylidine, polyheptilidine, and polyoctylidine form with a gold complex catalyst, $AuCl_3$-pyridine [34].

An entirely different route to preparation of macroparaffins is through a high-pressure reaction between hydrogen and carbon monoxide. Transition metals, like finely divided ruthenium, catalyze this reaction. At pressures of about 200 atm and temperatures below 140°C, polymethylene of molecular weight as high as 100,000 forms [35]:

6.2 Polypropylene

Propylene monomer, like ethylene, is obtained from petroleum sources. Free-radical polymerizations of propylene and other α-olefins are completely controlled by chain transferring [36]. They are, therefore, polymerized by coordination polymerization. At present, mainly isotactic polypropylene is being used in large commercial quantities. Also, there is some utilization of atactic polypropylene as well. Syndiotactic polypropylene, on the other hand, is still mainly a laboratory curiosity.

The polypropylene that was originally described by Natta contained less than 50% of isotactic fractions. The remainder was atactic material. Some stereoblocks composed of isotactic and atactic polypropylenes were also formed. This type of product forms when α-olefins are polymerized in inert hydrocarbons with catalysts prepared by reducing high valence metal compounds, like $TiCl_4$, with organometallic compounds like $Al(C_2H_5)$ prepared by reducing high valence metal compounds, like $TiCl_4$, with organometallic compounds like $Al(C_2H_5)_3$.

Later heterogeneous highly crystalline catalysts based on transition metals (valence 3 or less) like $TiCl_2$, $TiCl_3$, $ZrCl_3$, and VCl_3 were developed that yielded stereospecific polypropylene. The metal halides were combined with selected metal alkyls. Only those alkyls were picked that would not destroy the crystalline lattice of the transition metal salts in the process of the reaction. The resultant catalysts yielded crystalline polypropylenes with high fractions of the isotactic material. The products, however, also contained some low molecular weight fractions, some amorphous and stereoblock materials, that still required costly purification and separations to obtain relatively pure isotactic polypropylene. The atactic polymer is a wax-like substance that lacks toughness. Also, presence of amorphous materials, or very low molecular weight compounds, causes tackiness

Table 6.3 Polypropylenes prepared by Natta [37]

Transition metal halide	Metal alkyl halide	% Crystallinity
$TiCl_3$ (β)	$Al(C_2H_5)_3$	40–50
$TiCl_3$ (α, γ, or δ)	$Al(C_2H_5)_3$	96–98
$TiCl_3$ (α, γ, or δ)	$Al(C_2H_5)_2CI$	96–98
$TiCl_3$ (α, γ, or δ)	$Be(C_2H_5)_2$	94–96
$TiCl_3$ (α, γ, or δ)	$Mg(C_2H_5)_2$	78–85
$TiCl_3$ (α, γ, or δ)	$Zn(C_2H_5)_2$	30–40
VCl_3	$Al(C_2H_5)_3$	73
$TiCl_2$	$Al(C_2H_5)_3$	75

Table 6.4 Effect of addition of Lewis bases on the amount of crystalline fraction in polypropylene

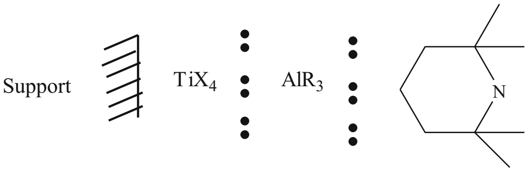
Transition metal halides	Aluminum alkyl	Lewis base	% Crystallinity
$TiCl_3$	$2Al(C_2H_5)Br_2$	Pyridine	>98.5
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$N(C_2H_5)_3$	95
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$NH(C_2H_5)_2$	93
$TiCl_3$	$2Al(C_2H_5)Br_2$	$N^+(C_4H_9)_4I^-$	>99
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$N^+(C_4H_9)_4Br^-$	96

[a] From Natta et al. [38]

and impedes processing. Table 6.3 lists some of the catalysts and the amounts of crystallinity in polymers that were reported by Natta et al. [37]. To avoid costly purification of isotactic polypropylene, three-component catalyst systems were developed. Some of the original ones appear to have been reported by Natta, himself, who found that addition of Lewis bases enhances the quantity of the crystalline material. Table 6.4 shows the effects of addition of Lewis bases on the amount of crystallinity, reported by Natta et al. [38].

Many other three-component systems were developed since [39–43]. Also, development of more active catalysts [44, 45] eliminates a need to remove them from the finished product [15]. The first improvement in catalyst productivity came from treating $TiCl_3$ (formed from $TiCl_4$ and $Al(C_2H_5)Cl_2$) with aliphatic ethers resulting in yields of 520 g of polymer for each gram of Ti [46]. Further improvement was achieved by supporting $TiCl_3$ on $MgCl_2$ or by producing a supported catalyst by reacting $TiCl_4$ with $Mg(OC_2H_5)$ or with other magnesium compounds. This raised the productivity to over 3,000 g of polymer for every gram of Ti [46]. The products, however, contained low percentages of the isotactic isomer (20–40%). Addition of a Lewis base like *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine in solid component and ethyl benzoate in solution raised the isotactic content to 93% with a productivity of 2,500 g of polymer per gram of Ti [41]. Claims are made today for much greater catalyst activity. It was reported, for instance, that catalyst efficiencies of 40 kg of polymer per 1 g of Ti can be achieved. Such yields require proper choice of catalysts and control over polymerization conditions. The isotactic fractions in the products are reported to range from 95 to 97% [47–49].

In a catalyst system $TiCl_3/MgCl_2/C_6H_5COOC_2H_5/Al(C_2H_5)_3$, the high activity was initially attributed to higher propagation rates rather than to an increase in the concentration of the active sites [50]. The higher activity of these catalysts, however, was shown instead to be due to higher numbers of active centers and only slightly higher values of K_P [51]. Subsequent trends in modifications of supported Ziegler–Natta catalysts consisted of using sterically hindered amines [52–54]. For instance, 2,2,6,6-tetramethylpiperidine might be used together with different trialkylaluminum compounds as modifier-cocatalyst systems for the supported catalysts:

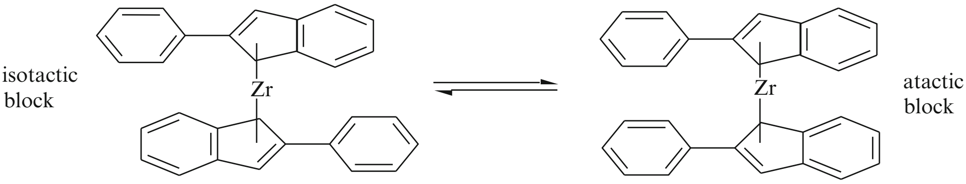


where X represents a halogen.

Other analogous amines, like 1,2,4-trimethylpiperazine and 2,3,4,5-tetraethylpiperidine, are also used in preparations of titanium halide catalysts supported on $MgCl_2$. The amine remains as a built-in modifier in the catalyst system [53].

Subsequent research efforts concentrated on soluble catalytic systems, like di-η^5-cyclopentadienyldiphenyltitanium and tetrabenzylzirconium complexed with methylaluminoxane, $(CH_3)_2Al–[–O–Al(CH_3)–]_n–Al(CH_3)_2$. Such catalysts, however, yield products that contain only about 85% isotactic polypropylene [55–61], and only if the reactions are conducted at low temperatures, $-45°C$ or lower. A major breakthrough occurred when rigid chiral metallocene initiators were developed, like 1,1-ethylene-di-η^5-indenylzirconium dichloride, complexed with methylaluminoxane. In place of zirconium, titanium and hafnium analogs can also be used. These catalysts are highly isospecific [62–64] when used at low temperatures. The compounds are illustrated in Chap. 4. Typical catalysts consist of aluminum to transition metal ratios of 103 or 104:1. Many of them yield 98–99% isotactic fractions of the polymer. In addition, these are very active catalysts, yielding large quantities of polymer per gram of zirconium.

It was also reported that elastomeric polypropylenes can be formed from the monomer with the aid of some metallocene catalysts [62–64]. Because rigid, chiral metallocene catalysts produce isotactic polypropylene, while the achiral ones produce the atactic form, Waymouth and Coates [62] prepared a bridged metallocene catalyst with indenyl ligands that rotate about the metal–ligand bond axis. The rotation causes the catalyst to isomerize between chivalric and nonchiral geometries:



Indenyl ligands, however, were found to rotate faster that the polymerization reaction. This prevents formation of stereoregular polymer blocks [62]. To overcome that, phenyl substituents were added to the ligands to slow down the rotation below the speed of monomer insertion, yet rotate faster than the time required for formation of the whole polymeric chain. The product, a catalytic system of bis(2-phenylindenyl)zirconium dichloride plus methylaluminoxane, was found to yield elastomeric block copolymers of isotactic and atactic polypropylene [62].

Vincenzo et al. [63] reported that ^{13}C NMR microstructural analysis of polypropylene samples produced with two representative "oscillating" metallocene catalysts was found to be largely different in steric hindrance. The original mechanistic proposal of an "oscillation" between the two enantiomorphous, a racemic-like (isotactic-selective) and a meso-like (non-stereoselective) conformation, according to them, cannot explain the observed polymer configuration.

They further feel that isotactic-stereoblock nature of the polymers obtained with this catalyst proves unambiguously that the active cation "oscillates" between the two enantiomorphous racemic-like conformations at an average frequency that, even at high propene concentration, is only slightly lower than that of monomer insertion. The less hindered catalyst gives instead a largely stereoirregular polypropylene, which is the logical consequence of a faster ligand rotation; however, depending on the use conditions (in particular, on the nature of the cocatalyst and the polarity of the solvent), the polymerization products may also contain appreciable amounts of a fairly isotactic fraction. The peculiar microstructure of this fraction, with isotactic blocks of the same relative configuration spanned by short atactic ones, rules out the possibility that the latter are due to an active species in meso-like conformation and point rather to a conformationally "locked" racemic-like species with restricted ring mobility. The hypothesis of a stereorigidity induced by the proximity to a counter anion, which would play the role of the inter-annular bridge in the racemic-bis(indenyl) ansa-metallocenes, was tested by computer modeling and found viable.

Preparation of elastomeric polypropylenes was also reported by Chien et al. [64]. Two metallocene catalysts of different stereospecificities were used. The isospecific catalyst precursors were either *rac*-ethylene bis-(1-η^5-indenyl)zirconium dichloride or *rac*-dimethylsilylene bis(1-η^5-indenyl)zirconium dichloride. The unspecific one was ethylene bis(9-η^5-fluorenyl)zirconium dichloride. The precursors were activated with triphenyl carbenium tetrakis(pentafluorophenyl)borate and triisobutylaluminum. The resultant catalysts exhibit very high activity, yielding products that range from tough plastomers to weak elastomers [64].

6.2.1 Manufacturing Techniques

The earliest commercial methods used slurry polymerizations with liquid hydrocarbon diluents, like hexane or heptane. These diluents carried the propylene and the catalyst. Small amounts of hydrogen were fed into the reaction mixtures to control molecular weights. The catalyst system consisted of a deep purple or violet-colored $TiCl_3$ reacted with diethyl aluminum chloride. The $TiCl_3$ was often prepared by reduction of $TiCl_4$ with an aluminum powder. These reactions were carried out in stirred autoclaves at temperatures below 90°C and at pressures sufficient to maintain a liquid phase. The concentration of propylene in the reaction mixtures ranged between 10 and 20%. The products formed in discrete particles and were removed at 20–40% concentrations of solids. Unreacted monomer was withdrawn from the product mixtures and reused. The catalysts were deactivated and dissolved out of the products with alcohol containing some HCl, or removed by steam extraction. This was followed by extraction of the amorphous fractions with hot liquid hydrocarbons.

Later bulk polymerization processes were developed where liquid propylene was either used as the only diluent in a loop reactor or permitted to boil out to remove the heat of reaction. The second was done in stirred vessels with vapor space at the top. More recently, gas-phase polymerizations of propylene were introduced. The technology is similar to the gas-phase technology in ethylene polymerizations [15] described in Sect. 6.1.

6.2.2 Syndiotactic Polypropylene

Isotactic polypropylene received most attention because it is commercially more desirable. Nevertheless, syndiotactic polypropylene, though less crystalline, has greater clarity, elasticity, and impact resistance. It melts, however, at lower temperature. This isomer was originally prepared with both, heterogeneous, titanium-based catalysts and soluble, vanadium-based ones. The heterogeneous catalysts gave very low yields of the syndiotactic fractions. In fact, original samples contained only a few percent of the desired material, almost an impurity. The yield of syndiotactic polypropylene increased with a decrease in polymerization temperature, but still remained low [65].

Highly syndiotactic polypropylene was prepared by Natta et al. [38] with homogeneous catalysts formed from VCl_4 or from vanadium tri-acetylacetonate, aluminum dialkyl halide, and anisole at -48 to -78°C.

Table 6.5 Comparison of isotactic and syndiotactic polypropylenes

				Typical	
Isomer	Crystal structure	Density at 25°C	MP (°C)	M_w	M_n
Isotactic	Monoclinic	0.92–0.43 g/cm^3	171–186	220–700 K	38–160 K
	Triclinic	0.943 g/cm^3			
	Hexagonal				
Syndiotactic	Orthorhombic	0.89–0.91 g/cm^3	138		

No isotactic fractions formed. This led to development of many effective soluble catalysts. The catalyst components and the conditions for their preparation are quite important in maintaining control over syndiotactic placement. For the most effective soluble catalyst the ratio of AIR_2X to the vanadium compound has to be maintained between 3 and 10 [66]. The organic portion of the organoaluminum compound can be either methyl, ethyl, isobutyl, neopentyl, phenyl, or methylstyryl [9, 67]. In addition to VCl_4 and to vanadium tri-acetylacetonate [66], various other vanadates can be used, like $[VO(OR)_xCl_{3-x}]$, where $x = 1, 2$, or 3 [65]. The exact nature of the vanadium compound, however, is very important to the resultant steric arrangement of the product. For instance, VCl_4 combined with $Al(C_2H_5)_2F$ forms a heterogeneous catalyst that yields the isotactic isomer [65]. Vanadium tri-acetylacetonate, on the other hand, upon reacting with $Al(C_2H_5)_2F$ forms a soluble catalyst that yields the syndiotactic isomer [66]. Addition of certain electron donors increases the amount of syndiotactic placement. These are anisole, furan, diethyl ether, cycloheptanone, ethyl acetate, and thiophene [67]. The optimum results are obtained when an anisole to vanadium ratio is 1:1. Also, the highest amount of syndiotactic polymer is obtained when the soluble catalysts are prepared and used at low temperatures. Even at low temperatures, however, like −78°C, the amount of syndiotacticity that can be obtained with a specific catalyst decreases with time [65, 66, 68]. This indicates a deterioration of the syndiotactic placing sites. On the other hand, polymerization of propylene with soluble vanadium tri-acetylacetonate–$Al(C_2C_5)_2Cl$ system was reported to be a “living” type polymerization [69]. The product has a narrow molecular weight distribution ($M_w/M_n = 1.05–1.20$). A kinetic study indicates an absence of chain transferring and termination at temperatures below −65°C.

More recent catalysts for syndiotactic polypropylene are complexes, like *i*-propyl(cyclopentadienyl-1-fluorenyl)hafnium dichloride with methyl aluminoxane [70]. Another, similar catalyst is *i*-propyl(η^5-cyclopentadienyl-η^3-fluorenyl)zirconium dichloride with methyl aluminoxane. These catalysts yield polymers that are high in syndiotactic material (the zirconium-based compound yields 86% of racemic pentads) [70, 71]. Commercial production of syndiotactic polypropylene is in the early stages. What catalytic system is used, however, is not disclosed at this time. Some of the properties of the two isomers, isotactic and syndiotactic polypropylenes, are compared in Table 6.5.

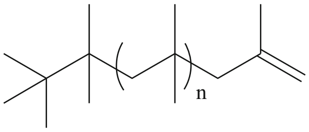
The molecular weights of syndiotactic polypropylenes can vary from a number average molecular weight of 25,000–60,000, depending upon reaction conditions [70]. Also, in isotactic polypropylene there is less than one double bond per 1,000 carbon atoms [72]. A typical $M_w/M_n = 5–12$.

6.3 Polyisobutylene

The original commercial methods for preparing high molecular weight polyisobutylene by cationic polymerization in good yields were reported in 1940. The reaction was carried out at −40 to −80°C in a diluent with BF_3 catalysis [72]. This developed into current commercial practices of polymerizing isobutylene at −80 to −100°C, using liquid ethylene or methyl chloride as a diluent [73, 74]. Even at these low temperatures the reaction is quite violent. Methods were developed, therefore, to dissipate the heat. In one of them, called “flash polymerization process” the catalyst (a Lewis acid, like BF_3 or $AlCl_3$, for instance) is added in solution to the cooled isobutylene solution. The polymerization takes place very rapidly and is complete in a few seconds with the heat of the reaction being removed by vaporization of the diluent. Such reactions, however, are very difficult to carry out in conventional batch reactors. Two types of procedures were, therefore, adopted [75]. The first one is built around a moving stainless steel belt contained inside a gas-tight reactor housing. Isobutylene and liquid ethylene from one source and a Lewis acid in ethylene solution (0.1–0.3% based on monomer) from another source are fed continuously onto the moving belt where they are mixed and moved. The movement of the belt is adjusted at such a speed that the polymerization is complete before the polymer arrives at the end of its travel, where it is removed with a scraper and further processed.

In the second process, the polymerization is carried out in multiple kneaders or mixers. These are arranged in a series of descending steps. Here the reaction mixture is carried from one kneader to another with the temperature being raised at each station and completed at the last one.

All commercially important polyisobutylenes are linear, head to tail polymers, with tertiary butyl groups at one end of the chains and vinylidene groups at the other:



The differences lie in molecular weights. They range from 2,000 to 20,000 for viscous liquids to between 100,000 and 400,000 for high molecular weight elastomers that resemble unmilled crepe rubber. The polymers degrade readily from thermal abuse. They can be stabilized effectively, however, by adding small quantities (0.1–1.0%) of such stabilizers as aromatic amines, phenols, or sulfur compounds. Polyisobutylenes are soluble in many hydrocarbons and are resistant to attacks by many chemicals.

Coordination polymerizations with Ziegler–Natta catalysts yield similar polymers that range from viscous liquids to rubbery solids. At 0°C, a catalyst with a 1:16 Ti to Al molar ratio yields a polymer with a molecular weight of 5,000–6,000 [76]. The molecular weight, however, is dependent upon the reaction time. This contrasts with polymerizations of ethylene, propylene, and 1-butene by such catalysts, where the molecular weights of the products are independent of the reaction time. In addition, there are some questions about the exact molecular structures of the products [76].

Bochmann and coworkers [77] carried out polymerizations of isobutylene and copolymerizations with isoprene using cationic zirconocene hydride complexes. The combination of $[Cp_2ZrH]$ with various trityl salts of weakly coordinating anions gives binuclear cationic hydrides $[Cp'_4Zr_2H(\mu\text{-}H)_2]^+X^-$ which are powerful initiators for the polymerization of isobutene and its copolymerization with isoprene. The temperature dependence of M is indicative of a cationic mechanism. The highest molecular weights are obtained only under scrupulously dry conditions.

High molecular weight polyisobutylene has fair tensile strength but suffers from the disadvantage of considerable cold flow. A copolymer of isobutylene with some isoprene for cross-linking is, therefore, used as a commercial elastomer and called “butyl rubber.” The isoprene is present in the copolymer in only minor proportions (1.4–4.5%). The uncross-linked material is very similar to polyisobutylene. Copolymers of isobutylene with other dienes are also called butyl rubbers. They can also be terpolymers, where the third component may be cyclopentadiene for improved ozone resistance.

The molecular weights of the copolymers vary inversely with the quantities of isoprene incorporated, the polymerization temperatures, and amount of impurities present during polymerization. Impurities like *n*-butene or water act as chain transferring agents [79].

To maintain uniform molecular weights, the conversions are usually kept from exceeding 60%.

6.4 Poly(α-olefin)s

Many α-olefins were polymerized by the Ziegler–Natta catalysts to yield high polymers and many such polymers were found to be stereospecific and crystalline. Polymerizations of α-olefins of the general structure of $CH_2 = CH - (CH_2)_x - R$, where x is 0–3 and R denotes CH_3, $CH–(CH_3)_2$, $C(CH_3)_3$, or C_6H_5, can be catalyzed by vanadium trichloride/triethyl aluminum [80]. The conversions are fairly high, though higher crystallinity can be obtained with titanium-based catalysts [81]. Addition of Lewis bases, such as $(C_4H_9)_2O$, $(C_4H_9)_3N$, or $(C_4H_9)_3P$, to the catalyst system further increases crystallinity [82].

6.4.1 *Properties of Poly(α-olefin)s*

Many poly(α-olefin)s reported in the literature are not used commercially for various reasons. Table 6.6 lists some of the olefins polymerized by the Ziegler–Natta catalysts [72, 83].

6.4.2 *Poly(butene-1)*

Isotactic poly(butene-1) is produced commercially with three-component coordination-type catalysts. It is manufactured by a continuous process with simultaneous additions to the reaction vessel of the monomer solution, a suspension of $TiCl_2–AlCl_3$, and a solution of diethyl aluminum chloride [84]. The effluent containing the suspension of the product is continually removed from the reactor. Molecular weight control is achieved through regulating the reaction temperature. The effluent contains approximately 5–8% of atactic polybutene that is dissolved in the liquid carrier. The suspended isotactic fractions (92–98%) are isolated after catalyst decomposition and removal. The product has a density of 0.92 g/cm^3 and melts at 124–130°C.

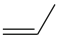
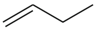
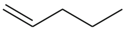
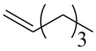
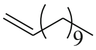
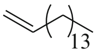
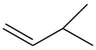
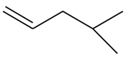
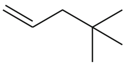
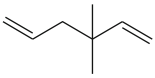
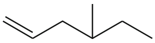
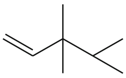
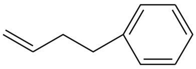
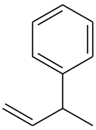
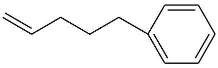
Isotactic polybutene crystallizes into three different forms. When it cools from the melt, it originally crystallizes into a metastable crystalline one. After several days, however, it transforms into a different form. Noticeable changes in melting point, density, flexural modulus, yield, and hardness accompany this transformation. The third crystalline form results from crystallization from solution. The polymer exhibits good impact and tear resistance. It is also resistant to environmental stress-cracking.

6.4.3 *Poly(4-methyl pentene-1)*

Another commercially produced polyolefin is isotactic poly(4-methyl pentene-1). The polymer carries a trade name of TPX. This material is known for high transparency, good electrical properties, and heat resistance. Poly(4-methyl pentene-1) has a density of 0.83 g/cm^3. This polyolefin exhibits poor load-bearing properties and is susceptible to UV degradation. It is also a poor barrier to moisture and gases and scratches readily. This limits its use in many applications.

Poly(4-methyl pentene) is produced by the same process and equipment as polypropylene. A post finishing de-ashing step, however, is required. In addition, aseptic conditions are maintained during manufacture to prevent contamination that may affect clarity.

Table 6.6 Properties of poly(α-olefin)s

Monomer	State	MP (°C)
	Crystalline	136
	Crystalline	165–168
	Crystalline	124–130
	Crystalline	75
	Rubber, amorphous	–
	Some crystallinity	45
	Crystallinity in pendant groups	70; 100
	Crystalline, hard	240–285
	Crystalline, hard	200–240
	Crystalline, hard	300–350
	Crystalline, hard	350
	Crystalline, hard	160
	Rubber, amorphous	–
	Crystalline, slightly rubbery	158
	Crystalline, intractable	360
	Rubber, amorphous	–

[a]From refs. [72, 83]

A number of similar polyolefins with pendant side groups are known. These include poly(3-methyl butene-1), poly(4,4-dimethyl pentene-1), and poly(vinyl cyclohexane). Due to their increased cohesive energy, ability to pack into tight structures, and the effect of increasing stiffness of the pendant groups, some of these polymers have a high melting point. This can be seen from Table 6.9. Many of these polymers, however, tend to undergo complex morphological changes on standing. This can result in fissures and planes of weakness in the structure.

6.5 Copolymers of Ethylene and Propylene

Many monomers have been copolymerized with ethylene by a variety of polymerization methods. When ethylene is copolymerized with other olefins, the resultant hydrocarbon polymers have reduced regularity and lower density, lower softening point, and lower brittle point.

Copolymers of ethylene and propylene are a commercially important family of materials. They vary from elastomers that can contain 80% ethylene and 20% propylene to polypropylene that is modified with small amounts of ethylene to improve impact resistance.

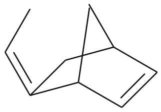
Metallocene catalysts can produce both random and alternating copolymers of ethylene and propylene [85]. At present there does not appear to be any commercial utilization of alternating copolymers. They were reported to form in polymerizations catalyzed by bridged fluorenyl catalysts [85].

6.5.1 Ethylene and Propylene Elastomers

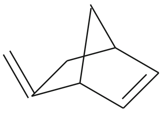
The commercial *ethylene-propylene rubbers* typically range in propylene content from 30 to 60%, depending upon intended use. Such copolymers are prepared with Ziegler–Natta type catalysts. Soluble catalysts and true solution processes are preferred. The common catalyst systems are based on VCl_4, $VOCl_3$, $V(Acac)_3$, $VO(OR)_3$, $VOCl(OR)_2$, $VOCl_2(OR)$, etc. with various organoaluminum derivatives. The products are predominantly amorphous. Polymerization reactions are usually carried out at 40°C in solvents like chlorobenzene or pentane. The resultant random copolymers are recovered by alcohol precipitation. Because these elastomers are almost completely saturated, cross-linking is difficult. A third monomer, a diene is, therefore, included in the preparation of these rubbers that carry the trade names EPTR or EPDM. Inclusion of third monomers presents some problems in copolymerization reactions. For instance, it is important to maintain constant feed mixtures of monomers to obtain constant compositions. Yet, two of the three monomers are gaseous and the third one is a liquid. Natta [86] developed a technique that depends upon maintaining violent agitation of the solvent while gaseous monomers were bubbled through the liquid phase. This was referred to as "semi-flow technique." The process allows the compositions of gaseous and liquid phases to be in equilibrium with each other and to be more or less constant [87]. Other techniques evolved since. All are designed to maintain constant polymerization mixtures.

The vanadium-based catalyst systems deteriorate with time and decrease in the number of catalytic centers as the polymerizations progress. The rate of decay is affected by conditions used for catalyst preparation, compositions of the catalysts, temperature, solvents, and Lewis bases. It is also affected by the type and concentration of the third monomer [88–90]. Additions of chlorinated compounds to the deactivated catalysts, however, help restore activity [91, 92]. Catalyst decay can also be overcome by continually feeding catalyst components into the polymerization medium [93].

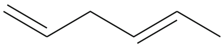
While third monomer can be a common diene, like isoprene, more often it is a bridged ring structure with at least one double bond in the ring. In typical terpolymer rubbers with 60–40 ratios of ethylene to propylene the diene components usually comprise about 3% of the total. Some specialty rubbers, however, may contain 10% of the diene or even more. Reaction conditions are always chosen to obtain 1,2 placement of the diene. Dienes in common use are ethylidine norbornene, methylene norbornene, 1,4-hexadiene, dicyclopentadiene, and cycloocatadiene:



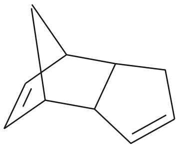
ethylidine
norbornene



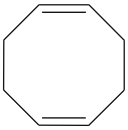
methyle
norbornene



1,4-hexadiene

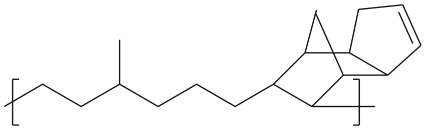


dicyclopentadiene



cyclooctadiene

In addition to the above, the patent literature describes many other dienes. An idealized picture of a segment of an uncross-linked gum stock might be shown as having the following structure:



6.5.2 Copolymers of Ethylene with α-Olefins and Ethylene with Carbon Monoxide

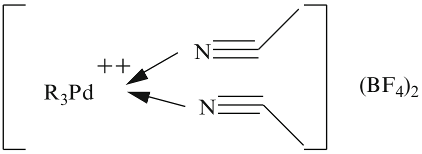
Many copolymers of ethylene with α-olefins are prepared commercially. Thus ethylene is copolymerized with butene-1, where a comonomer is included to lower the regularity and the density of the polymer. Many copolymers are prepared with transition metal oxide catalysts on support. The comonomer is usually present in approximately 5% quantities. This is sufficient to lower the crystallinity and to markedly improve the impact strength and resistance to environmental stress-cracking. Copolymers of ethylene with hexene-1, where the hexene-1 content is less than 5%, are also produced for the same reason.

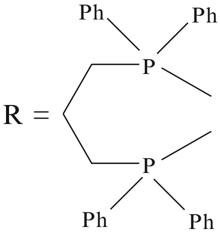
In most cases, the monomers that homopolymerize by Ziegler–Natta coordination catalysts also copolymerize by them [94]. In addition, some monomers that do not homopolymerize may still copolymerize to form alternating copolymers. Because the lifetime of a growing polymer molecule is relatively long (can be as long as several minutes), block copolymerization is possible through changes in the monomer feeds. Also, the nature of the transition metal compound influences the reactivity ratios of the monomers in copolymerizations. On the other hand, the nature of the organometallic compound has no such effect [95]. It also appears that changes in the reaction temperature between 0 and 75°C have no effect on the *r* values. Copolymers can be formed using either soluble or heterogeneous Ziegler–Natta. One problem encountered with the heterogeneous catalysts is the tendency by the formed polymers to coat the active sites. This forces the monomers to diffuse to the sites and may cause starvation of the more active monomer if both diffuse at equal rates.

Many different block copolymers of olefins, like ethylene with propylene and ethylene with butene-1, are manufactured. Use of the anionic coordination catalysts enables variations in the molecular structures of the products. It is possible to vary the length and stereoregularity of the blocks. This is accomplished by feeding alternately different monomers into the reactor. When it is necessary that the blocks consist of pure homopolymers, then after each addition the reaction is allowed to subside. If any residual monomer remains, it is removed [96]. This requires a long lifetime for the growing chains and an insignificant amount of termination. The stability of the anion depends upon the catalyst system. One technique for catalyst preparation is to form $TiCl_3$ by reducing $TiCl_4$ with diethyl aluminum chloride followed by careful washing of the product of reduction to remove the by-product $Al(C_2H_5)Cl$. Other reports describe using the α-form of $TiCl_3$ or heat treating it to form the β or γ-forms that yields more stereospecific products.

The transition metal oxide catalysts on support, such as the CrO_3/silica–alumina (Phillips) and MoO_3/Al_2O_3 (Standard Oil), are used to copolymerize minor quantities of α-olefins with ethylene. Such copolymerizations introduce short pendant groups into polymer backbones.

Ethylene and other olefins can also be copolymerized with carbon monoxide to form polymers of aliphatic ketones, using transition metal catalysts, like palladium(II) coupled with non-coordinating anions. There are numerous reports of such catalysts in the literature. One example is a compound composed of bidentate diarylphosphinopropane ligand and two acetonitrile molecules coordinating Pd^{2+} coupled with BF_3 counterions. This compound, bis(acetonitrile)palladium(II)-1,3-bis(diphenylphosphino)propane-(tetrafluoborate), can be illustrated as follows [97]:

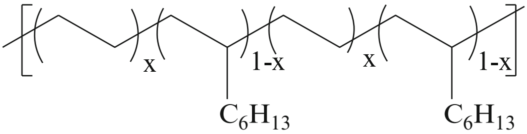




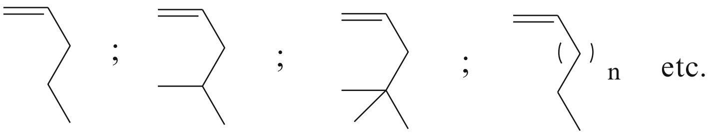
When the tetrafluoroborate is replaced with a perchlorate, the compound is a very active catalyst [97].

One copolymer of ethylene and carbon monoxide are available commercially. The material offered under the trade name of Carilon is actually a terpolymer, because it contains a small quantity of propylene. It is reported [98] that use of a palladium catalyst permits formation of perfectly alternating interpolymer.^{08} The product is reported to be a tough, chemical resistant material.

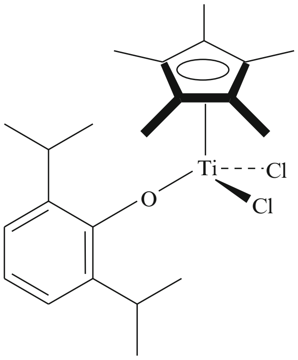
Hustad et al. [99] developed a technique to make polydisperse polyethylene diblock copolymers with 1-octene with a distribution of block lengths. When melted and compressed into films, the distinct polymeric segments self-assemble into layered patterns of semi-crystalline and hard and amorphous phases. Because each phase has a different refractive index, the block copolymer, shown below, can function as a photonic crystal and scatter visible light.

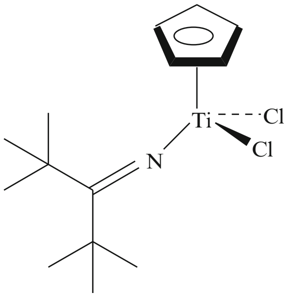


Nomura and coworkers [100] studied copolymerization of ethylene with various pentenes:



where $n = 8, 12$. The polymerizations were carried out with titanium catalysts illustrated below. Titanium compound were combined with methyl aluminoxane:

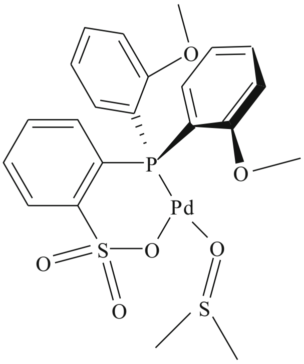




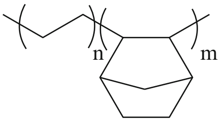
Their results show that the monomer reactivities are influenced not only by substituents on the olefins but also by the nature of the catalytically active species.

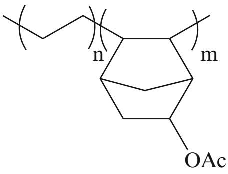
Derlin and Kaminsky [101] reported copolymerizations of ethylene and propylene with a sterically hindered monomer, 3-methyl-1-butene, using titanium and zirconium metallocenes with methyl aluminoxane cocatalyst.

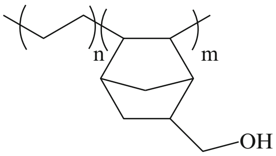
Tritto and coworkers [102] reported that the complex [Pd(k^2-P,O-{2-(2-MeOC$_6$H$_4$)$_2$P}C$_6$H$_4$SO$_3$) Me(DMSO)] was investigated as a single-component catalyst for the copolymerization of ethylene with norbornene. The catalyst was illustrated as follows:



The copolymers were obtained in very good yields and molar masses were significantly higher than those of polyethylene. Three copolymers were formed:

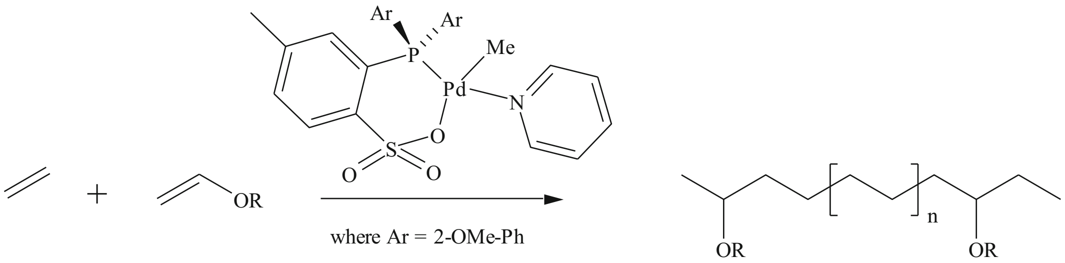






Determination of microstructure and reactivity ratios revealed a strong inherent tendency to form alternating copolymers.

Jordan [103] described copolymerization of ethylene with vinyl ethers and with vinyl fluoride. The catalyst used was (*ortho*-phospheno-arenesulfonate)PdMe(pyridine). The reaction was illustrated as follows:



6.5.3 Copolymers of Propylene with Dienes

Although presently lacking industrial importance, alternating copolymers can be made from propylene and butadiene [104] and also from propylene and isoprene [105]. Copolymers of propylene and butadiene form with vanadium- or titanium-based catalysts combined with aluminum alkyls. The catalysts have to be prepared at very low temperature (−70°C). Also, it was found that a presence of halogen atoms in the catalyst is essential [75]. Carbonyl compounds, such as ketones, esters, and others, are very effective additives. A reaction mechanism based on alternating coordination of propylene and butadiene with the transition metal was proposed by Furukawa [104].

6.5.4 Copolymers of Ethylene with Vinyl Acetate

Various copolymers of ethylene with vinyl acetate are prepared by free-radical mechanism in emulsion polymerizations. Both reactivity ratios are close to 1.0 [106]. The degree of branching in these copolymers is strongly temperature-dependent [107]. These materials find wide use in such areas as paper coatings and adhesives. In addition, some are hydrolyzed to form copolymers of ethylene with vinyl alcohol. Such resins are available commercially in various ratios of polyethylene to poly(vinyl alcohol), can range from 30% poly(vinyl alcohol) to as high as 70%.

Vinyl acetate residues in ethylene–vinyl acetate copolymers reduce regularity of polyethylene. This reduces crystallinity in the polymer. Materials containing 45% vinyl acetate are elastomers and can be cross-linked with peroxides.

6.5.5 Ionomers

Another group of commercial copolymers of ethylene is those formed with acrylic and methacrylic acids, where ethylene is the major component. The copolymerizations are carried out under high pressures. These materials range in comonomer content from 3 to 20%. Typical values are 10%. A large proportion of the carboxylic acid groups (40–50%) are prereacted with metal ions like sodium or zinc. The copolymer salts are called ionomers with a trade name like Syrlin. The materials tend to behave similarly to cross-linked polymers at ambient temperature by being stiff and tough. Yet they can be processed at elevated temperatures, because aggregation of the ionic segments from different polymeric molecules is destroyed. The material becomes mobile but after cooling the aggregates reform. Ionomers exhibit good low temperature flexibility. They are tough, abrasion-resistant resins that adhere well to metal surfaces.

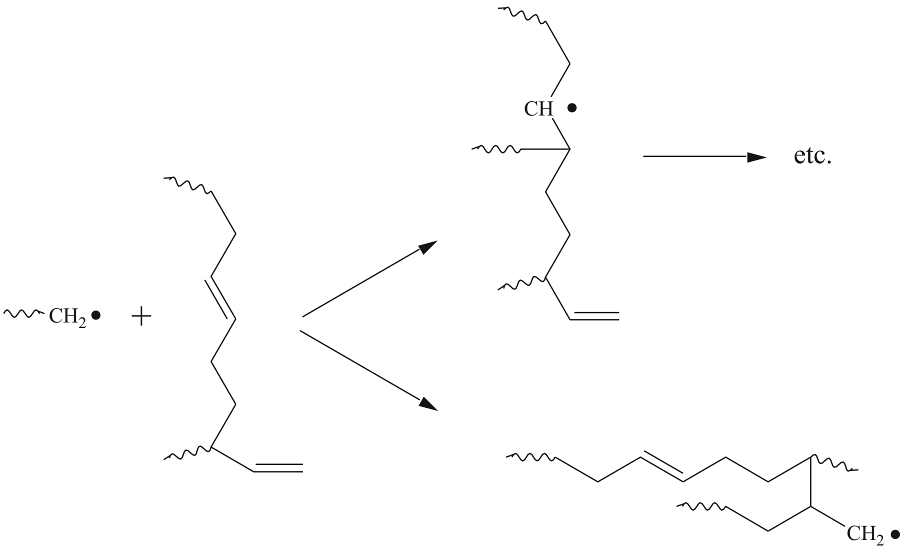
6.6 Homopolymers of Conjugated Dienes

Many different polymers of conjugated dienes are prepared commercially by a variety of processes, depending upon the need. They are formed by free-radical, ionic, and coordinated anionic polymerizations. In addition, various molecular weights homopolymers and copolymers, ranging from a few thousand for liquid polymers to high molecular weight ones for synthetic rubbers, are on the market.

6.6.1 Polybutadiene

1,3-Butadiene, the simplest of the conjugated dienes, is produced commercially by thermal cracking of petroleum fractions and catalytic dehydrogenation of butane and butene. Polymerization of butadiene can potentially lead to three poly(1,2-butadiene)s, atactic, isotactic, and syndiotactic and two *cis* and *trans* forms of poly(1,4-butadiene). This is discussed in Chaps. 3 and 4.

Free-radical polymerizations of 1,3-butadiene usually result in polymers with 78–82% of 1,4-type placement and 18–22% of 1,2-adducts. The ratio of 1,4 to 1,2 adducts is independent of the temperature of polymerization. Moreover, this ratio is obtained in polymerizations that are carried out in bulk and in emulsion. The ratio of *trans*-1,4 to *cis*-1,4 tends to decrease, however, as the temperature of the reaction decreases. Polybutadiene polymers formed by free-radical mechanism are branched because the residual unsaturations in the polymeric chains are subjects to free-radical attacks:



Should branching become excessive, infinite networks can form. The products become cross-linked, insoluble, and infusible. Such materials are called *popcorn* polymers. This phenomenon is more common in bulk polymerizations. The cross-linked polymers form nodules that occupy much more volume than the monomers from which they formed and often clog up the polymerization equipment, sometimes even rupturing it.

High molecular weight homopolymers of 1,3-butadiene formed by free-radical mechanism lack the type of elastomeric properties that are needed from commercial rubbers. Copolymers of butadiene, however, with styrene or acrylonitrile are more useful and are prepared on a large scale. This is discussed in another section.

6.6.1.1 Liquid Polybutadiene

Low molecular weight liquid homopolymers of 1,3 butadiene, also some liquid copolymers, find industrial uses in many applications. These materials can range in molecular weights from 500 to 5,000 depending upon the mode of polymerization. Liquid polybutadienes formed by cationic polymerizations are high *trans*-1,4 content. Such materials find applications in industrial coatings. They are usually prepared with Lewis acids in chlorinated solvents. When the reactions are catalyzed by $AlCl_3$ at −78°C, two types of polymers form [108]. One is soluble and the other is insoluble, depending upon the extent of conversion. $AlCl_3$, $AlBr_3$, and BF_3–Et_2O produce polymers with the same ratios of *trans*-1,4 to 1,2 adducts. These range from 4 to 5. Polymerizations carried out in ethylene chloride [108] catalyzed by $TiCl_4$ yield products with lower ratios of *trans*-1,4 to 1,2 adducts. The ratios of the two placements are affected by the solvents. They are also affected by additions of complexing agents, such as nitroethane and nitrobenzene [108]. The changes, however, are small.

Hydroxyl-terminated liquid polybutadienes are prepared for reactions with diisocyanates to form elastomeric polyurethanes (see Chap. 6). Such materials can be prepared by anionic polymerizations as “living” polymers and then quenched at the appropriate molecular weight. These polybutadienes can also be formed by free-radical mechanism. The microstructures of the two products differ, however, and this may affect the properties of the finished products. To form hydroxyl-terminated polymers by free-radical mechanism, the polymerization reactions may be initiated by hydroxyl radicals from hydrogen peroxide.

A new approach to preparation of hydroxyl-terminated liquid polybutadiene is to use a cyclic monomer, 1,5-cyclooctadiene, a ruthenium metathesis catalyst (see Chap. 5, Grubbs catalysts in section on metathesis ring opening polymerization) and an acetate functionalized chain transfer agent [109, 110]. The acetate-functionalized chain transfer agent is *cis*-2-butene-1,4-diacetate. The reaction can be carried out without a solvent and proceeds at 50°C over 6 h under an inert gas purge [111]. The acetate protecting groups provide compatibility with the ruthenium catalyst. Subsequent to polymerization the acetate groups can be converted to hydroxyl end groups with the aid of a base, like sodium methoxide.

Liquid polybutadienes that are high in 1,2 placement are also available commercially. These range from reactive polymers containing approximately 70% of vinyl groups to very reactive ones containing more than 90% of 1,2 units. The materials are formed by anionic polymerization with either sodium naphthalene, or with sodium dispersions, or with organolithium initiators in polar solvents. Carboxyl group terminated liquid polybutadienes are predominantly used as modifiers for epoxy resins (Chap. 7). They are formed by anionic mechanisms in solution with organolithium catalysts like diphenylethanedilithium, butanedilithium, isoprenelithium, or lithium methylnaphthalene complexes. Cyclohexane is the choice solvent. The reaction is quenched with carbon dioxide to introduce the terminal carboxyl groups.

Table 6.7 Microstructures of polybutadienes prepared with some coordination catalysts

	Microstructure (%)		
Catalyst	*Cis*-1,4	*Trans*-1,4	1,2
$TiI_4/Al(C_2H_5)_3$	95	2	3
$TiBr_4/Al(C_4H_9)_3$	88	3	9
β-$TiCl_3/Al(C_2H_5)_3$	80	12	8
$Ti(OC_4H_9)_4/Al(_2H_5)_3$	–	–	99–100
$Ti(OC_6H_5)_4/R_3Al$	90–100	–	–
(π-Cycloocatadiene)$_2$Ni,CF_3CO_2H	100	–	–
Bis(π-Crotyl NiCl)	92	–	–
Bis(π-Crotyl NiI)	–	94	–
$CoCl_2/Al(C_2H_5)_2Cl$	96–97	2.5	1–1.5
$CoCl_2/Al(C_2H_5)_3$	94	3	3
$CoCl_2/Al(C_2H_5)_3$/pyridine	90–97	–	–
Co-stearate/AlR_2Cl	98	1	1
VCl_3/AlR_3	–	99	1
$VOCl_3/Al(C_2H_5)_3$	–	97–9	2–3
$VCl_4/AlCl_3$	–	95	–
$Cr(C_6H_5CN)_6/Al(C_2H_5)_3$	100	–	–
$MoO_2(OR)_3/Al(C_2H_5)_3$	–	–	75

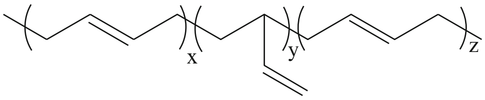
[a] From various sources in the literature

6.6.1.2 High Molecular Weight Polybutadiene

High molecular weight polybutadiene homopolymers are prepared commercially with anionic catalysts and with coordination ones. Polybutadiene formed with sodium dispersions was prepared industrially in the former USSR, and perhaps might still be produced in that area today. This sodium-catalyzed polybutadiene contains 65% of 1,2-adducts [112]. Many of the preparations by others, however, utilize either alkyllithium or Ziegler–Natta type catalysts prepared with titanium tetra iodide or preferably containing cobalt.

Because high molecular weight polybutadiene can be prepared by different catalytic systems, the choice of catalyst is usually governed by the desired microstructure of the product. Alfin catalysts yield very high molecular weight polymers with a large amount of *trans*-1,4 structures. Both the molecular weight and microstructure can be affected significantly, however, by variations in the Alfin catalyst components. These can be the alkyl groups of the organometallic compounds or alkoxide portions.

When butadiene is polymerized with lithium metal or with alkyllithium catalysts, inert solvents like hexane or heptane must be used to obtain high *cis*-1,4 placement (see Chap. 4). Based on ^{13}C NMR spectra, 1,4-polybutadiene formed with *n*-butyllithium consists of blocks of *cis*-1,4 units and *trans*-1,4 units that are separated by isolated vinyl structures [113]:

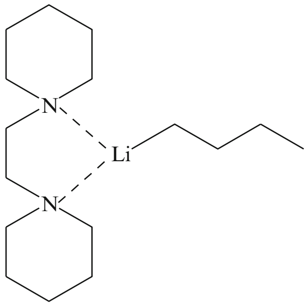


The quantity of such units in the above polybutadienes is approximately 48–58% *trans*-1,4, 33–45% *cis*-1,4, and 7–10% 1,2 units [112]. There is little effect of the reaction temperatures upon this composition. As described in Chap. 3, however, addition of Lewis bases has a profound effect. Reactions in tetrahydrofuran solvent result in 1,2 placement that can be as high as 87%.

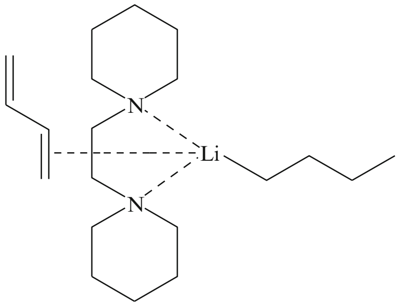
The microstructures of polybutadienes prepared with Ziegler–Natta catalysts vary with catalyst composition. It is possible to form polymers that are high either in 1,2 placement or in 1,4 units. The catalysts and the type of placement are summarized in Table 6.7.

Butadiene can be polymerized with chromium oxide catalyst on support to form solid homopolymers. The products, however, tend to coat the catalyst within a few hours after the start of the reaction and interfere with further polymerization. Polybutadiene can also be prepared in the presence of molybdenum catalyst promoted by calcium hydride. The product contains 80% of 1,4 units and 20% of 1,2 units. Of the 1,4 units, 62.5% are *cis* and 37.5% are *trans* [110].

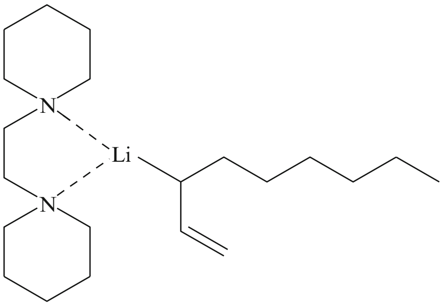
Cobalt oxide on silica–alumina in the presence of alkyl aluminum also yields high *cis*-1,4 structure polymers. An all 1,2 polybutadiene can be prepared with *n*-butyllithium modified with bis-piperidino ethane. The atactic polymer can be formed in hexane at −5 to +20°C temperature [111]. The 100% 1,2 placement was postulated to proceed according to the following scheme [111]. First a complex forms between the base and butyllithium:



The above complex reacts with butadiene to form a new complex:



This is followed by insertion of butadiene into the carbon–lithium bond:



Annunziata et al. [114] reported that Group 4 metals complexes bearing anilidomethylpyridine ligands were prepared by them. After activation by $AlBu_2H$ and methylalumoxane, the catalysts were tested in 1,3-butadiene and α-olefin polymerization. The zirconium complexes showed higher activity than the titanium analogous. Polymerization of ethylene resulted in all cases in the production of high molecular weight linear polyethylene. On the other hand, propylene polymerization tests provided substantially atactic polypropylene. 1,3-Butadiene polymerizations produced *cis*-1,4 polybutadiene. Use of zirconium complexes produced polymers with a content of *cis*-1,4 units higher than 99.9% were claimed.

6.6.2 Polyisoprene

Polyisoprenes occur in nature. They are also prepared synthetically. Most commercial processes try to duplicate the naturally occurring material.

6.6.2.1 Natural Polyisoprenes

Rubber hydrocarbon is the principle component of raw rubber. The subject is discussed in greater detail in Chap. 7. Natural rubber is 97% *cis*-1,4 polyisoprene. It is obtained by tapping the bark of rubber trees (*Hevea brasiliensis*) and collecting the exudates, a latex consisting of about 32–35% rubber. A similar material can also be found in the sap of many other plants and shrubs. The structure of natural rubber has been investigated over 100 years, but it was only after 1920, however, that the chemical structure was elucidated. It was shown to be a linear polymer consisting of head to tail links of isoprene units, 98% bonded 1,4.

6.6.2.2 Synthetic Polyisoprenes

In following natural rubber, the synthetic efforts are devoted to obtaining very high *cis*-1,4 polyisoprene and to forming a synthetic "natural" rubber. Two types of polymerizations yield products that approach this. One is through use of Ziegler–Natta type catalysts and the other through anionic polymerization with alkyllithium compounds in hydrocarbon solvents. One commercial process, for instance, uses reaction products of $TiCl_4$ with triisobutylaluminum at an Al/Ti ratio of 0.9–1.1 as the catalyst. Diphenyl ether or other Lewis bases are sometimes added as catalyst modifiers [113–116]. The process results in an approximately 95% *cis*-1,4 polyisoprene product. Typically, such reactions are carried out on continuous basis, usually in hexane and take 2–4 h. Polymerizations are often done in two reaction lines, each consisting of four kettles arranged in series. The heat of the reaction is partially absorbed by precooling the feed streams. The remaining heat is absorbed on cooled surfaces. When the stream exits, the conversion is about 80%. Addition of a shortstop solution stabilizes the product.

Alkyllithium-initiated polymerizations of isoprene yield polymers with 92–93% *cis*-1,4 content. One industrial process uses butyllithium in a continuous reaction in two lines each consisting of four reaction kettles. The heat of the reaction is removed by vaporization of the solvent and the monomer. The catalyst solution is added to the solvent stream just before it is intensively mixed with the isoprene monomer stream and fed to the first reactor. After the stream leaves each reactor, small quantities of methanol are injected between stages into the reaction mixture. This limits the molecular weight by stopping the reaction. Fresh butyllithium catalyst is added again at the next stage in the next reactor to initiate new polymer growth [117–119].

As is described in Chaps. 3 and 4, the monomer placement into the polyisoprene chain can occur potentially in nine different ways. These are the three tactic forms of the 1,2 adducts, two 1,4 adducts, *cis* and *trans*, and three tactic forms of 3,4-adducts. In addition, there is some possibility of head to head and tail to tail insertion, though the common addition is head to tail. Table 6.8 presents the various microstructures that can be obtained in polymerizations of isoprene with different catalysts.

Table 6.8 Polymerization products of isoprene

		Approximate			
Mode of polymerization	Solvent	% *Cis*-1,4	% *Trans*-1,4	% 1,2	% 3,4
Free radical	Emulsion in water	32	65	6	7
Cationic	–	37	51	4	9
	Chloroform (30°C)	–	90	4	6
Anionic					
Lithium	Pentane	94	0		6
Ethyllithium	Pentene	94	0		6
Butyllithium	Pentene	93	0		7
Sodium	Pentene	0	43	6	51
Ethylsodium	Pentene	6	42	7	45
Butylsodium	Pentane	4	35	7	54
Potassium	Pentane	0	52	8	40
Ethylpotassium	Pentane	24	39	6	31
Butylpotassium	Pentane	20	41	6	34
Rubidium	Pentane	5	47	8	39
Cesium	Pentene	4	51	8	37
Ethyllithium	Ethyl ether	6	29	5	60
Ethylsodium	Ethyl ether	0	14	10	76
Lithium	Ethyl ether	4	27	5–7	63–65
Alfin	Pentane	27	52	5	16
Coordination catalysis					
α-$TiCl_3/AlR_3$			91		
$VCl_3/Al(C_2H_5)_3$			99		
$TiCl_4/Al(C_2H_5)_3$		95–96			
Ti I_4/AlR_3 + amine		100	–		–
$CoCl_2/AlR_3$ + pyridine		96			
V(acetylacetonate)$_3/AlR_3$		90			
$Ti(OR)_4/Al(C_2H_5)_3$		95			

[a] From various sources in the literature

Cationic polymerizations of isoprene proceed more readily than those of butadiene, though both yield low molecular weight liquid polymers. $AlCl_3$ and stannic chloride can be used in chlorinated solvents at temperatures below 0°C. Without chlorinated solvents, however, polymerizations of isoprene require temperatures above 0°C. At high conversions, cationic polymerizations of isoprene result in formations of some cross-linked material [120]. The soluble portions of the polymers are high in *trans*-1,4 structures. Alfin catalysts yield polymers that are higher in *trans*-1,4 structures than free-radical emulsion polymerizations [121].

Chromium oxide catalysts on support polymerize isoprene-like butadiene to solid polymers. Here too, however, during the polymerization process, polymer particles cover the catalyst completely within a few hours from the start of the reaction and retard or stop further polymer formation. The polymerization conditions are the same as those used for butadiene. The reactions can be carried out over fixed bed catalysts containing 3% chromium oxide on $SiO_2–Al_2O_3$. Conditions are 88°C and 42 kg/cm^2 pressure with the charge containing 20% of isoprene and 80% isobutane [122]. The mixed molybdenum–alumina catalyst with calcium hydride also yields polyisoprene.

Lithium metal dispersions form polymers of isoprene that are high in *cis*-1,4 contents as shown in Table 6.8. These polymers form in hydrocarbon solvents. This is done industrially and the products are called Coral rubbers. They contain only a small percentage of 3,4-structures and no *trans*-1,4 or 1,2 units. The materials strongly resemble *Hevea* rubber.

Use of Ziegler–Natta catalysts, as seen from Table 6.8, can yield an almost all *cis*-1,4-polyisoprene or an almost all *trans*-1,4-polyisoprene. The microstructure depends upon the ratio of titanium to aluminum. Ratios of Ti:Al between 0.5:1 and 1.5:1 yield the *cis* isomer. A 1:1 ratio is the optimum. Ratios of Ti:Al between 1.5:1 and 3:1 yield the *trans* structures [123]. The titanium to aluminum ratios also affect the yields of the polymers as well as the microstructures. There also is an influence on the molecular weight of the product [124]. Variations in catalyst compositions, however, do not affect the relative amounts of 1,4 to 3,4 or to 1,2 placements. Only *cis* and *trans* arrangements are affected. In addition, the molecular weights of the polymers and the microstructures are relatively insensitive to the catalyst concentrations. The temperatures of the reactions, however, do affect the rates, the molecular weights, and the microstructures.

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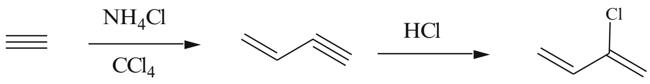
6.7 Methyl Rubber, Poly(2,3-dimethylbutadiene)

Early attempts at preparations of synthetic rubbers resulted in developments of elastomers from 2,3-dimethylbutadiene. The material, called “methyl rubber,” was claimed to yield better elastomeric properties than polybutadiene. Methyl rubber was produced in Germany during World War I where the monomer was prepared from acetone. The polymerizations were carried out by free-radical mechanism and anionically, using sodium metal dispersions for initiation. Later, it was demonstrated that 2,3-dimethyl polybutadiene can be polymerized to very high *cis*-1,4 polymer with Ziegler–Natta catalysts [125, 126].

6.8 Chloroprene Rubber, Poly(2-chloro-1,3-butadiene)

2-Chloro-1,3-butadiene (chloroprene) was originally synthesized in 1930. The material can polymerize spontaneously to an elastomer that has good resistance to oil and weathering. Commercial production of chloroprene rubber started in 1932. Since then, many types of polymers and copolymers were developed with the trivial generic name of *neoprene*.

The monomer can be prepared from acetylene:



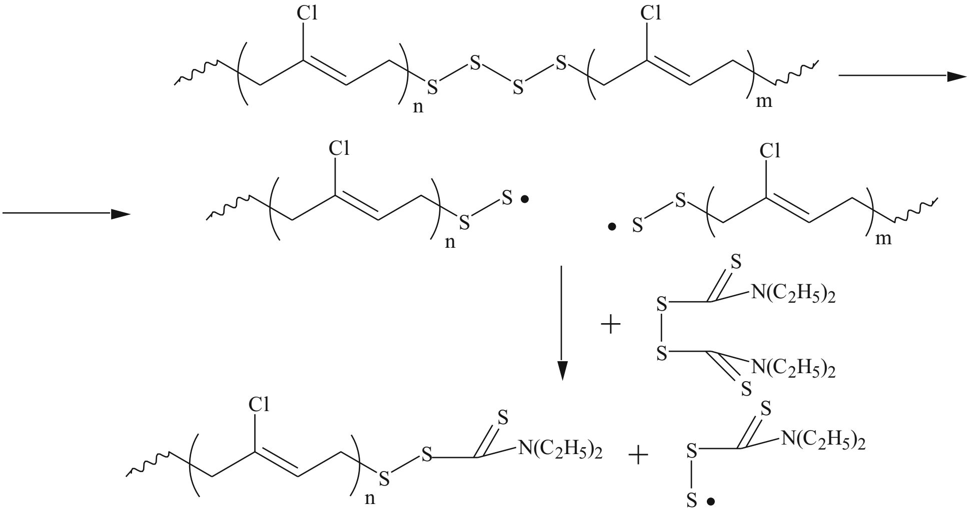
It can also be formed from butadiene.

Chloroprene is polymerized commercially by free-radical emulsion polymerization. The reaction is carried out at 40°C to a 90% conversion. A typical recipe for such an emulsion polymerization is as follows [127]:

Material	Parts
Water	150
Chloroprene	100
Rosin	4 (stabilizer)
NaOH	0.8 (stabilizer)
$K_2S_2O_8$	
Sulfur	
Methylene-bis-(Na-naphthalenesulfonic acid)	0.7

When the polymerization reaches 90% conversion, the reaction mixture is cooled to 20°C and tetraethylthiuram disulfide is added. This is done to prevent the pendant unsaturation in the polychloroprene backbones from cross-linking or forming branches. An unmodified polymer is difficult to process even at a 70% conversion. To overcome this, a sulfur–tetraethylthiuram modification is carried out.

When the product is treated with the thiuram, an exchange reaction takes place to yield a stable, thiuram-modified polymer of reduced molecular weight. It is believed that the reaction takes place through cleavage of the sulfur links, formed during polymerization in the presence of sulfur, and formation of free radicals [128]



After the reaction with tetraethylthiuram disulfide is completed, the latex is acidified with acetic acid, short of coagulation. The rubber is then recovered at a low temperature (about −15°C) in the form of sheets by deposition of the latex on cooled rotating drums [127, 128].

The polymer, formed by this technique, consists of about 85% of *trans*-1,4 units, 10% of *cis*-1,4 units, 1.5% of 1,2 units, and 1.0% of 3,4 units. The polymer is essentially linear with a molecular weight equal to approximately 100,000. The sulfur-modified polychloroprenes are sold under a trade name of Neoprene-G. An unmodified version prepared with mercaptan chain transferring agents (Neoprene W) is a polymer with a molecular weight of about 200,000 [128, 130].

Table 6.9 lists the structures of polychloroprenes that form by free-radical polymerization at different temperatures. Chloroprene polymerizes by cationic polymerization with the aid of Lewis acids in chlorinated solvents. When aluminum chloride is used in a mixture of ethyl chloride–methylene chloride solvent mixture at −80°C, the polymer has 50% 1,4 units [131, 132]. If it is polymerized with boron trifluoride, the product consists of a 50–70% 1,4-adducts. A very high *trans*-1,4 poly(2-chloro-1,3-butadiene) forms by X-ray radiation polymerization of large crystals of chloroprene at −130 to −180°C. It is 97.8% *trans*-1,4 [130]. Presumably the mechanism of polymerization is free radical.

Table 6.9 Structures of polychloroprenes formed by free-radical polymerization

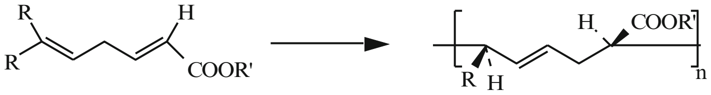
	% 1,4				
Polymerization temperature (°C)	*Cis*	*Trans*	% 1,2	% 3,4	References
−40	5	94	0.9	0.3	[112]
−20	6	91.5	0.7	0.5	[113]
−10	7	–	–	–	[112]
10	9	84	1.1	1.0	[112]
40	10	86, 81	1.6	1.0	[112]
40	13	88.9	0.9	0.3	[113]
100	13	71	2.4	2.4	[112]

[a] From refs. [127–132]

6.9 Special Polymers from Dienes

There are many reports in the literature of preparations of polymers from various other substituted dienes. Most have no commercial significance. Some are, however, interesting materials. An example is a polymer of 2-*t*-butyl-1,3-butadiene formed with $TiCl_4$ and either alkylaluminum or aluminum hydride catalysts [132]. The polymer is crystalline and melts at 106°C. It can be dissolved in common solvents. Based on X-ray data, the monomer placement is high *cis*-1,4.

Poly(carboxybutadiene)s also forms with coordination catalysts [133–135]:



where R = CH_3; R′ = CH_3, C_2H_5, C_4H_9, or C_6H_5.

X-ray crystallography [133–135] showed that the placement is *trans*-isotactic.

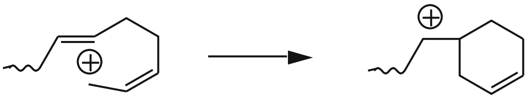
Based on the mode of packing of the chains in the crystalline regions and from the encumbrance of the side groups in relationship to the main chain, an *erythro* configuration can be assigned [134]. The polymers, therefore, are *trans*-*erythro*-isotactic.

Polymerization of 1,3-pentadiene can potentially result in five different insertions of the monomers. These are 1,4-*cis*, 1,4-*trans*, 1,2-*cis*, 1,2-*trans*, and 3,4. In addition, there are potentially 3-*cis*-1,4 and 3 *trans*-1,4 structures (isotactic, syndiotactic, and atactic). Formations of *trans*-1,4 isotactic, *cis*-1,4 isotactic, and *cis*-1,4 syndiotactic polymers are possible with Ziegler–Natta catalysts [136–138]. Amorphous polymers also form that are predominantly *cis*-1,4 or *trans*-1,4, but lack tactic order. Stereospecificity in poly(1,3-pentadiene) is strongly dependent upon the solvent used during the polymerization. Thus, *cis*-1,4 syndiotactic polymers form in aromatic solvents and *trans*-1,2 in aliphatic ones. The preparations require cobalt halide/aluminum alkyl dichloride(or dialkyl chloride) catalysts in combinations with Lewis bases. To form a *trans*-1,4 structure, a catalyst containing aluminum to titanium ratio close to 5 must be used [139].

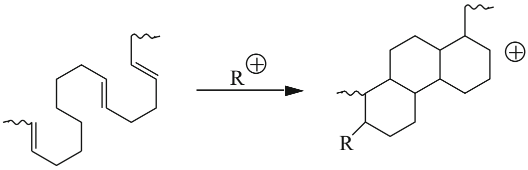
6.10 Cyclopolymerization of Conjugated Dienes

Conjugated dienes like isoprene, butadiene, and chloroprene cyclopolymerize with catalysts consisting of aluminum alkyls, like ethylaluminum dichloride, and titanium tetrachloride [141]. The ladder polymers that form contain fused cyclic structures. The products prepared in hexane are generally insoluble powders, while those prepared in aromatic solvents are soluble even when the molecular weights are high [142]. A high ratio of the transition metal halide to that of the aluminum alkyl must be used. Such a ratio might, conceivably, mean that the mechanism of polymerization is cationic. Also, conventional cationic initiators can be used to yield similar products. The cyclization occurs during propagation. Unsaturation in the products can vary from none to as high as 80%, depending upon the initiator used [142].

Different mechanisms were offered to explain the cyclization of 1,3 dienes [142, 143]. The cyclization might conceivably occur by a sequential process:



or, perhaps from attacks by the propagating carbon cation on *trans*-1,4 double bonds:



where R^+ can represent either a propagating carbon cation or an initiating species. The extensive cyclization may be a result of a sequential process [142, 143].

Cyclopolymerizations typically result in low conversions and dormant reaction mixtures. When additional monomer is added, the dormant mixtures reinitiate polymerizations that again proceed to some limited conversions. If the original dormant mixtures are allowed to stand for a long time the unreacted monomers are slowly consumed [142].

Polymerization of 2,3-dimethylbutadiene-1,3 with Ziegler–Natta catalysts consisting of $Al(i\text{-}C_4H_9)_3–TiCl_4$ yields *cis*-1,4-polydimethylbutadiene as described earlier. This, however, takes place when the aluminum alkyl is in excess. If, on the other hand, the ratio of Al to Ti is 1 or less, cyclic polymer forms instead. The product has reduced unsaturation and some *trans*-1,4 units in the chain [144]. A complex catalyst, consisting of $Al(i\text{-}C_4H_9)_3–CoCl_2$, yields polymers that are predominantly *cis*-1,4 with about 20% of 1,2 units. On the other hand, acid catalysts, like $Al(C_2H_5)Cl_2$, yield cyclic polymers [143, 144]. A polymer formed with the aid of X-ray radiation at low temperatures also contains cyclic units and some *trans*-1,4 [145]. Butadiene and isoprene also form this type of polymer at the same conditions [145].

6.11 Copolymers of Dienes

Several different elastomers, copolymers of butadiene, are produced commercially. The major ones are copolymers of butadiene with styrene and butadiene with acrylonitrile. Some terpolymers, where the third component is an unsaturated carboxylic acid, are also manufactured. Block copolymers of isoprene with styrene and butadiene with styrene are important commercial elastomers.

6.11.1 GR-S Rubber

Copolymerization of butadiene with styrene by free-radical mechanism has been explored very thoroughly [146]. The original efforts started during World War I in Germany. Subsequent work

Table 6.10 Typical recipes for preparation of butadiene–styrene rubbers by emulsion polymerization

	"Hot" process		"Cold" process	
Material	Parts	Purpose	Parts	Purpose
Butadiene	75	Comonomer	72	Comonomer
Styrene	25	Comonomer	28	Comonomer
Water	180	Carrier	180	Carrier
Fatty acid soap	5.0	Emulsifier	4.5	Emulsifier
n-Dodecyl mercaptan	0.5	Chain transferring agent	–	–
t-Dodecyl mercaptan	–	–	0.2	Chain transferring agent
Potassium persulfate	0.3	Initiator	–	–
Auxiliary surfactant	–	–	0.3	Stabilizer
Potassium chloride	–	–	0.3	Stabilizer
p-Menthane hydroperoxide	–	–	0.06	Initiator system
Ferrous sulfate	–	–	0.01	
Ethylenediamine tetraacetic acid sodium salt	–	–	0.05	
Sodiumformaldehyde sulfoxylate			0.05	

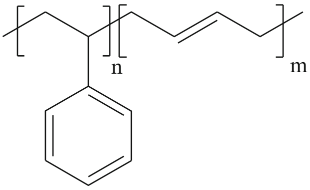
[a] From ref. [127] and other patent literature

during the 1930s was followed by a particularly strong impetus in the United States during World War II. This led to a development of GR-S rubber in the United States and Buna-S rubber in Germany. After World War II further refinements were introduced into the preparatory procedures and "cold" rubber was developed. Industrially, the copolymer is prepared by emulsion copolymerization of butadiene and styrene at low temperatures in a continuous process. A typical product is a random distribution copolymer, with the butadiene content ranging from 70 to 75%. The diene monomer placement is roughly 18% *cis*-1,4; 65% *trans*-1,4; and 17% 1,2. M_n of these copolymers is about 100,000.

A "redox" initiator is used in the cold process, but not in the "hot" one. Also, the "hot" process is carried out at about 50°C for 12 h to approximately 72% conversion. The "cold" process is also carried for 12 h, but at about 5°C to a 60% conversion. The two recipes for preparation of GR-S rubbers are shown in Table 6.10 for comparison of the "hot" and "cold" processes.

In both polymerizations, the unreacted monomer has to be removed. In the "hot" one the reaction is often quenched by addition of hydroquinone, and in the "cold" one by addition of *N*, *N*-diethyldithiocarbamate. After the monomers are steam stripped in both processes, an antioxidant like *N*-phenyl-2-naphthylamine is added. The latex is usually coagulated by addition of a sodium chloride–sulfuric acid solution. The "cold" process yields polymers with less branching than the "hot" one, slightly higher *trans* to *cis* ratios.

During the middle 1960s a series of butadiene–styrene and isoprene–styrene *block-copolymer-elastomers* were developed. These materials possess typical rubber-like properties at ambient temperatures, but act like thermoplastic resins at elevated ones. The copolymers vary from diblock structures of styrene and butadiene



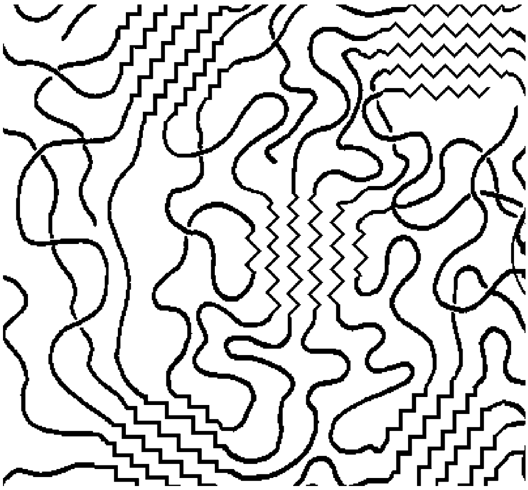
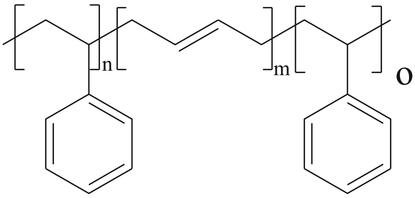


Fig. 6.4 Illustration of polystyrene and polybutadiene domains

to triblock ones, like styrene–butadiene–styrene:



A typical triblock copolymer may consist of about 150 styrene units at each end of the macromolecule and some 1,000 butadiene units in the center. The special physical properties of these block copolymers are due to inherent incompatibility of polystyrene with polybutadiene or polyisoprene blocks. Within the bulk material, there are separations and aggregations of the domains. The polystyrene domains are dispersed in continuous matrixes of the polydienes that are the major components. At ambient temperature, below the T_g of the polystyrene, these domains are rigid and immobilize the ends of the polydiene segments. In effect they serve both as filler particles and as cross-links. Above T_g of polystyrene, however, the domains are easily disrupted and the material can be processed as a thermoplastic polymer. The separation into domains is illustrated in Fig. 6.4.

These thermoplastic elastomers are prepared by anionic solution polymerization with organometallic catalysts. A typical example of such preparation is polymerization of a 75/25 mixture of butadiene/styrene in the presence of *sec*-butyllithium in a hydrocarbon–ether solvent blend. At these reaction conditions butadiene blocks form first and when all the butadiene is consumed, styrene blocks form. In other preparations, monomers are added sequentially, taking advantage of the "living" nature of these anionic polymerizations.

These block copolymers have very narrow molecular weight distributions. Also, the sizes of the blocks are restricted to narrow ranges to maintain optimum elastomeric properties.

6.11.2 GR-N Rubber

Butadiene–acrylonitrile rubbers are another group of useful synthetic elastomers. These copolymers were originally developed in Germany where they were found superior in oil resistance to the butadiene–styrene rubbers. Commercially, these materials are produced by free-radical emulsion polymerization very similarly to the butadiene–styrene copolymers. Similarly, "hot" and "cold" processes are employed. "Low," "medium," and "high" grades of solvent-resistant copolymers are formed, depending upon the amount of acrylonitrile in the copolymer that can range from 25 to 40%. The butadiene placement in these copolymers is approximately 77.5% *trans*-1,4, 12.5% *cis*-1,4, and 10% of 1,2-units. Also, the polymers formed by the "cold" process are less branched and have a narrower molecular weight distribution than those formed by the "hot" process.

An interesting alternating copolymer of butadiene and acrylonitrile was developed in Japan [147]. The copolymer is formed with coordination catalysts consisting of AlR_3, $AlCl_3$, and $VOCl_3$ in a suspension polymerization process. The product is more than 94% alternate and is reported to have very good mechanical properties and good oil resistance.

6.12 Polystyrene and Polystyrene-Like Polymers

Styrene is produced in the United States from benzene and ethylene by a Friedel–Craft reaction that is followed by dehydrogenation over alumina at 600°C. Polystyrene was first prepared in 1839, though the material was confused for an oxidation product of the styrene monomer [148]. Today polystyrene is produced in very large quantities and much is known about this material.

6.12.1 Preparation of Polystyrene by Free-Radical Mechanism

Styrene is one of those monomers that lends itself to polymerization by free-radical, cationic, anionic and coordination mechanisms. This is due to several reasons. One is resonance stabilization of the reactive polystyryl species in the transition state that lowers the activation energy of the propagation reaction. Another is the low polarity of the monomer. This facilitates attack by free-radicals, differently charged ions, and metal complexes. In addition, no side reactions that occur in ionic polymerizations of monomers with functional groups are possible. Styrene polymerizes in the dark by free-radical mechanism more slowly than it does in the presence of light [149]. Also, styrene formed in the dark is reported to have greater amount of syndiotactic placement [150]. The amount of branching in the polymer prepared by free-radical mechanism increases with temperature [136]. This also depends upon the initiator used [151].

The following information has evolved about the free-radical polymerization of styrene:

1. Styrene polymerizes thermally [151–155]. This is discussed in Chap. 3.
2. Oxygen retards polymerizations of styrene. At higher temperatures, however, the rate is accelerated due to peroxide formation [156].
3. The rate of styrene polymerizations in bulk is initially, at low conversions, first order with respect to monomer concentrations. In solution, however, it is a second order with respect to monomer [157].

Polystyrene that is manufactured by free-radical polymerization is atactic. Isotactic polystyrene formed with Ziegler–Natta catalysts was introduced commercially in the 1960s, but failed to gain acceptance. Syndiotactic polystyrene is now being produced commercially.

Industrially, free-radical styrene polymerizations are carried out in bulk, in emulsion, in solution, and in suspension. The clear plastic is generally prepared by mass polymerization. Because polystyrene is soluble in the monomer, mass polymerization, when carried out to completion, results in a tremendous increase in melt viscosity. To avoid this, when styrene is polymerized in bulk in an agitated kettle, the reaction is only carried out to 30–40% conversion. After that, the viscous syrup is transferred to another type of reactor for the completion of the reaction. According to one early

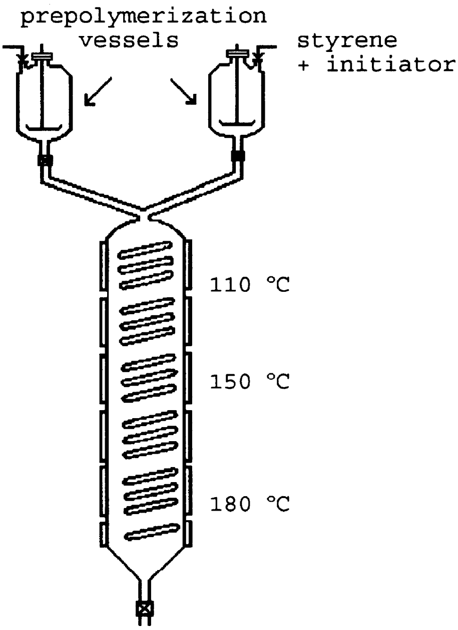


Fig. 6.5 Adiabatic tower for mass polymerization of styrene

German patent, polymerization is completed in a plate and frame filter press [157]. Water circulating through the press removes the heat of the reaction, and the solid polymer is formed inside the frames. This process is still used in some places [158].

Another approach is to use adiabatic towers. Styrene is first partially polymerized in two agitated reaction kettles at 80–100°C. The syrup solution of the polymer in the monomer is then fed continually into the towers from the top. The temperatures in the towers are gradually increased from 100–110°C at the top to 180–200°C at the bottom. By the time the material reaches the bottom, in about 3 h, the polymerization is 92–98% complete [159]. The unreacted monomer is removed and recycled. A modification of the process is to remove the monomer vapor at the top of the tower for reuse.

An improvement in the above procedure is the use of agitated towers [160]. To avoid channeling inside the towers and for better heat transfer, three towers are arranged in series. They are equipped with slow agitators and with grids of pipes for cooling and heating [160]. Polymeric melt is heated from 95 to 225°C to reduce viscosity and help heat transfer. A solvent like ethyl benzene may be added. A vacuum devolatalizer removes both monomer and solvent from the product (Fig. 6.5).

6.12.2 *Polystyrene Prepared by Ionic Chain-Growth Polymerization*

Much research was devoted to both cationic and anionic polymerizations. An investigation of cationic polymerization of styrene with $Al(C_2H_5)_2Cl/RCl$ (R = alkyl or aryl) catalyst/cocatalyst system was reported by Kennedy [161, 162]. The efficiency (polymerization initiation) is determined by the relative stability and/or concentration of the initiating carbocations that are provided by the cocatalyst RCl. *N*-butyl, isopropyl, and *sec*-butyl chlorides exhibit low cocatalytic efficiencies because of low tendency for ion formation. Triphenylmethyl chloride is also a poor cocatalyst because the triphenylmethyl ion that forms is more stable than the propagating styryl ion. Initiation of styrene polymerizations by carbocations is now well established [163].

Anionic polymerization of styrene with amyl sodium yields an isotactic polymer [164]. Polymerizations catalyzed by triphenylmethylpotassium also yield the same stereospecific polystyrene [165]. The same is true of organolithium compounds [166, 167].

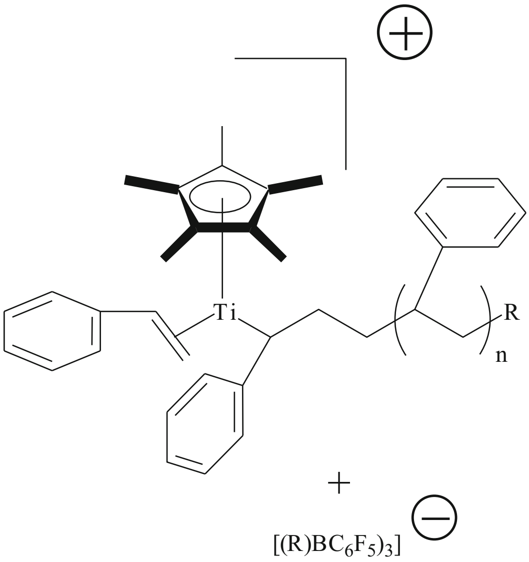
In butyllithium initiated polymerizations of styrene in benzene termination were claimed to occur by association between the propagating anions and the lithium counterions with another butyllithium molecule [168]. This was contradicted by claims that terminations result from association of two propagating chains [169]. Alfin catalysts polymerize styrene to yield stereospecific products [170].

Coordination catalysts based on aluminum alkyls and titanium halides yield isotactic polystyrene [171–174]. The polymer matches isotactic polystyrene formed with amylsodium. It is composed of head-to-tail sequences with the main chain fold being helical. There are three monomer units per each helical fold [171, 172]. The catalyst composition, however, has a strong bearing on the microstructure of the resultant polymer [175, 176].

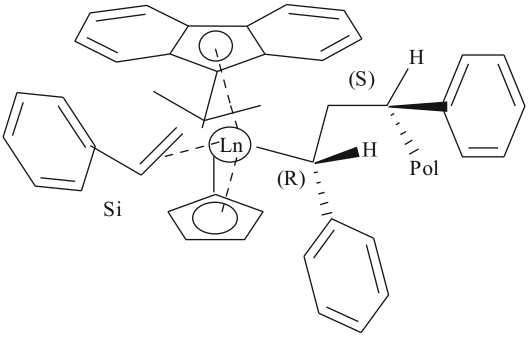
Ishihara et al. reported in 1986 that syndiotactic polystyrene can be prepared with the aid of organic or inorganic titanium compounds activated with methylaluminoxane [177]. There is much greater incentive to commercialize syndiotactic polystyrene than the isotactic one. This is because isotactic polystyrene crystallizes at a slow rate. That makes it impractical for many industrial applications. Syndiotactic polystyrene, on the other hand, crystallizes at a fast rate, has a melting point of 275°C, compared to 240°C for the isotactic one, and is suitable for use as a strong structural material.

Many catalysts were investigated for the preparation of syndiotactic polystyrene. High activity is claimed for half-sandwich titanocenes of the type $CpTiCl_3$, $IndTiCl_3$, and substituted $IndTiCl_3$ with methylaluminoxane as cocatalyst [178]. It was also reported that $BMe(C_6F_5)_3$ and other borates can be used as precursors instead of methyl-aluminoxane [178]. In addition, it was disclosed that fluorinated catalysts exhibit very high activities and produce polymers with higher molecular weight polymers [178].

The mechanism of polymerization was investigated by different groups. Grassi and Zambelli claim that the syndiotactic styrene polymerization proceeds through a secondary insertion of styrene into Ti–alkyl (or growing polymer chain) bond. In the half titanocene catalyst, the polymer chain appears to be η^6-coordinated to the metal of the active species [179]:



Maron and coworkers [180] reported that theoretical methods were used to investigate the syndiospecificity of the styrene polymerization catalyzed by single-site, single-component allyl ansa-lanthanidocenes:



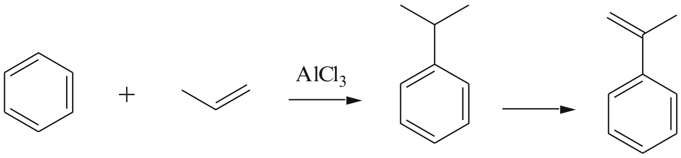
Two limiting chain end stereocontrol mechanisms were studied by them, namely, migratory insertion through a site epimerization and site stereoconfiguration independent of backside insertion on a "stationary" polymer chain. Four consecutive insertions of styrene were computed to reveal that (i) backside insertions are more favorable than, or at least as favorable as, frontside insertions. The formation of a syndiotactic polymer is controlled by the thermodynamics. Moreover, the odd (first and third) insertions are of 2,1-down-*si*-type and are kinetically favored over the 2,1-up-*re*-ones. This control is the conjunction of two effects: minimization of styrene–styrene and styrene (phenyl ring)–fluorenyl repulsions. The steric hindrance of the polymer chain induces a fourth insertion by an exocyclic coordination of the fluorenyl ligand that is compensated by the η^6 coordination of one of the phenyl ring in the growing chain.

Syndiotactic polystyrene is available commercially under the trade name of Questra. This material is produced with the aid of a metallocene catalyst and is sold in several grades [181].

There is a small interest in forming isotactic polystyrenes with vary narrow molecular weight distributions, because of some very limited practical applications, and from purely academic interests. Several preparations of virtually monodisperse polystyrenes of $M_w/M_n = 1.06$ by anionic polymerizations were developed. The materials are available commercially [181–186], small quantities for use as standards for GPC.

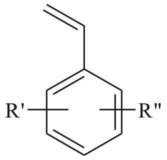
6.12.3 Polymers from Substituted Styrenes

Many derivatives of styrene can be readily synthesized. Some are commercially available. One of them is α-methyl styrene. It is formed from propylene and benzene by a process that is very similar to styrene preparation:

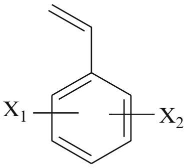


Due to the allylic nature of α-methyl styrene it cannot be polymerized by free-radical mechanism. It polymerizes readily, however, by an ionic one. Resins based on copolymers of α-methyl styrene are available commercially. Other styrene derivatives that can be obtained commercially are:

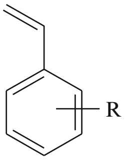
1. Alkyl or aryl substituted styrenes,



where R_1 and R_2 are alkyl or aryl groups.
2. Halogen derivatives,



where X_1 and X_2 = F, Cl, Br, or I.
3. Polar-substituted styrenes,

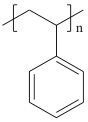
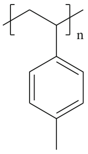
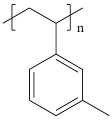
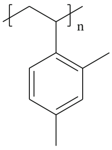
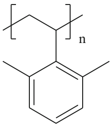
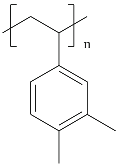
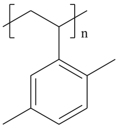
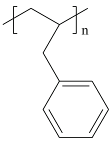
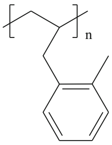


where R = CN, CHO, COOH, $OCOCH_3$, OH, OCH_3, NO_2, NH_2, and SO_3H.

Vinyl toluene polymerizes readily by free-radical mechanism at 100°C. The absolute rate at that temperature is greater than for styrene. The activation energy for vinyl toluene polymerization is 17–19 kcal per mole while that for styrene is 21 kcal mole. This monomer can also be polymerized by ionic and coordination mechanisms. Earlier attempts at polymerization of α-methyl styrene with Ziegler–Natta catalysts were not successful [187, 188]. Later, however, it was shown that polymerization does take place with $TiCl_4/Al(C_2H_5)_3$ at −78°C. The activity of the catalyst and the DP depend on the ratio of aluminum to titanium, the nature of the solvent, and on the aging of the catalyst [189]. The optimum ratio of the aluminum alkyl to titanium chloride is 1.0–1.2. Mixing and aging of the catalyst must be done below room temperature, and the valence of titanium must be maintained between 3 and 4 [189]. This led Sakurada to suggest that the reaction actually proceeds via a cationic rather than a coordinated anionic mechanism [189].

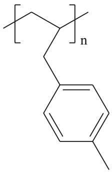
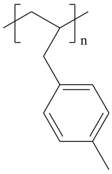
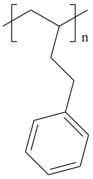
Various reports in the literature describe cationic polymerizations of α-methyl styrene with Lewis acids [190–192]. The products are mostly low molecular weight polymers, some containing unsaturation with pendant phenylindane groups. A high molecular weight polymer can be prepared from α-methyl styrene by cationic polymerization at −90 to −130°C with $AlCl_3$ in ethyl chloride or in carbon disulfide [193]. The product has a narrow molecular weight distribution. Some T_g and T_m values of polystyrene-like materials, including isotactic polystyrene, are presented in Table 6.11.

Table 6.11 Transition temperatures of poly(phenylene alkene)s

Polymer	T_g (°C)	References	T_m (°C)	References
	80	[178]	(i) 240; (s) 272	[178]
	73.81	[178]	Amorphous	[176]
	77	[178]	219	[176]
	92	[178]	310	[176]
	123	[178]	330	[176]
	91	[178]	240	[176]
	84	[177]	290	[176]
	60	[177]	207–208	[176]
	80	[177]	2	[177]

(continued)

Table 6.11 (continued)

Polymer	T_g (°C)	References	T_m (°C)	References
	34–40	[177]	180	[177]
	60–65	[177]	240	[177]
	10	[177]	162–168	[177]

[a] From refs. [196–198]

6.13 Copolymers of Styrene

Many copolymers of styrene are manufactured on a large commercial scale. Because styrene copolymerizes readily with many other monomers, it is possible to obtain a wide distribution of properties. Random copolymers form quite readily by free-radical mechanism [185, 194]. Some can also be formed by ionic mechanism. In addition, graft and block copolymers of styrene are also among commercially important materials.

Most comonomers differ from styrene in polarity and reactivity. A desired copolymer composition can be achieved, however, through utilization of copolymerization parameters based on kinetic data and on quantum-chemical considerations. This is done industrially in preparations of styrene–acrylonitrile, styrene–methyl methacrylate, and styrene–maleic anhydride copolymers of different compositions.

6.13.1 High-Impact Polystyrene

For many applications, the homopolymer of styrene is too brittle. To overcome that, many different approaches were originally tried. These included use of high molecular weight polymers, use of plasticizers, fillers (glass fiber, wood flour, etc.), deliberate orientation of the polymeric chains, copolymerization and addition of rubbery substances. Effect of plasticizers is too severe for practical use, and use of high molecular weight polymers exhibits only marginal improvement. Use of fillers, though beneficial, is mostly confined to United States. Orientation is limited to sheets and filaments, and copolymerization usually lowers the softening point too much.

Addition of rubbery materials, however, does improve the impact resistance of polystyrene. This is done, therefore, extensively. The most common rubbers used for this purpose are butadiene–styrene copolymers. Some butadiene homopolymers are also used but to a lesser extent. The high-impact polystyrene is presently prepared by dissolving the rubber in a styrene monomer and then polymerizing the styrene. This polymerization is either done in bulk or in suspension. The product contains styrene–butadiene rubber, styrene homopolymer, and a considerable portion of styrene-graft copolymer that forms when polystyrene radicals attack the rubber molecules. The product has very enhanced impact resistance.

Past practices, however, consisted simply in blending a mixture of polystyrene and rubber on a two-roll mill, or in a high shear internal mixer, or passing through an extruder. The impact strength of the product was only moderately better than that of the unmodified polymer. Another procedure was to blend polystyrene emulsion latex with a styrene–butadiene rubber emulsion latex and then to coagulate the two together. The product is also only marginally better in impact strength than styrene homopolymer. This practice, however, may still be in existence in some places.

In high-impact polystyrene, the rubber exists in discrete droplets, less than 50 μm in diameter. In effect the polymerization serves to form an oil in oil emulsion [199] where the polystyrene is in the continuous phase and the rubber is in a dispersed phase. The graft copolymer that forms serves to "emulsify" this heterogeneous polymer solution [200].

Commercial high-impact polystyrene usually contains 5–20% styrene–butadiene rubber. The particle size ranges from 1 to 10 μm. High-impact polystyrene may have as much as seven times the impact strength of polystyrene, but it has only half its tensile strength, lower hardness, and lower softening point.

6.13.2 ABS Resins

Styrene–acrylonitrile copolymers are produced commercially for use as structural plastics. The typical acrylonitrile content in such resins is between 20 and 30%. These materials have better solvent and oil resistance than polystyrene and a higher softening point. In addition, they exhibit better resistance to cracking and crazing and an enhanced impact strength. Although the acrylonitrile copolymers have enhanced properties over polystyrene, they are still inadequate for many applications. Acrylonitrile–butadiene–styrene polymers, known as ABS resins, were therefore developed.

Although ABS resins can potentially be produced in a variety of ways, there are only two main processes. In one of them acrylonitrile–styrene copolymer is blended with a butadiene–acrylonitrile rubber. In the other one, interpolymers are formed of polybutadiene with styrene and acrylonitrile.

In the first one, the two materials are blended on a rubber mill or in an internal mixer. Blending of the two materials can also be achieved by combining emulsion latexes of the two materials together and then coagulating the mixture. Peroxide must be added to the blends in order to achieve some -cross-linking of the elastomer to attain optimum properties. A wide range of blends are made by this technique with various properties [201]. Most common commercial blends of ABS resins may contain 70 parts of styrene–acrylonitrile copolymer (70/30) and 40 parts of butadiene–nitrile rubber (65/35).

In the second process, styrene and acrylonitrile are copolymerized in the presence of polybutadiene latex. The product is a mixture of butadiene homopolymer and a graft copolymer.

6.13.3 Copolymers of Styrene with Maleic Anhydride

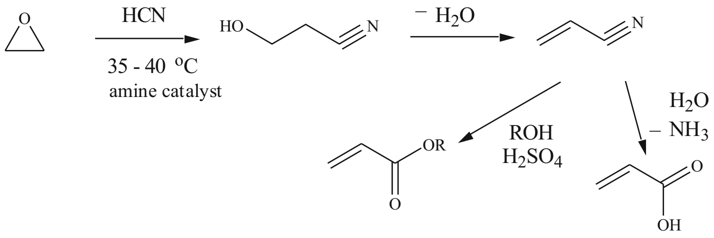
Many styrene–maleic anhydride copolymers are produced commercially for special uses. These are formed by free-radical copolymerization and many commercial grades are partially esterified. Molecular weights of such polymers may range from 1,500 to 50,000, depending upon the source. The melting points of these copolymers can vary from 110 to 220°C, depending upon molecular weight, degree of hydrolysis and esterification, and also the ratio of styrene to maleic anhydride.

Only a small percent of styrene copolymers reported in the literature achieved industrial importance. Some of the interesting copolymers of styrene that were reported but not utilized commercially are copolymers with various unsaturated nitriles. This includes vinylidene cyanide, fumaronitrile, malononitrile, methacrylonitrile, acrylonitrile, and cinnamonitrile [292]. Often, copolymerization of styrene with nitriles yields copolymers with higher heat distortion temperature, higher tensiles, better craze resistance, and higher percent elongation.

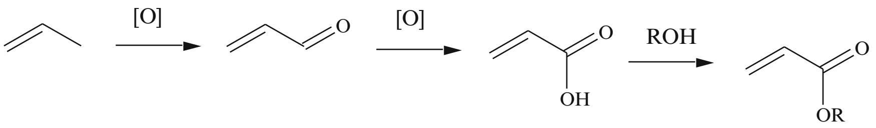
Styrene was also copolymerized with many acrylic and methacrylic esters. Products with better weathering properties often form. Copolymerization with some acrylates lowers the value of T_g [203].

6.14 Polymers of Acrylic and Methacrylic Esters

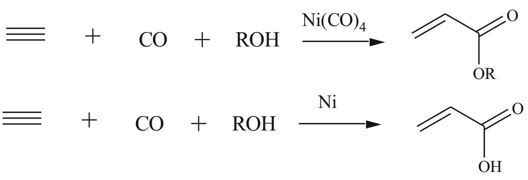
There are many synthetic procedures for preparing acrylic acid and its esters. One way, used early, is to make acrylic esters from ethylene oxide:



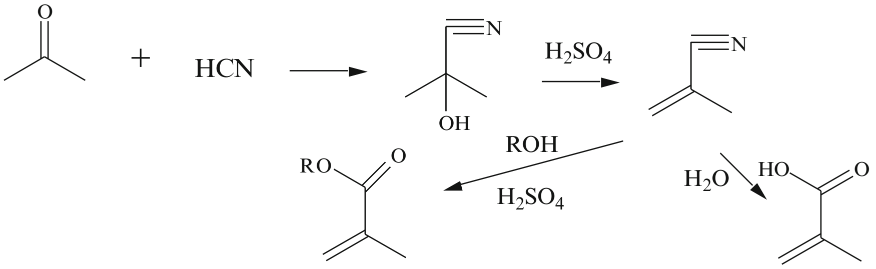
Another route is through oxidation of propylene over cobalt molybdenum catalyst at 400–500°C:



Many industrial preparations start with acetylene, carbon monoxide, and alcohol or water:



One route to α-methyl acrylic acid (or methacrylic acid) and its esters is by a cyanohydrin reaction of acetone:

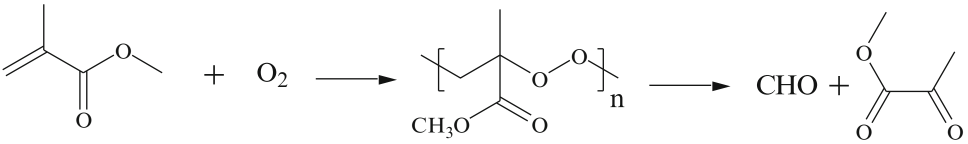


6.14.1 Polymerizations of Acrylic and Methacrylic Esters

Free-radical bulk polymerizations of acrylate esters exhibit rapid rate accelerations at low conversions. This often results in formation of some very high molecular weight polymer and some cross-linked material. The cross-linking is a result of chain transferring by abstractions of labile tertiary hydrogens from already formed "dead" polymeric chains [204]. Eventually, termination by combination of the branched radicals leads to cross-linked structures. Addition of chain transferring agents, like mercaptans (that reduces the length of the primary chains), helps prevent gel formation. There are no labile tertiary hydrogens in methacrylic esters. The growing methacrylate radicals are still capable of abstracting hydrogens from the α-methyl groups. Such abstractions, however, require more energy and are not an important problem in polymerizations of methacrylic esters [205]. Nevertheless, occasional formation of cross-linked poly(alkyl methacrylate)s does occur. This is due to chain transferring to the alcohol moiety [206, 210].

The termination reaction in free-radical polymerizations of the esters of acrylic and methacrylic acids takes place by recombination and by disproportionation [206, 207]. Methyl methacrylate polymerizations, however, terminate at 25°C predominantly by disproportionation [205].

Oxygen inhibits free-radical polymerization of α-methyl methacrylate [208]. The reaction with oxygen results in formation of low molecular weight polymeric peroxides that subsequently decompose to formaldehyde and methyl pyruvate [210]:



Oxygen is less effective in inhibiting polymerizations of acrylic esters. It reacts 400 times faster with the methacrylic radicals than with the acrylic ones. Nevertheless, even small quantities of oxygen affect polymerization rates of acrylic esters [216]. This includes photopolymerizations of gaseous ethyl acrylate that are affected by oxygen and by moisture [217].

Acrylic and methacrylic esters polymerize by free-radical mechanism to atactic polymers. The sizes of the alcohol portions of the esters determine the T_g values of the resultant polymers. They also determine the solubility of the resultant polymers in hydrocarbon solvents and in oils.

Solvents influence the rate of free-radical homopolymerization acrylic acid and its copolymerization with other monomers. Hydrogen bonding solvents slow down the reaction rates [219]. Due to electron withdrawing nature of the ester groups, acrylic and methacrylic ester polymerize by anionic but not by cationic mechanisms. Lithium alkyls are very effective initiators of α-methyl methacrylate polymerization yielding stereospecific polymers [213]. Isotactic poly(methyl methacrylate) forms in hydrocarbon solvents [214]. Block copolymers of isotactic and syndiotactic poly(methyl methacrylate) form in solvents of medium polarity. Syndiotactic polymers form in polar solvents, like ethylene glycol dimethyl ether, or pyridine. This solvent influence is related to Lewis basicity [215] in the following order:

$$\text{tetrahydrofuran} > \text{tetrahydropyran} > \text{dioxane} > \text{diethyl ether}$$

Furthermore, polymerizations in solvating media, like ethylene glycol dimethyl ether, tetrahydrofuran, or pyridine, using biphenylsodium or biphenyllithium yield virtually monodisperse syndiotactic poly(methyl methacrylate) [216].

The nature of the counterion in anionic polymerizations of methyl methacrylate in liquid ammonia with alkali metal amide or alkali earth metal amide catalysts is an important variable [217]. Lithium and calcium amides yield high molecular weight polymers, though the reactions tend to be slow. Sodium amide, on the other hand, yields rapid polymerizations but low molecular weight polymers. Polymers formed with sodium amide, however, have a narrower molecular weight distribution than those obtained with lithium and calcium amides. Calcium amide also yields high molecular weight polymers from ethyl acrylate and methyl methacrylate monomers in aromatic and aliphatic solvents at temperatures from −8 to 110°C. When, however, tetrahydrofuran or acetonitrile is used as solvents much lower molecular weight products form [218].

Products from anionic polymerizations of methyl methacrylate catalyzed by Grignard reagents (RMgX) vary with the nature of the R and X groups, the reaction temperature, and the nature of the solvent [219–221]. Secondary alkyl Grignard reagents give the highest yields and the fastest rates of the reactions. Isotacticity of the products increases with the temperature. When anion-radicals from alkali metal ketyls of benzophenone initiate polymerizations of methyl methacrylate, amorphous polymers form at temperatures from −78 to +65°C [222].

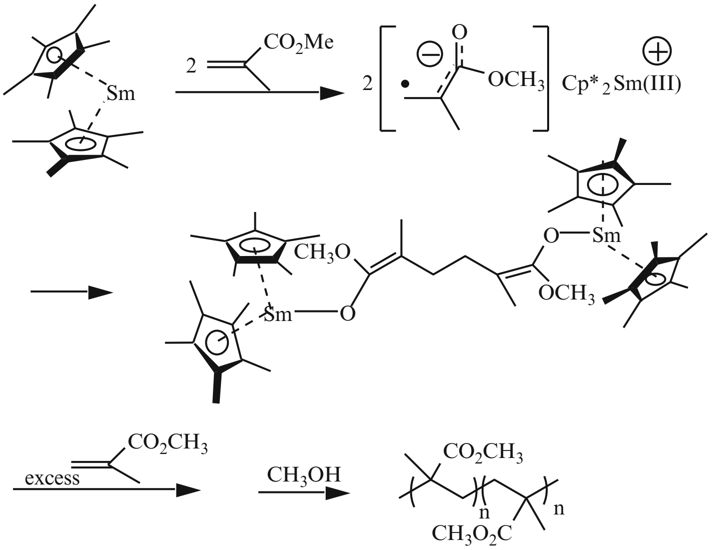
Sodium dispersions in hexane yield syndiotactic poly(methyl methacrylate) [223]. A 60–65% conversion is obtained over a 24-h period at a reaction temperature of 20–25°C. Lithium dispersions [224], butyllithium [203], and Grignard reagents [225, 226] yield crystalline isotactic poly(*t*-butyl acrylate). The reactions take place in bulk and in hydrocarbon solvents. Isotactic poly(isopropyl acrylate) forms with Grignard reagents [226, 227].

Coordination polymerizations of methyl methacrylate with diethyliron–bipyridyl complex in nonpolar solvents like benzene or toluene yield stereoblock polymers. In polar solvents, however, like dimethylformamide or acetonitrile, the products are rich in isotactic placement [229].

There are many reports in the literature on polymerizations of acrylic and methacrylic esters with Ziegler–Natta catalysts [230–233]. The molecular weights of the products, the microstructures, and rates of the polymerizations depend upon the metal alkyl and the transition metal salt used. The ratios of the catalyst components to each other are also important [234, 235].

In 1992 Yasuda et al. [236, 237] reported that organolanthanide complexes of the type $Cp^*_2Sm\text{-}R$ (where Cp* is pentamethyl cyclopentadienyl, and R is either an alkyl, alkylaluminum or a hydride) initiate highly syndiotactic, living polymerizations of methacrylates. It was also reported that lanthanide complexes such as $Cp^*_2Yb(THF)_{1-3}$, $Cp^*_2Sm(THF)_2$, and $(indenyl)_2Yb(THF)_2$ can also initiate polymerizations of methylmethacrylate [238]. Although very low initiator efficiencies were observed, these were living polymerizations. The polymers that formed had the dispersity of 1.1 and were high in syndiotactic sequences.

Novak and Boffa, in studying lanthanide complexes, observed an unusual facile organometallic electron transfer process takes place that generates in situ bimetallic lanthanide(III) initiators for polymerizations of methacrylates [239]. They concluded that methyl methacrylate polymerizations initiated by the Cp^*_2Sm complexes occur through reductive dimerizations of methyl methacrylate molecules to form "bisinitiators" that consists of two samarium(III) enolates joined through their double bond terminally [239]. Their conclusion is based on the tendency of Cp^*_2Sm complexes to reductively couple unsaturated molecules:

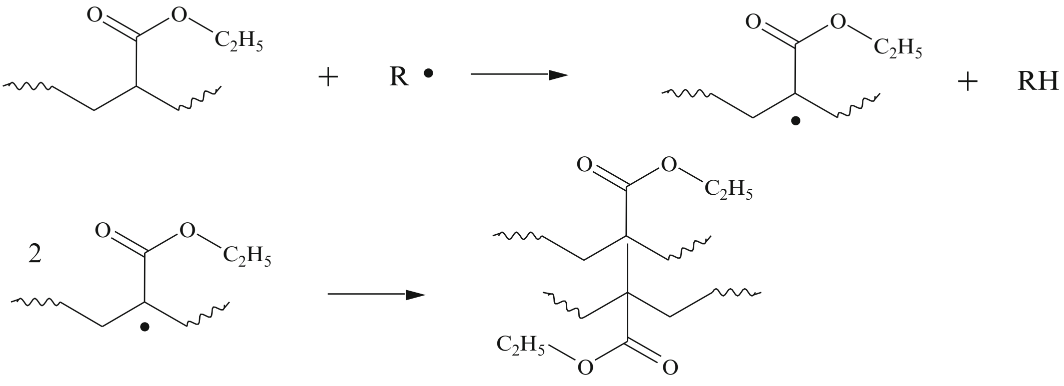


Montei and coworkers [240] reported that Nickel complexes [(X,O)NiR(PPh_3)] (X = N or P), designed for the polymerization of ethylene, are effective for home- and copolymerization of butyl acrylate, methyl methacrylate, and styrene. Their role as radical initiators was demonstrated from the calculation of the copolymerization reactivity ratios. It was shown that the efficiency of the radical initiation is improved by the addition of PPh_3 to the nickel complexes as well as by increasing the temperature. The dual role of nickel complex as radical initiators and catalysts was exploited to succeed in the copolymerization of ethylene with butyl acrylate and methyl methacrylate.

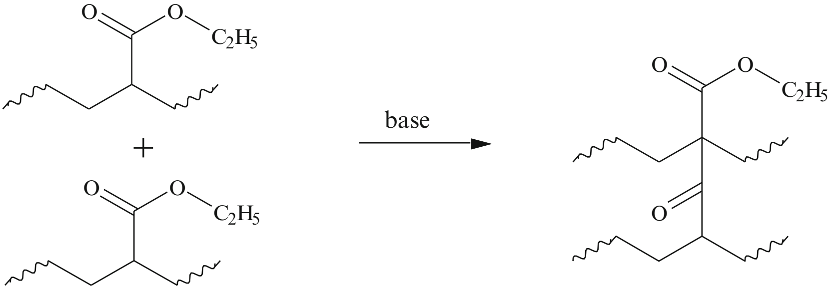
Multiblock copolymers containing sequences of both ethylene and polar monomers were thus prepared.

6.14.2 Acrylic Elastomers

Polymers of lower *n*-alkyl acrylates are used commercially to only a limited extent. Ethyl and butyl acrylates are, however, major components of ***acrylic elastomers***. The polymers are usually formed by free-radical emulsion polymerization. Because acrylate esters are sensitive to hydrolysis under basic conditions, the polymerizations are usually conducted at neutral or acidic pH. The acrylic rubbers, like other elastomers must be cross-linked or ***vulcanized*** to obtain optimum properties. Cross-linking can be accomplished by reactions with peroxides through abstractions of tertiary hydrogens with free radicals:



Another way to cross-link acrylic elastomers is through a Claisen condensation:



The above illustrated cross-linking reactions of homopolymers, however, form elastomers with poor aging properties. Commercial acrylic rubbers are, therefore, copolymers of ethyl or butyl acrylate with small quantities of comonomers that carry special functional groups for cross-linking. Such comonomers are 2-chloroethylvinyl ether or vinyl chloroacetate, used in small quantities (about 5%). These copolymers cross-link through reactions with polyamines.

6.14.3 Thermoplastic and Thermoset Acrylic Resins

Among methacrylic ester polymers, poly(methyl methacrylate) is the most important one industrially. Most of it is prepared by free-radical polymerizations of the monomer and a great deal of these polymerizations are carried out in bulk. Typical methods of preparation of clear sheets and rods consist of initial partial polymerizations in reaction kettles at about 90°C with peroxide initiators. This is done by heating and stirring for about 10 min to form syrups. The products are cooled to room

Table 6.12 Typical components of thermoset acrylic resins

Monomers that contribute rigidity	Flexibilizing monomers	Monomers used for cross-linking
Methyl methacrylate	Ethyl acrylate	Acrylic acid
Ethyl methacrylate	Isopropyl acrylate	Methacrylic acid
Styrene	Butyl acrylate	Hydroxyethyl acrylate
Vinyl toluene	*i*-Octyl acrylate	Hydroxypropyl acrylate
Acrylonitrile	Decyl acrylate	Glycidyl acrylate
Methacrylonitrile	Lauryl methacrylate	Glycidyl methacrylate
		Acrylamide
		Aminoethyl acrylate

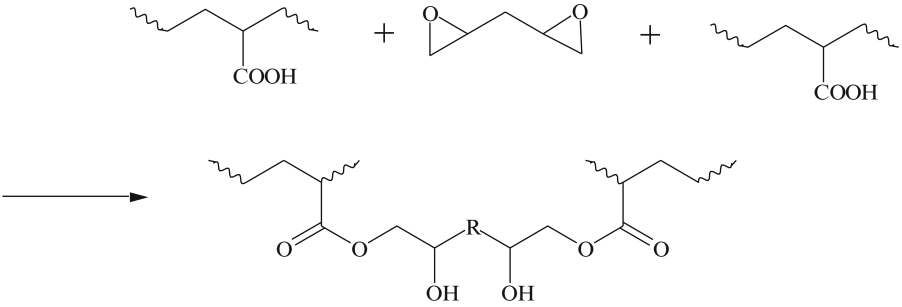
temperature and various additives may be added. The syrups are solutions of about 20% polymer dissolved in the monomer. They are poured into casting cells where the polymerizations are completed. The final polymers are high in molecular weight, about 1,000,000.

Poly(methyl methacrylate) intended for surface coatings is prepared by solution polymerization. The molecular weights of the polymers are about 90,000 and the reaction products that are 40–60% solutions are often used directly in coatings.

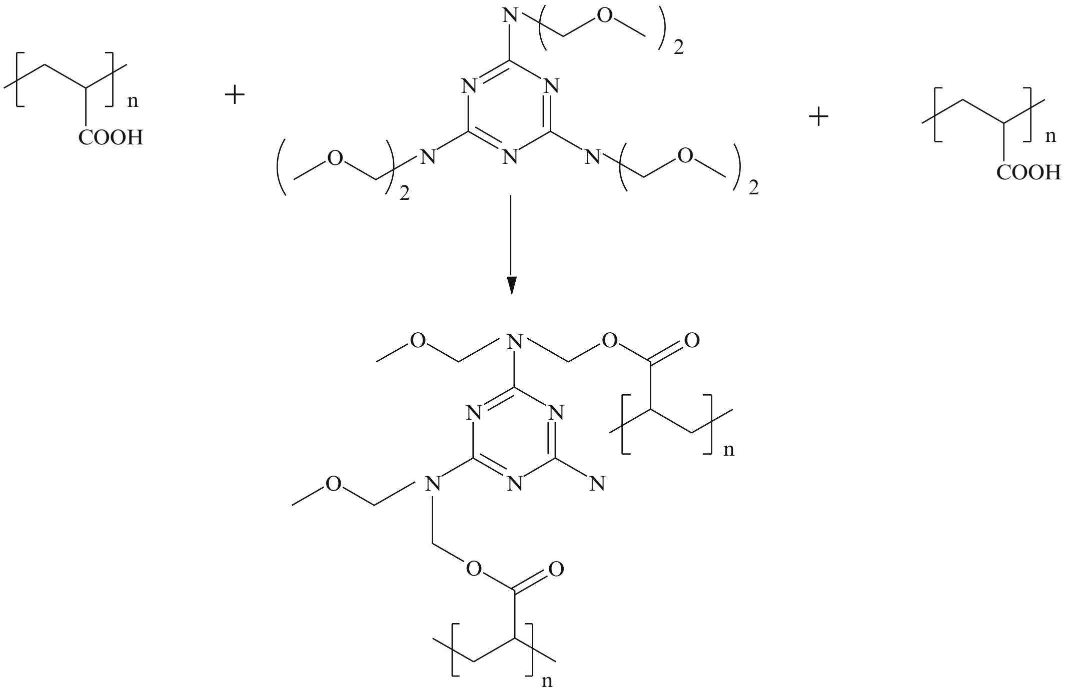
A certain amount of poly(methyl methacrylate) is also prepared by suspension polymerization. The molecular weights of these polymers are about 60,000 and they are used in injection molding and extrusion.

Thermosetting acrylic resins are used widely in surface coatings. Both acrylic and methacrylic esters are utilized and the term is applied to both of them. Often such resins are terpolymers or even tetra polymers where each monomer is chosen for a special function [214]. One is selected for rigidity, surface hardness, and scratch resistance; another for the ability to flexibilize the film, and the third one for cross-linking it. In addition, not all comonomers are necessarily acrylic or methacrylic esters or acids. For instance, among the monomers that may be chosen for rigidity may be methyl methacrylate. On the other hand, it may be styrene instead, or vinyl toluene, etc. The same is true of the other components. Table 6.12 illustrates some common components that can be found in thermoset acrylic resins.

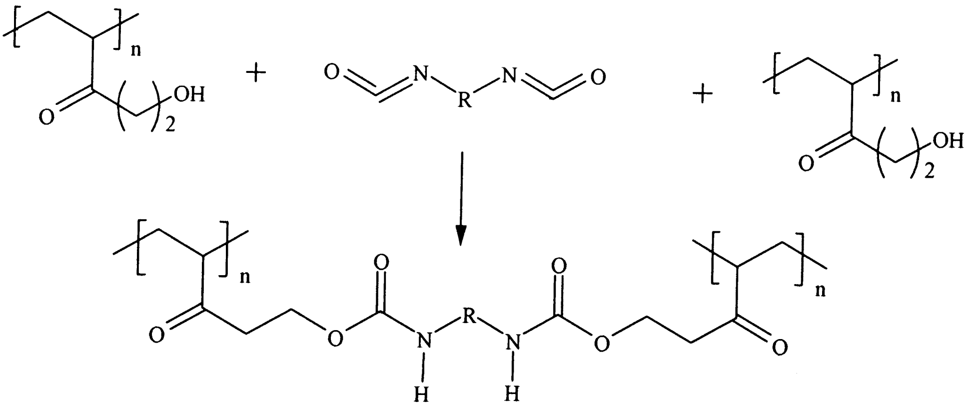
The choice of the cross-linking reaction may depend upon desired application. It may also simply depend upon price, or a particular company that manufactures the resin, or simply to overcome patent restrictions. Some common cross-linking reactions will be illustrated in the remaining portion of this section. If the functional groups are carboxylic acids in the copolymer or terpolymer, cross-linking can be accomplished by adding a diepoxide.



Other reactions can also cross-link resins with pendant carboxylic acid groups. For instance, one can add a melamine formaldehyde condensate:

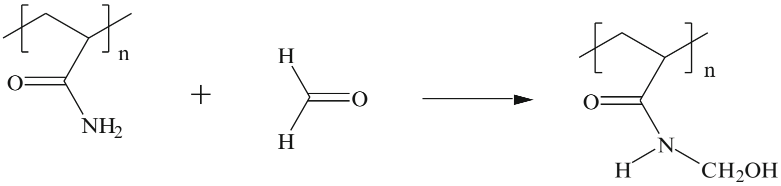


A diisocyanate, a phenolic, or a melamine–formaldehyde resin can be used as well. Resins with pendant hydroxyl groups can also be cross-linked by these materials. A diisocyanate is effective in forming urethane linkages:



When the pendant groups are epoxides, like glycidyl esters, cross-linking can be carried out with dianhydrides or with compounds containing two or more carboxylic acid groups [241]. Aminoplast resins (urea–formaldehyde or melamine–formaldehyde and similar ones) are also very effective [242].

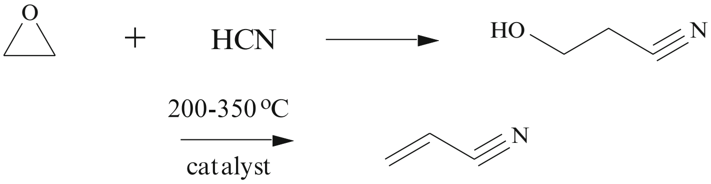
Pendant amide groups from terpolymers containing acrylamide can be reacted with formaldehyde to form methylol groups for cross-linking [243]:



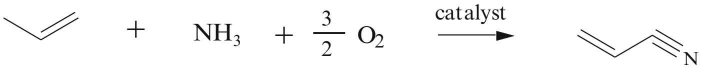
The product of the above reaction can be thermoset like any urea–formaldehyde resin (see Chaps. 7 and 9). Many cross-linking routes are described in the patent literature, because there are many different functional groups available.

6.15 Acrylonitrile and Methacrylonitrile Polymers

Polymers from acrylonitrile are used in synthetic fibers, in elastomers, and in plastic materials. The monomer can be formed by dehydration of ethylene cyanohydrin:

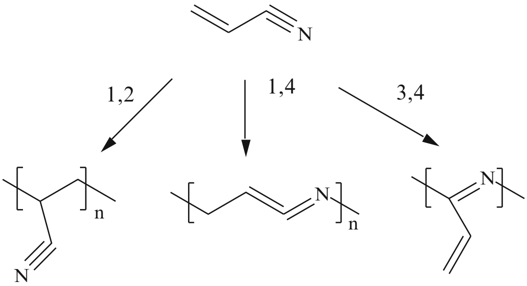


Other commercial processes exist, like condensation of acetylene with hydrogen cyanide, or ammoxidation of propylene:



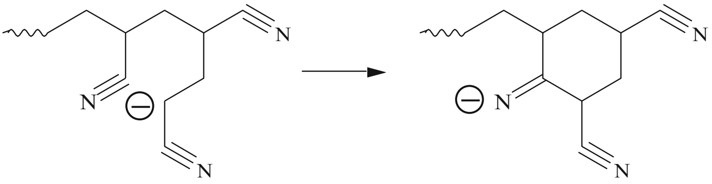
Acrylonitrile polymerizes readily by free-radical mechanism. Oxygen acts as a strong inhibitor. When the polymerization is carried out in bulk, the reaction is autocatalytic [242, 243]. In solvents, like dimethylformamide, however, the rate is proportional to the square root of the monomer concentration [242]. The homopolymer is insoluble in the monomer and in many solvents.

Acrylonitrile polymerizes also by anionic mechanism. There are many reports in the literature of polymerizations initiated by various bases. These are alkali metal alkoxides [246], butyllithium [247, 248], metal ketyls [249, 250], solutions of alkali metals in ethers [251, 252], sodium malonic esters [232], and others. The propagation reaction is quite sensitive to termination by proton donors. This requires use of aprotic solvents. The products, however, are often insoluble in such solvents. In addition, there is a tendency for the polymer to be yellow. This is due to some propagation taking place by 1,4 and by 3,4 insertion in addition to the 1,2 placement [253, 254]:



Another disadvantage of anionic polymerization of acrylonitrile is formation of cyanoethylate as a side reaction. It can be overcome, however, by running the reaction at low temperatures. An example is polymerizations initiated by KCN at −50°C in dimethylformamide [254], or by butyllithium in toluene at −78°C [255]. Both polymerizations yield white, high molecular weight products that are free from cyanoethylation.

It was suggested that the terminations in anionic polymerizations of acrylonitrile proceed by proton transfer from the monomer. This, however, depends upon catalyst concentrations [256, 257]. At low concentrations, the terminations can apparently occur by a cyclization reaction [257] instead:



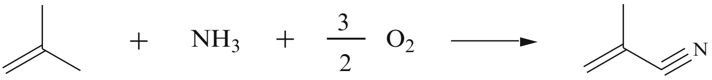
Industrially, polyacrylonitrile homopolymers and copolymers are prepared mainly by free-radical mechanism. The reactions are often conducted at low temperatures, in aqueous systems, either in emulsions or in suspensions, using redox initiation. Colorless, high molecular weight materials form. Bulk polymerizations are difficult to control on a large scale.

Over half the polymer that is prepared industrially is for use in textiles. Most of these are copolymers containing about 10% of a comonomer. The comonomers can be methyl methacrylate, vinyl acetate, or 2-vinylpyridine. The purpose of comonomers is to make the fibers more dyeable. Polymerizations in solution offer an advantage of direct fiber spinning.

Polyacrylonitrile copolymers are also used in barrier resins for packaging. One such resin contains at least 70% acrylonitrile and often methyl acrylate as the comonomer. The material has poor impact resistance and in one industrial process the copolymer is prepared in the presence of about 10% butadiene–acrylonitrile rubber by emulsion polymerization. The product contains some graft copolymer and some polymer blend. In another process the impact resistance of the copolymer is improved by biaxial orientation. The package, however, may have a tendency to shrink at elevated temperature, because the copolymer does not crystallize.

It is possible to form clear transparent polyacrylonitrile plastic shapes by a special bulk polymerization technique [258, 259]. The reaction is initiated with *p*-toluenesulfinic acid–hydrogen peroxide. Initially, heterogeneous polymerizations take place. They are followed by spontaneous transformations, at high conversion, to homogeneous, transparent polyacrylonitrile plastics [260]. A major condition for forming transparent solid polymer is continuous supply of monomer to fill the gaps formed by volume contraction during the polymerization process [261].

Methacrylonitrile, $CH_2{=}C(CH_3)CN$, can also be prepared by several routes. Some commercial processes are based on acetone cyanohydrin intermediate and others on dehydrogenation (or oxydehydrogenation) of isobutyronitrile. It is also prepared from isobutylene by ammoxidation:



Just like acrylonitrile, methacrylonitrile does not polymerize thermally but polymerizes readily in the presence of free-radical initiators. Unlike polyacrylonitrile, polymethacrylonitrile is soluble in some ketone solvents. Bulk polymerizations of methacrylonitrile have the disadvantage of long reaction time. The rate, however, accelerates with temperature. The polymer is soluble in the monomer at ambient conditions [262].

Emulsion polymerization of methacrylonitrile is a convenient way to form high molecular weight polymers. With proper choices of emulsifiers, the rates may be increased by increasing the numbers of particles in the latexes. At a constant rate of initiation, the degree of polymerization of methacrylonitrile increases rather than decreases as the rate of polymerization rises [263].

Methacrylonitrile polymerizes readily in inert solvents. The polymer, depending on the initiator and on reaction conditions, is either amorphous or crystalline. Polymerizations take place over a broad range of temperatures from ambient to −5°C, when initiated by Grignard reagents, triphenyl ethylsodium, or sodium in liquid ammonia [264]. The properties of these polymers are essentially the same as those of the polymers formed by free-radical mechanism.

The homopolymer, prepared by polymerization in liquid ammonia with sodium initiator at −77°C, is insoluble in acetone, but it is soluble in dimethylformamide [265]. When it is formed with lithium in liquid ammonia, at −75°C, the molecular weight of the product increases with monomer concentration and decreases with initiator concentration. If, however, potassium initiates the reaction rather than lithium, the molecular weight is independent of the monomer concentration [266, 267]. Polymethacrylonitrile prepared with *n*-butyllithium in toluene or in dioxane is crystalline and insoluble in solvents like acetone [268]. When polymerized in petroleum ether with *n*-butyllithium, methacrylonitrile forms a living polymer [269]. Highly crystalline polymethacrylonitrile can also be prepared with beryllium and magnesium alkyls in toluene over a wide range of temperatures.

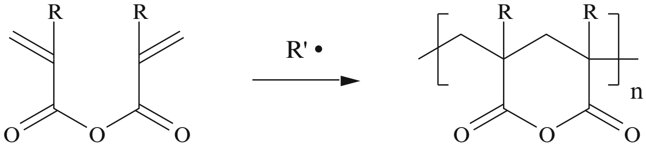
6.16 Polyacrylamide, Poly(acrylic acid), and Poly(methacrylic acid)

Commercially, acrylamide is formed from acrylonitrile by reaction with water. Similarly, the preferred commercial route to methacrylamide is through methacrylonitrile. Acrylamide polymerizes by free-radical mechanism [270]. Water is the common solvent for acrylamide and methacrylamide polymerizations because the polymers precipitate out from organic solvents.

Crystalline polyacrylamide forms with metal alkyls in hydrocarbon solvents by anionic mechanism [271]. The product is insoluble in water and in dimethylformamide.

Both acrylic and methacrylic acids can be converted to anhydrides and acid chlorides. The acids polymerize in aqueous systems by free-radical mechanism. Polymerizations of these monomers in nonpolar solvents like benzene result in precipitations of the products.

Polymerizations of anhydrides proceed by inter- and intramolecular propagations [272]:



where R = H, CH_3.

The above shown cyclopolymerizations produce soluble polymers rather than gels.

The *acid chlorides* of both acrylic and methacrylic acids polymerize by free-radical mechanism in dry aromatic and aliphatic solvents. Molecular weights of the products, however, are low, usually under 10,000 [273, 274]. Polyacrylic and polymethacrylic acids are used industrially as thickeners in cosmetics, as flocculating agents, and when copolymerized with divinyl benzene in ion-exchange resins.

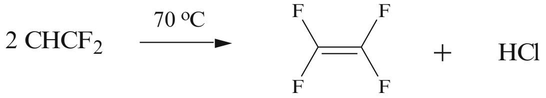
6.17 Halogen-Bearing Polymers

The volume of commercial fluorine-containing polymers is not large when compared with other polymers like, for instance, poly(vinyl chloride). Fluoropolymers, however, are required in many important applications. The main monomers are tetrafluoroethylene, trifluorochloroethylene, vinyl fluoride, vinylidine fluoride, and hexafluoropropylene.

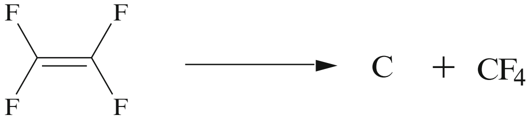
6.17.1 *Polytetrafluoroethylene*

This monomer can be prepared from chloroform [275]:

$$CHCl_3 + 2HF \xrightarrow[\text{up to 39 atm pressure}]{50\text{ -}100\ ^{o}C} CHCF_2 + 2HCl$$



Tetrafluoroethylene boils at −76.3°C. It is not the only product from the above pyrolytic reaction of difluorochloromethane. Other fluorine by-products form as well and the monomer must be isolated. The monomer polymerizes in water at moderate pressures by free-radical mechanism. Various initiators appear effective [276]. Redox initiation is preferred. The polymerization reaction is strongly exothermic, and water helps dissipate the high heat of the reaction. A runaway, uncontrolled polymerization can lead to explosive decomposition of the monomer to carbon and carbon tetrafluoride [277]:



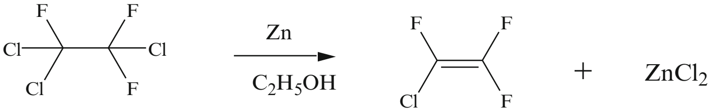
Polytetrafluoroethylene is linear and highly crystalline [278]. Absence of terminal $CF_2 = CF$-- groups shows that few, if any, polymerization terminations occur by disproportionation but probably all take place by combination [279]. The molecular weights of commercially available polymers range from 39,000 to 9,000,000. Polytetrafluoroethylene is inert to many chemical attacks and is only swollen by fluorocarbon oils at temperatures above 300°C. The T_m of this polymer is 327°C and the T_g is below −100°C.

The physical properties of polytetrafluoroethylene depend upon crystallinity and on the molecular weight of the polymer. Two crystalline forms are known. In both cases the chains assume helical arrangements to fit into the crystalloids. One such arrangement has 15 CF_2 groups per turn and the other has 13.

Polytetrafluoroethylene does not flow even above its melting point. This is attributed to restricted rotation around the C–C bonds and to high molecular weights. The stiffness of the solid polymer is also attributed to restricted rotation. The polymer exhibits high thermal stability and retains its physical properties over a wide range of temperatures. The loss of strength occurs at about the crystalline melting point. It is possible to use the material for long periods at 300°C without any significant loss of its strength.

6.17.2 Polychlorotrifluoroethylene

The monomer can be prepared by dechlorination of trichlorotrifluoroethane with zinc dust and ethanol.

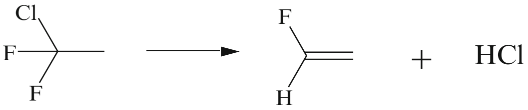


It is a toxic gas that boils at −26.8°C. Polymerization of chlorotrifluoroethylene is usually carried out commercially by free-radical suspension polymerization. Reaction temperatures are kept between 0 and 40°C to obtain a high molecular weight product. A redox initiation based on reactions of persulfate, bisulfite, and ferrous ions is often used. Commercial polymers range in molecular weights from 50,000 to 500,000.

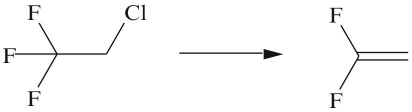
Polychlorotrifluoroethylene exhibits greater strength, hardness, and creep resistance than does polytetrafluoroethylene. Due to the presence of chlorine atoms in the chains, however, packing cannot be as tight as in polytetrafluoroethylene, and it melts at a lower temperature. The melting point is 214°C. The degree of crystallinity varies from 30 to 85%, depending upon the thermal history of the polymer. Polytrifluorochloroethylene is soluble in certain chloro fluoro compounds above 100°C. It flows above its melting point. The chemical resistance of this material is good, but inferior to polytetrafluoroethylene.

6.17.3 Poly(vinylidine fluoride)

The monomer can be prepared by dehydrochlorination of 1,1,1-chlorodifluoroethane:



or by dechlorination of 1,2-dichloro-1,1-difluoroethane [280]:



Vinylidine fluoride boils at −84°C. The monomer is polymerized in aqueous systems under pressure. Details of the process, however, are kept as trade secrets. Two different molecular weight materials are available commercially, 300,000 and 6,000,000. Poly(vinylidine fluoride) is crystalline and melts at 171°C. The material exhibits fair resistance to solvents and chemicals, but is inferior to polytetrafluoroethylene and to polytrifluorochloroethylene.

6.17.4 Poly(vinyl fluoride)

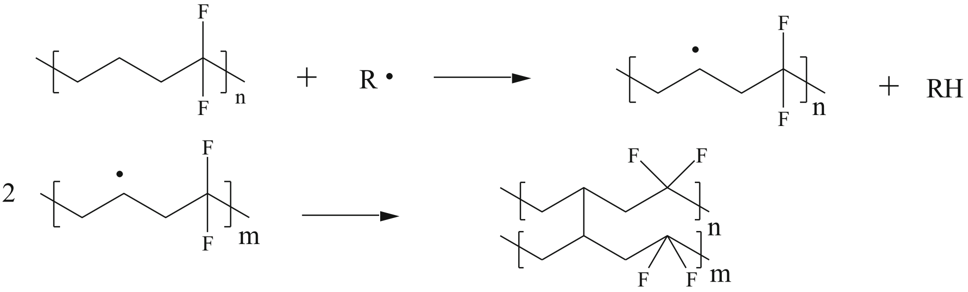
Vinyl fluoride monomer can be prepared by addition of HF to acetylene. The monomer is a gas at room temperature and boils at −72.2°C. Commercially, vinyl fluoride is polymerized in aqueous medium using either redox initiation or one from thermal decomposition of peroxides. Pressures of up to 1,000 atm may be used. Radicals generated at temperatures between 50 and 100°C yield very high molecular weight polymers.

Poly(vinyl fluoride) is moderately crystalline. The crystal melting point, T_m, is approximately 200°C. The high molecular weight polymers dissolve in dimethylformamide and in tetramethyl urea at temperatures above 100°C. The polymer is very resistant to hydrolytic attack. It does, however, loose HF at elevated temperatures.

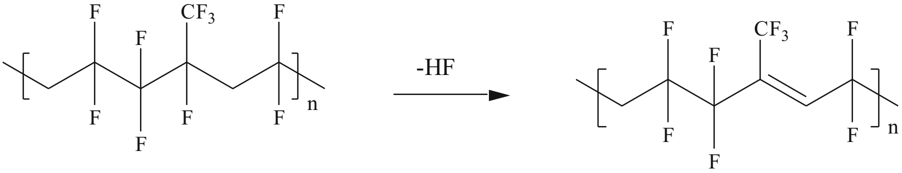
6.17.5 Copolymers of Fluoroolefins

Mary different copolymers of fluoroolefins are possible and were reported in the literature. Commercial use of fluoroolefin copolymers, however, is restricted mainly to elastomers. Such materials offer superior solvent resistance and good thermal stability.

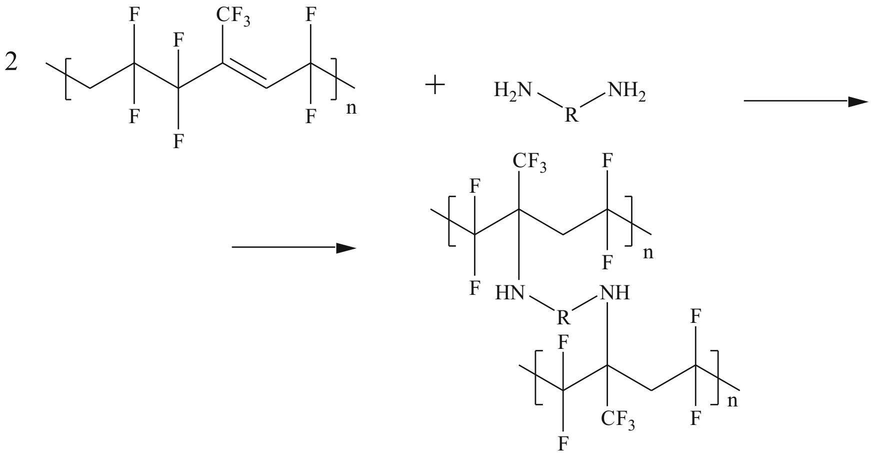
The elastomers that are most important industrially are vinylidine fluoride–chlorotrifluoroethylene [260] and vinylidine fluoride–hexafluoropropylene copolymers [282]. These copolymers are amorphous due to irregularities in their structures and can range in properties from resinous to elastomeric, depending upon composition [283]. Those that contain 50–70 mole percent of vinylidine fluoride are elastomers. The T_g ranges from 0 to −15°C, also depending upon vinylidine fluoride content [284]. They may be cross-linked with various peroxides, polyamines [284], or ionizing radiation. The cross-linking reactions by peroxides take place through hydrogen abstraction by primary radicals:



Copolymers of vinylidine fluoride with hexafluoropropylene are prepared in aqueous dispersions using persulfate initiators. Hexafluoropropylene does not homopolymerize but it does copolymerize. This means that its content in the copolymer cannot exceed 50%. Preferred compositions appear to contain about 80% of vinylidine fluoride. The cross-linking reactions with diamines are not completely understood. It is believed that the reaction takes place in two steps [285, 286]. In the first one, a dehydrofluorination occurs:



The above elimination is catalyzed by basic materials. These may be in the form of MgO, which is often included in the reaction medium. In the second step the amine groups add across the double bonds:

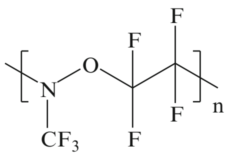


Free diamines, used for cross-linking, are too reactive and can cause premature gelation. It is common practice, therefore, to add these diamine compounds in the form of carbamates, like ethylenediamine carbamate or hexamethylene diamine carbamate. The above fluoro elastomers exhibit good resistance to chemicals and maintain useful properties from −50 to +300°C.

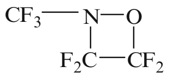
Copolymers of tetrafluoroethylene with hexafluoropropylene are truly thermoplastic polyperfluorolefins that can be fabricated by common techniques. Such copolymers soften at about 285°C and have a continuous use temperature of −260 to +205°C. Their properties are similar to, though somewhat inferior to, polytetrafluoroethylene.

6.17.6 *Miscellaneous Fluorine Containing Chain-Growth Polymers*

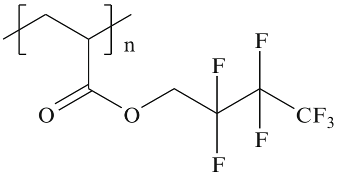
One of the miscellaneous fluoroolefin polymers is a copolymer of trifluoronitrosomethane and tetrafluoroethylene [287], an elastomer:



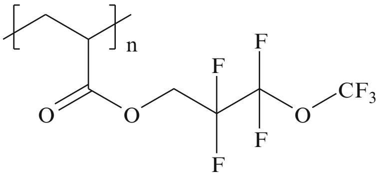
It can be formed by suspension polymerization. One procedure is to carry out the reaction in an aqueous solution of lithium bromide at −25°C with magnesium carbonate as the suspending agent. No initiator is added and the reaction takes about 20 h. Because the reaction in inhibited by hydroquinone and accelerated by ultra-violet light, it is believed to take place by a free-radical mechanism. Whether it is chain-growth polymerization, however, is not certain. A 1:1 copolymer is always formed regardless of the composition of the monomer feed, and the copolymerization takes place only at low temperatures. At elevated temperatures, however, cyclic oxazetidines form instead:



Two polyfluoroacrylates are manufactured on a small commercial scale for some special uses in jet engines. These are poly(1,1-dihyroperfluorobutyl acrylate):

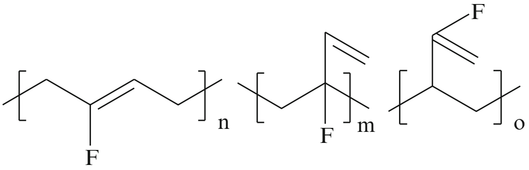


and poly(3-perfluoromethoxy-1,1-dihydroperfluoropropyl acrylate):



The polymers are prepared by emulsion polymerization with persulfate initiators.

Although many other fluorine containing polymers were described in the literature, it is not possible to describe all of them here. They are not utilized commercially on a large scale. A few, however, will be mentioned as examples. One of them is polyfluoroprene [288]:

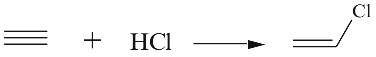


The polymer is formed by free-radical mechanism, in an emulsion polymerization using redox initiation. All three possible placements of the monomer occur [267].

Polyfluorostyrenes are described in many publications. A β-fluorostyrene can be formed by cationic mechanism [289]. The material softens at 240–260°C. An α,β,β-trifluorostyrene can be polymerized by free-radical mechanism to yield an amorphous polymer that softens at 240°C [290]. Ring-substituted styrenes apparently polymerize similarly to styrene. Isotactic poly(*o*-fluorostyrene) melts at 265°C. It forms by polymerization with Ziegler–Natta catalysts [291]. The *meta* analog, however, polymerized under the same conditions yields an amorphous material [291].

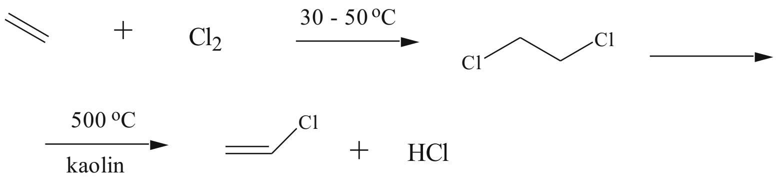
6.17.7 Poly(vinyl chloride)

Poly(vinyl chloride) is used in industry on a very large scale in many applications, such as rigid plastics, plastisols, and surface coatings. The monomer, vinyl chloride, can be prepared from acetylene:



The reaction is exothermic and requires cooling to maintain the temperature between 100 and 108°C.

The monomer can also be prepared from ethylene:



The reaction of dehydrochlorination is carried out at elevated pressure of about 3 atm.

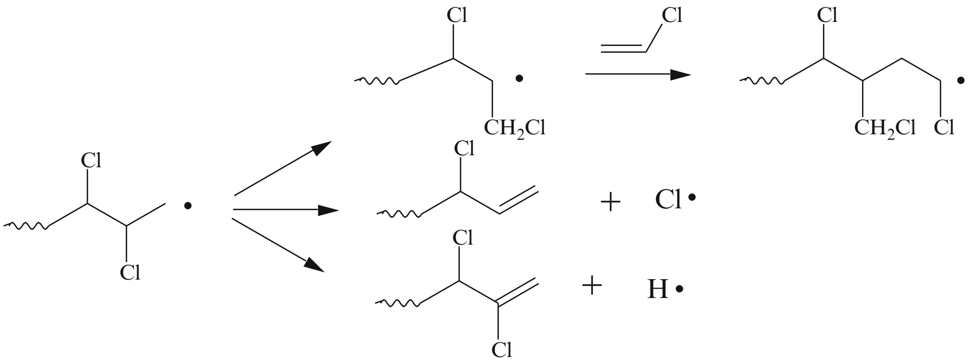
Free-radical polymerization of vinyl chloride was studied extensively. For reactions that are carried out in bulk the following observations were made [292]:

1. The polymer is insoluble in the monomer and precipitates out during the polymerization.
2. The polymerization rate accelerates from the start of the reaction. Vinyl chloride is a relatively unreactive monomer. The main sites of initiation occur in the continuous monomer phase.
3. The molecular weight of the product does not depend upon conversion nor does it depend upon the concentration of the initiator.
4. The molecular weight of the polymer increases as the temperature of the polymerization decreases. The maximum for this relationship, however, is at 30°C.

There is autoacceleration in bulk polymerization rate of vinyl chloride [293]. It was suggested by Schindler and Breitenbach [294] that the acceleration is due to trapped radicals that are present in the precipitated polymer swollen by monomer molecules. This influences the rate of the termination that decreases progressively with the extent of the reaction, while the propagation rate remains constant. The autocatalytic effect in vinyl chloride bulk polymerizations, however, depends on the type of initiator used [295]. Thus, when 2, 2′-azobisisobutyronitrile initiates the polymerization, the autocatalytic effect can be observed up to 80% of conversion. Yet, when benzoyl peroxide initiates the reaction, it only occurs up to 20–30% of conversion.

When vinyl chloride is polymerized in solution, there is no autoacceleration. Also, a major feature of vinyl chloride free-radical polymerization is chain transferring to monomer [296]. This is supported by experimental evidence [297, 298]. In addition, the growing radical chains can terminate by chain transferring to “dead” polymer molecules. The propagations then proceed from the polymer backbone [297]. Such new growth radicals, however, are probably short lived as they are destroyed by transfer to monomer [299].

The ^{13}C NMR spectroscopy of poly(vinyl chloride), which was reduced with tributyltin hydride, showed that the original polymer contained a number of short four-carbon branches [300]. This, however, may not be typical of all poly(vinyl chloride) polymers formed by free-radical polymerization. It conflicts with other evidence from ^{13}C NMR spectroscopy that chloromethyl groups are the principal short chain branches in poly(vinyl chloride) [301, 302]. The pendant chloromethyl groups were found to occur with a frequency of 2–3/1,000 carbons. The formation of these branches, as seen by Bovey and coworkers, depends upon head to head additions of monomers during the polymer formation. Such additions are followed by 1,2 chlorine shifts with subsequent propagations [301, 302]. Evidence from still other studies also shows that some head to head placement occurs in the growth reaction [303]. It was suggested that this may be not only an essential step in formation of branches but also one leading to formation of unsaturation at the chain ends [303, 304]:



Poly(vinyl chloride) prepared with boron alkyl catalysts at low temperatures possesses higher amounts of syndiotactic placement and is essentially free from branches [305–307].

Many attempts were made to polymerize vinyl chloride by ionic mechanisms using different organometallic compounds, some in combinations with metal salts [308–312]. Attempts were also made to polymerize vinyl chloride with Ziegler–Natta catalysts complexed with Lewis bases. To date, however, it has not been established unequivocally that vinyl chloride does polymerize by ionic mechanism. Use of the above catalysts did yield polymers with higher crystallinity. These reactions, however, were carried out at low temperatures where greater amount of syndiotactic placement occurs by the free-radical mechanism [313]. Vinyl chloride was also polymerized by $AlCl(C_2H_5)O_2H_5 + VO(C_3H_7O_2)$ without Lewis bases [312]. Here too, however, the evidence indicates a free-radical mechanism.

On the other hand, butyllithium–aluminum alkyl-initiated polymerizations of vinyl chloride are unaffected by free-radical inhibitors [313]. Also the molecular weights of the resultant polymers are unaffected by additions of CCl_4 that acts as a chain transferring agent in free-radical polymerizations. This suggests an ionic mechanism of chain growth. Furthermore, the reactivity ratios in copolymerization reactions by this catalytic system differ from those in typical free-radical polymerizations [313]. An anionic mechanism was also postulated for polymerization of vinyl chloride with *t*-butylmagnesium in tetrahydrofuran [314].

Commercially, by far the biggest amount of poly(vinyl chloride) homopolymer is produced by suspension polymerization and to a lesser extent by emulsion and bulk polymerization. Very little polymer is formed by solution polymerization.

One process for bulk polymerization of vinyl chloride was developed in France where the initiator and monomer are heated at 60°C for approximately 12 h inside a rotating drum containing stainless steel balls. Typical initiators for this reaction are benzoyl peroxide or azobisisobutyronitrile. The speed of rotation of the drum controls the particle size of the final product. The process is also carried out in a two-reactor arrangement. In the first one approximately 10% of the monomer is converted. The material is then transferred to the second reactor where the polymerization is continued until it reaches 75–80% conversion. Special ribbon blenders are present in the second reactor. Control of the operation in the second reactor is quite critical [315].

Industrial suspension polymerizations of vinyl chloride are often carried out in large batch reactors or stirred jacketed autoclaves. Continuous reactors, however, have been introduced in several manufacturing facilities [315]. Typical recipes call for 100 parts of vinyl chloride for 180 parts of water, a suspending agent, like maleic acid–vinyl acetate copolymer, a chain transferring agent, and a monomer soluble initiator. The reaction may be carried out at 100 lb/in.^{2} pressure and 50°C for approximately 15 h. As the monomer is consumed the pressure drops. The reaction is stopped at an internal pressure of about 10 lb/in.^{2} and remaining monomer (about 10%) is drawn off and recycled. The product is discharged.

Emulsion polymerizations of vinyl chloride are usually conducted with redox initiation. Such reactions are rapid and can be carried out at 20°C in 1–2 h with a high degree of conversion. Commercial poly(vinyl chloride)s range in molecular weights from 40,000 to 80,000. The polymers are mostly amorphous with small amounts of crystallinity, about 5%. The crystalline areas are syndiotactic [317, 318].

Poly(vinyl chloride) is soluble at room temperature in oxygen-containing solvents, such as ketones, esters, ethers, and others. It is also soluble in chlorinated solvents. The polymer, however, is not soluble in aliphatic and aromatic hydrocarbons. It is unaffected by acid and alkali solutions but has poor heat and light stability. Poly(vinyl chloride) degrades at temperatures of 70°C or higher or when exposed to sun light, unless it is stabilized. Heating changes the material from colorless to yellow, orange, brown, and finally black. Many compounds tend to stabilize poly(vinyl chloride). The more important ones include lead compounds, like dibasic lead phthalate and lead carbonate. Also effective are metal salts, like barium, calcium, and zinc octoates, stearates, and laurates. Organotin compounds, like dibutyl tin maleate or laurate, also belong to that list. Epoxidized drying oils are effective heat stabilizers, particularly in coatings based on poly(vinyl chloride). Some coating materials may also include aminoplast resins, like benzoguanamine–formaldehyde condensate.

The process of degradation is complex. It involves loss of hydrochloric acid. The reactions are free radical in nature, though some ionic reactions appear to take place as well. The process of dehydrochlorination results in formations of long sequences of conjugated double bonds. It is commonly believed that formation of conjugated polyenes, which are chromophores, is responsible for the darkening of poly(vinyl chloride). In addition, the polymer degrades faster in open air than it does in an inert atmosphere. This shows that oxidation contributes to the degradation process. All effective stabilizers are hydrochloric acid scavengers. This feature alone, however, can probably not account for the stabilization process. There must be some interaction between the stabilizers and the polymers. Such interaction might vary, depending upon a particular stabilizer.

6.17.7.1 Copolymers of Vinyl Chloride

A very common copolymer of vinyl chloride is vinyl acetate. Copolymerization with vinyl acetate improves stability and molding characteristics. The copolymers are also used as fibers and as coatings. Copolymers intended for use in moldings are usually prepared by suspension polymerization. Those intended for coating purposes are prepared by solution, emulsion, and suspension polymerizations. The copolymers used in molding typically contain about 10% of poly(vinyl acetate). Copolymers that are prepared for coating purposes can contain from 10 to 17% of poly(vinyl acetate). For coatings, a third comonomer may be included in some resins. This third component may, for instance, be maleic anhydride, in small quantities, like 1%, to improve adhesion to surfaces.

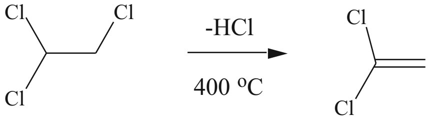
Copolymers of vinyl chloride with vinylidine chloride are similar in properties to copolymers with vinyl acetate. They contain from 5 to 12% of poly(vinylidine chloride) and are intended for use in stabilized calendaring.

Copolymers containing 60% vinyl chloride and 40% acrylonitrile are used in fibers. The fibers are spun from acetone solution. They are nonflammable and have good chemical resistance.

6.17.8 Poly(vinylidine chloride)

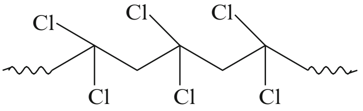
Vinylidine chloride homopolymers form readily by free-radical polymerization, but lack sufficient thermal stability for commercial use. Copolymers, however, with small amounts of comonomers find many applications.

The monomer, vinylidine chloride, can be prepared by dehydrochlorination of 1,1,2-trichloroethylene:



It is a colorless liquid that boils at 32°C. Also, it is rather hard to handle as it polymerizes on standing. This takes place upon exposure to air, water, or light. Storage under an inert atmosphere does not completely prevent polymer formation.

Poly(vinylidine chloride) can be formed in bulk, solution, suspension, and emulsion polymerization processes. The products are highly crystalline with regular structures and a melting point of 220°C. The structure can be illustrated as follows:



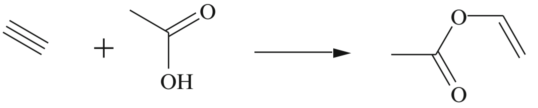
This regularity in structure is probably due to little chain transferring to the polymer backbone during polymerization. Such regularity of structure allows close packing of the chains and, as a result, there are no effective solvents for the polymer at room temperature.

Copolymerization of vinylidine chloride with vinyl chloride reduces the regularity of the structure. It increases flexibility and allows processing the polymer at reasonable temperatures. Due to extensive crystallization, however, that is still present in 85:15 copolymers of vinylidine chloride with vinyl chloride, they melt at 170°C. The copolymerization reactions proceed at slower rates than do homopolymerizations of either one of the monomers alone. Higher initiator levels and temperatures are, therefore, used. The molecular weights of the products range from 20,000 to 50,000. These materials are good barriers for gases and moisture. This makes them very useful in films for food packaging. Such films are formed by extrusion and biaxial orientation. The main application, however, is in filaments. These are prepared by extrusion and drawing. The tensile strength of the unoriented material is 10,000 lb/in.^{2} and the oriented one 30,000 lb/in.^{2}.

Vinylidine chloride is also copolymerized with acrylonitrile. This copolymer is used mainly as a barrier coating for paper, polyethylene, and cellophane. It has the advantage of being heat sealable.

6.18 Poly(vinyl acetate)

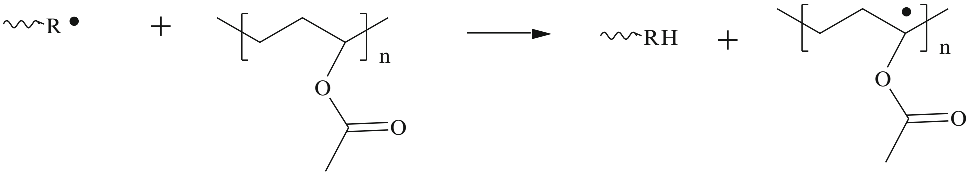
Vinyl acetate monomer can be prepared by reacting acetylene with acetic acid:



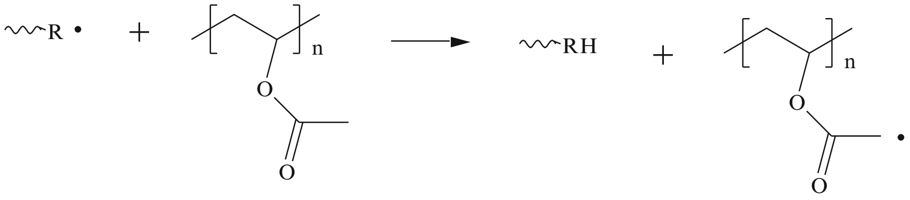
The reaction can be carried out in a liquid or in a vapor phase. A liquid phase reaction requires 75–80°C temperatures and a mercuric sulfate catalyst. The acetylene gas is bubbled through glacial acetic acid and acetic anhydride. Vapor phase reactions are carried out at 210–250°C.

Typical catalysts are cadmium acetate or zinc acetate. There are other routes to vinyl acetate as well, based on ethylene.

Commercially, poly(vinyl acetate) is formed in bulk, solution, emulsion, and suspension polymerizations by free-radical mechanism. In such polymerizations, chain transferring to the polymer may be as high as 30%. The transfer can be to a polymer backbone through abstraction of a tertiary hydrogen:



It can also take place to the methyl proton of the acetate group:



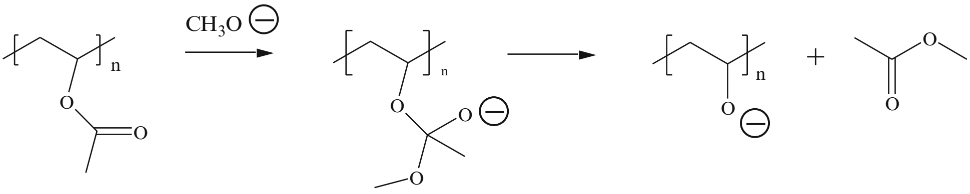
The polymer has a head to tail structure and is highly branched. It is quite brittle and exhibits cold flow. This makes it useless as a structural plastic. It is, however, quite useful as a coating material and as an adhesive for wood. The polymer is soluble in a wide range of solvents and swells and softens upon prolonged immersion in water. At higher temperatures or at extended exposures to temperatures above 70°C, the material loses acetic acid.

A number of copolymers are known where vinyl acetate is the major component. In coatings, vinyl acetate is often used in copolymers with alkyl acrylates (line 2-ethylhexyl acrylate) or with esters of maleic or fumaric acids. Such copolymers typically contain 50–20% by weight of the comonomer and are usually formed by emulsion polymerization in batch processes. They are used extensively as vehicles for emulsion paints.

Shaver and coworkers [319] investigated the mechanism of bis(imino)pyridine ligand framework for transition metal systems-mediated polymerization of vinyl acetate. Initiation using azobisisobutyronitrile at 120°C results in excellent control over poly(vinyl acetate) molecular weights and polymer dispersities. The reaction yields vanadium-terminated polymer chains which can be readily converted to both proton-terminated poly(vinyl acetate) or poly(vinyl alcohol). Irreversible halogen transfer from the parent complex to a radical derived from azobisisobutyronitrile generates the active species.

6.19 Poly(vinyl alcohol) and Poly(vinyl acetal)s

Vinyl alcohol monomer does not exist because its keto tautomer is much more stable. Poly(vinyl alcohol) can be prepared from either poly(vinyl esters) or from poly(vinyl ethers). Commercially, however, it is prepared exclusively from poly(vinyl acetate). The preferred procedure is through a transesterification reaction using methyl or ethyl alcohols. Alkaline catalysts yield rapid alcoholyses. A typical reaction employs about 1% of sodium methoxide and can be carried to completion in 1 h at 60°C. The product is contaminated with sodium acetate that must be removed. The reaction of transesterification can be illustrated as follows:



The branches of poly(vinyl acetate) that form during polymerization as a result of chain transferring to the acetate groups cleave during transesterification. As a result, poly(vinyl alcohol) is lower in molecular weight than its parent material.

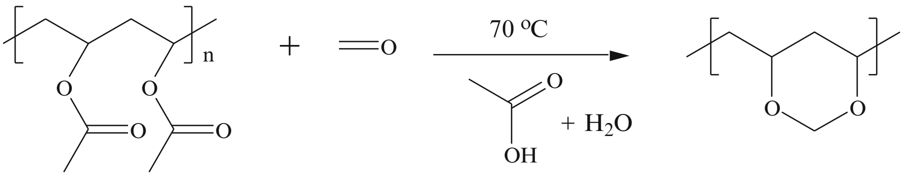
Poly(vinyl alcohol) is very high in head to tail structures, based on NMR data. It shows the presence of only a small amount of adjacent hydroxyl groups. The polymer prepared from amorphous poly(vinyl acetate) is crystalline, because the relatively small size of the hydroxyl groups permits the chains to line-up into crystalline domains. Synthesis of isotactic poly(vinyl alcohol) was reported from isotactic poly(vinyl ethers), like poly(benzyl vinyl ether), poly(*t*-butyl vinyl ether), poly (trimethylsilyl vinyl ether), and some divinyl compounds.

Poly(vinyl alcohol) is water soluble. The hydroxyl groups attached to the polymer backbone, however, exert a significant effect on the solubility. When the ester groups of poly(vinyl acetate) are cleaved to a hydroxyl content of 87–89%, the polymer is soluble in cold water. Further cleavage of the ester groups results in a reduction of the solubility and the products require heating of the water to 85°C to dissolve. This is due to strong hydrogen bonding that also causes unplasticized poly(vinyl alcohol) to decompose below its flow temperature. On the other hand, due to hydrogen bonding the polymer is very tough.

Poly(vinyl acetals) are prepared by reacting poly(vinyl alcohol) with aldehydes. Reactions of poly (vinyl alcohol) with ketones yield ketals. These are not used commercially.

Not all hydroxyl groups participate in formations of acetals and some become isolated. A typical poly(vinyl acetal) contains acetal groups, residual hydroxyl groups, and residual acetate groups from incomplete transesterification of the parent polymer.

Poly(vinyl acetal)s can be formed directly from poly(vinyl acetate) and this is actually done commercially in preparations of poly(vinyl formal). A typical reaction is carried out in the presence of acetic acid, formalin, and sulfuric acid catalyst at 70°C:



Poly(vinyl butyral), on the other hand, is prepared from poly(vinyl alcohol) and butyraldehyde. Sulfuric acid is used as the catalyst. Commercially only poly(vinyl formal) and poly(vinyl butyral) are utilized on a large scale in coating materials.

Review Questions

Section 6.1

1. What are the two types of polyethylene that are currently manufactured commercially?
2. Describe the chemical structure of low-density polyethylene produced by free-radical mechanism and show by chemical equations how all the groups that are present form. How can low-density polyethylene be prepared by ionic mechanism?
3. Describe conditions and procedure for commercial preparation of polyethylene by free-radical mechanism, the role of oxygen, and the problems associated with oxygen.
4. Describe a tubular reactor for preparation of polyethylene.
5. What are the industrial conditions for preparations of high-density polyethylene. Describe the continuous solution process, the slurry process, and the gas-phase process.
6. Show with chemical reactions how polymethylene forms from diazomethane.

Section 6.2

1. Discuss high activity catalysts for the manufacturing of isotactic polypropylene, heterogeneous and homogeneous.
2. What are the current techniques for polypropylene manufacture?
3. How can syndiotactic polypropylene be prepared and what are its properties?

Section 6.3

1. Describe the two industrial processes for manufacturing polybutylene.

Section 6.4

1. Draw the chemical structure of isotactic poly(butene-1). How is it prepared and used?
2. What is TPX, how is it prepared, and what are its properties?

Section 6.5

1. Discuss copolymers of ethylene with propylene. How are they prepared? What catalysts are used in the preparations? How are ethylene–propylene rubbers cross-linked?
2. What are the copolymers of ethylene with higher α-olefins and why are they prepared and how?
3. Discuss the copolymers of ethylene with vinyl acetate? How are they prepared and used?
4. What are ionomers? Describe each type. How are they used?
5. Describe the catalysts used in preparations of aliphatic ketones by copolymerization of ethylene with carbon monoxide.

Section 6.6

1. Discuss polybutadiene homopolymers. How are they prepared? What are their uses?
2. What are popcorn polymers? What causes their formation?
3. Discuss liquid polybutadienes. How are they prepared and used?
4. How are high molecular weight polybutadienes prepared and used?
5. Discuss polyisoprenes. What is natural rubber? Where does it come from? What are synthetic polyisoprenes? How are they prepared?

Section 6.7

1. What is methyl rubber?

Section 6.8

1. What is chloroprene rubber? How is it made and used?

Section 6.9

1. What are poly(carboxybutadiene)s?

Section 6.10

1. Discuss cyclopolymerization of conjugated dienes.

Section 6.11

1. What is SBR rubber? Explain and describe preparation and properties.
2. What are block copolymer elastomers? How are they prepared and what gives them their unique properties?
3. What is GR-N rubber? Explain and describe preparation and properties.

Section 6.12

1. How are atactic and syndiotactic polystyrenes prepared commercially? Describe and explain.
2. What polymers of substituted styrenes are available commercially? How are they prepared?

Section 6.13

1. What is high-impact polystyrene and how is it prepared?
2. Discuss ABS resins. How are they prepared?

Section 6.14

1. Discuss the chemistry of free-radical polymerization of acrylic and methacrylic esters.
2. What are acrylic elastomers and how are they vulcanized?
3. How is poly(methyl methacrylate) prepared commercially, such as Plexiglas in the form of sheets and rods? Is poly(methyl methacrylate) prepared in any other way, how? For what applications?
4. Describe the thermosetting acrylic resins used in industrial coatings. How are they prepared? How are they cross-linked?

Section 6.15

1. Discuss industrial polymers and copolymers of acrylonitrile and methacrylonitrile. How are they prepared and used?

Section 6.16

1. Describe preparation and uses of polyacrylamide, poly(acrylic acid), and polymethacrylic acid.

Section 6.17

1. How is polytetrafluoroethylene prepared, and what are its properties and uses?
2. Discuss the chemistry of polychlorotrifluoroethylene, poly(vinylidine fluoride), and poly(vinyl fluoride).
3. What common copolymers of fluoroolefins are used commercially?
4. Discuss the chemistry of poly(vinyl chloride) and poly(vinylidine chloride).
5. Discuss the important commercial copolymers of vinyl chloride. What are their main uses?
6. Discuss the chemistry of poly(vinylidine chloride).

Section 6.18

1. Discuss preparation, properties, and uses of poly(vinyl acetate).

Section 6.19

1. How is poly(vinyl alcohol) prepared, used, and converted to poly(vinyl acetal)s?

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Chapter 7
Step-Growth Polymerization and Step-Growth Polymers

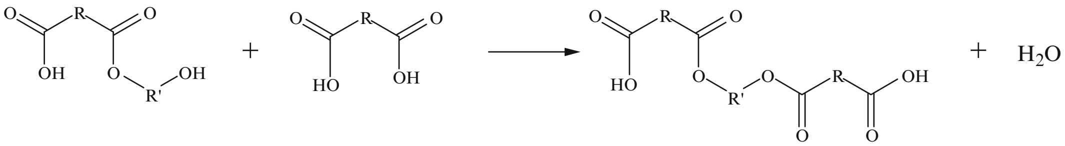
7.1 Mechanism and Kinetics of Step-Growth Polymerization

Two types of monomers can undergo step-growth polymerizations [1, 4, 5]. Both are polyfunctional, but one type possesses only one kind of functionality. An example is adipic acid that has two functional groups, but both are carboxylic acid groups. Another one is hexamethylene diamine with two amine functional groups. To the second type belong monomers that have both functional groups needed for condensation on the same molecule. An example of such a monomer is *p*-amino benzoic acid, where both amino and carboxylic acid groups are present in the same molecule. Chain growths proceed from reactions between two different functional groups with both types of molecules. An exception is formation of polyanhydrides, where the polymeric chains are formed from two carboxylic acid groups reacting with each other and splitting out water. There are some other exceptions as well.

7.1.1 *Reactions of Functional Groups*

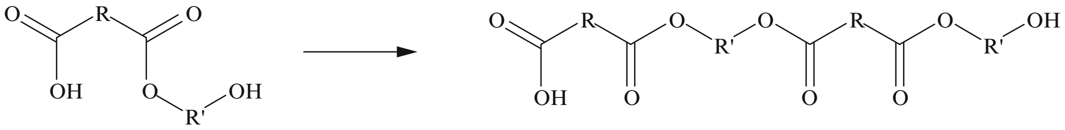
Kinetic considerations are of paramount importance in understanding the mechanism of step-growth polymerization [1]. As stated in Chap. 1, chain-growth polymerizations take place in discreet steps. Each step is a reaction between two functional groups, like, for instance, in a polyesterification reaction, it is a reaction between –COOH and –OH. The increase in molecular weight is slow. The first step is a condensation between two monomers to form a dimer:

A dimer can react next with another monomer to form a trimer:



A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_7,

Two dimers can combine to form a tetramer:

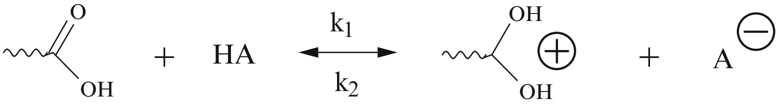


These step condensations continue slowly with the molecular weights of the polymers increasing with each step. In such reactions, the monomeric species disappear early from the reaction mixtures, long before any large molecular weight species develop. In most step-growth polymerizations, on a weight basis, less than 1% of monomeric species remain by the time the average chain length attains the size of ten combined monomeric units [1, 3, 4, 6].

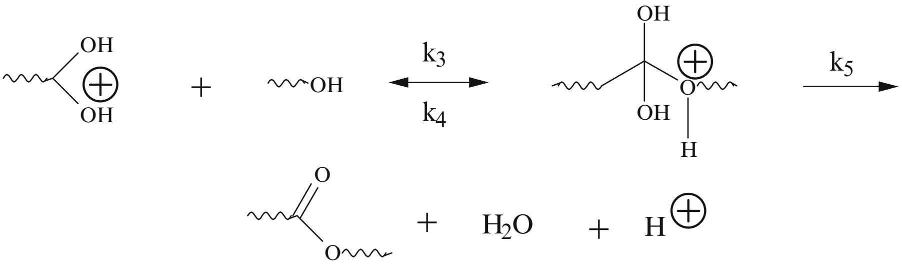
One important characteristic of step-growth polymerizations is that any functional group on any one molecule is capable of reacting with any opposite functional group on any other molecule. Thus, for instance, if it is a reaction of polyesterification, any carboxylic acid group on any one molecule, regardless of size, can react with any hydroxy on another one. This is true of all other step-growth polymerizations. It means that the rates of step-growth polymerizations are the sums of the rates of all reactions between molecules of various sizes. A useful assumption that can be applied here is that the reactivities of both functional groups remain the same throughout the reaction, regardless of the size of the molecules to which they are attached. This allows treating step-growth polymerizations like reactions of small molecules. General observations would suggest slower reactivity of functional groups attached to large molecules. This, however, is usually due to lower diffusion rates of large molecules. The actual reactivity of the functional groups depends upon collision frequencies (number of collisions per unit of time) of the groups and not upon the rate of diffusion. Functional groups on the terminal ends of large molecules have greater mobility than the remaining portions of the molecules as a whole. In addition, the reactivity of one given functional group in a bifunctional molecule is not altered by the reaction of the other group (if there is no neighboring group effect). This implies that the reactivities of functional groups are not altered during the polymerization.

The kinetics of step-growth polymerization can be derived from a polyesterification reaction that follows the same course as all acid-catalyzed esterifications [2].

1. Protonation step:



2. Reaction of the protonated carboxylic acid group with the alcohol:



The above polyesterifications, like many other reactions, are equilibrium reactions. They must be conducted in a way that allows the equilibrium to shift to the right to attain high molecular weights.

One way is by continual removal of the by-products. In such situations, the reactions take place at nonequilibrium conditions and there is no K_4.

7.1.2 Kinetic Considerations

The rate of polymerization can be expressed as the *rate of disappearance of one of the functional groups*. In reactions of polyesterification, this can be the rate of disappearance of carboxyl groups, $-\mathrm{d}[\mathrm{CO_2H}]/\mathrm{d}t$.

$$R_\mathrm{P} = \frac{-\mathrm{d}[\mathrm{CO_2H}]}{\mathrm{d}t} = k_3[\mathrm{C(OH^{\oplus})_2}][\mathrm{OH}]$$

In the above equation $[\mathrm{CO_2H}]$, [OH], and $[\mathrm{C(OH^{\oplus})_2}]$ represent carboxyl, hydroxy, and protonated carboxyl groups, respectively. Also, it is possible to write an equilibrium expression for the protonation reaction of the acid as follows:

$$K = \frac{k_1}{k_2} = \frac{[\mathrm{C(OH^{\oplus})_2}][\mathrm{A^{\ominus}}]}{[\mathrm{COOH}][\mathrm{HA}]}$$

This equation can be combined with the above rate expression:

$$\frac{-\mathrm{d}[\mathrm{COOH}]}{\mathrm{d}t} = \frac{k_1k_3[\mathrm{COOH}][\mathrm{OH}][\mathrm{HA}]}{k_2[\mathrm{A^{\ominus}}]} = k_3K[\mathrm{COOH}][\mathrm{OH}][\mathrm{HA}]$$

If there is no catalyst present and the dicarboxylic acid acts as its own catalyst, HA is replaced by [COOH] and the expression becomes:

$$\frac{-\mathrm{d}[\mathrm{COOH}]}{\mathrm{d}t} = k[\mathrm{COOH}]^2[\mathrm{OH}]$$

In the above expression k_1, k_2, k_3, and the concentration of the $[\mathrm{A^{\ominus}}]$ ions have been replaced by an experimentally determined rate constant, k.

In most step-growth polymerization reactions, the concentrations of the two functional groups are very close to stoichiometric. This allows writing the above rate equation as follows:

$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k[\mathrm{M}]^3$$

In this equation, M represents the concentration of each of the reacting species. They can be hydroxy and carboxylic acid groups in a polyesterification reaction, or amino and carboxylic acid groups in polyamidation reaction, and so on.

The above equation can also be written as follows:

$$k\,\mathrm{d}t = -\mathrm{d}[\mathrm{M}]/[\mathrm{M}]^3$$

after integrating of the above, we get:

$$2kt = 1/[\mathrm{M}]^2 + \text{constant}$$

The constant in the above equation equals $1/[M_o]^2$, where $[M_o]$ represents the initial concentration of the reactants (of hydroxyl or carboxyl groups in a polyesterification) at time $t = 0$.

At the start of the polymerization, there are $[\mathrm{M_o}]$ molecules present. After some progress of the reaction, there are [M] molecules left; $[\mathrm{M_o}] - [\mathrm{M}]$ is then the number of molecules that participated in the formation of polymeric chains. The conversion, p, can be written, according to Carothers [6], as

$$p = \frac{[\mathrm{M_o}] - [\mathrm{M}]}{[\mathrm{M_o}]}$$

or, the concentration of [M] at any given time t is

$$[\mathrm{M}] = [\mathrm{M_o}](1 - p)$$

and the degree of polymerization,

$$\overline{\mathrm{DP}} = \frac{1}{1 - p}$$

It is important to realize from the above equation that in order to a $\overline{\mathrm{DP}}$ of only 50, it is necessary to achieve 98% conversion (p must equal 0.98).

The value of $\overline{\mathrm{DP}}$, at any given time, t is equal to the ratio of monomer molecules that were present at the start of the reaction divided by the number of molecules that are still present at that particular time:

$$\overline{\mathrm{DP}} = \frac{[\mathrm{M_o}]}{[\mathrm{M}]}$$

By combining the above expression with Caruthers equation and solving for $[M]$, one obtains

$$[\mathrm{M}] = [\mathrm{M_o}](1 - p)$$

For a second-order rate expression, the above equation can be written as

$$1/\{[\mathrm{M_o}](1 - p)\} - 1[\mathrm{M_o}] = kt$$

and by replacing $1/(1 - p)$ with $\overline{\mathrm{DP}}$, one obtains

$$\mathrm{DP} = [\mathrm{M_o}]kt + 1$$

Using the above equation, it is possible to calculate from the rate constant (if it is known) and the concentration of monomers the time required to reach a desired number average molecular weight. When there is no catalyst present and the carboxylic acid assumes the role of a catalyst itself, then a third-order rate expression (shown above) must be employed:

$$-\,\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k[\mathrm{M}]^3$$

By integrating the third-order rate expression, one obtains:

$$1/[\mathrm{M}]^2 - 1/[\mathrm{M_o}]^2 = 2kt$$

and, by substituting for [*M*] the Carothers equation and then rearranging the resultant equation, one obtains:

$$\frac{1}{[\mathrm{M_o}]^2(1-p)^2}-\frac{1}{[\mathrm{M_o}]^2}=2kt$$

this can also be written as:

$$1/(1-p)^2=2kt[\mathrm{M_o}]^2+1$$

or

$$\overline{\mathrm{DP}}^2=2kt[\mathrm{M_o}]^2+1$$

The above equation shows that without a catalyst the molecular weight increases more gradually.

It can be deduced from the above discussion that a high stoichiometric balance is essential for attaining high molecular weight. This means that any presence of a monofunctional impurity has a strong limiting effect on the molecular weight of the product. The impurity blocks one end of the chain by reacting with it. This is useful, however, when it is required to limit the DP of the product. For instance, small quantities of acetic acid are sometimes added to preparations of some polyamides to limit their molecular weight.

In polymerizations of monomers with the same functional groups on each molecule, like A —— A and B —— B (i.e., a diamine and a diacid), the number of functional groups present can be designated as N_A^o for A type and N_B^o for B type. These numbers N_A^o and N_B^o represent the number of functional groups present at the start of the reaction. They are twice the number of A —— A and B —— B molecules that are present. If the number N_B^o is slightly larger than N_A^o, then we have a *stoichiometric imbalance* in the reaction mixture. This imbalance is designated as *r*.

$$r=N_\mathrm{A}^\mathrm{o}/N_\mathrm{B}^\mathrm{o}$$

(It is common to define the ratio *r* as less than or equal to unity, so, in the above, B groups are present in excess.) The total number of monomers at the start of the reaction are $(N_\mathrm{A}^\mathrm{o}+N_\mathrm{B}^\mathrm{o})/2$ or $N_\mathrm{A}^\mathrm{o}(1+(1/r))/2$.

The extent of the reaction, *p,* can be defined as the portion of the functional groups A that reacted at any given time. The portion of the functional groups B that reacted at the same time can be designated by *rp*. The unreacted portions of A and B groups can then be designated as $1-p$ and $1-rp$, respectively. The total number of unreacted A groups in the reaction mixture would then be $N_\mathrm{A}^\mathrm{o}(1-p)$. This reaction mixture also contains $N_\mathrm{B}^\mathrm{o}(1-rp)$ unreacted B groups. The total number of chain ends on the polymer molecules is the sum of the unreacted A and B groups. Because each polymer molecule has two chain ends, the total number of chain ends is then $[N_\mathrm{A}^\mathrm{o}(1-p)+N_\mathrm{B}^\mathrm{o}(1-rp)]/2$.

The number average degree of polymerization is equal to the total number of A —— A and B —— B molecules present at the start of the reaction divided by the number of polymer molecules at the end. This can be represented as follows:

$$\overline{\mathrm{DP}}_n=\frac{N_\mathrm{A}^\mathrm{o}(1+1/r)/2}{[N_\mathrm{A}^\mathrm{o}(1-p)+N_\mathrm{B}^\mathrm{o}(1-rp)]/2}$$

the expression can be reduced (since $r=N_\mathrm{A}^\mathrm{o}/N_\mathrm{B}^\mathrm{o}$) to

$$\overline{\mathrm{DP}} = \frac{1+r}{2+r-2rp}$$

The molecular weight of the product can be controlled by precise stoichiometry of the polymerization reaction. This can be done by simply quenching the reaction mixture at a specified time when the desired molecular weight is achieved.

Flory derived statistical methods for relating the molecular weight distribution to the degree of conversion [1, 3]. In these polymerizations, each reaction step links two monomer molecules together. This means that the number of mers in the polymer backbone is always larger by one than the number of each kind of functional groups, A or B. If there are x monomers in a chain, then the number of functional groups that have reacted is $x - 1$. The functional groups that are unreacted remain at the ends of the chains. If we designate p as the extent of the reaction or the degree of conversion, as above, then the probability that $x - 1$ of A or B has reacted is p^{x-1}, where

$$p = (N_{\mathrm{o}} - N)/N_{\mathrm{o}}$$

and the probability of finding an unreacted functional group is $p - 1$. The probability of finding a polymer molecule that contains x monomer units and an unreacted functional group A or B is $p^{x-1}(1-p)$. At a given time t, the number of molecules present in the reaction mixture is N.

The fraction that contains x units can be designated as N_x and can be defined as:

$$N_x = Np^{x-1}(1-p)$$

The Carothers equation defines $N/N_{\mathrm{o}} = 1 - p$. The above expression for N_x can, therefore, be written as:

$$N_x = N_{\mathrm{o}}(1-p)^2 p^{x-1}$$

where N_{o} is, of course, the number of monomer units that are present at the start of the reaction.

To determine the molecular weight distribution of the polymeric species that form at any given degree of conversion, it is desirable to express the weight average and number average molecular weights by terms, like p. By defining $\mathrm{M_o}$ as the mass of the repeating unit, the number average molecular weight is:

$$\overline{M}_{\mathrm{n}} = \mathrm{M_o}\overline{\mathrm{DP}} = \mathrm{M_o}(1/1-p)$$

and the weight average molecular weight is:

$$\overline{M}_{\mathrm{w}} = \sum w_x x M_{\mathrm{o}}$$

where w_x is the weight fraction of molecules containing x monomer units. It is equal to xN_x/N_{o} and that can be written, based on the above equation for N_x, as $w_x = x(1-p)^2 p^{x-1}$. The weight average molecular weight can now be expressed as:

$$\overline{M}_{\mathrm{w}} = \mathrm{M_o}(1-p)^2 \sum x^2 p^{x-1}$$

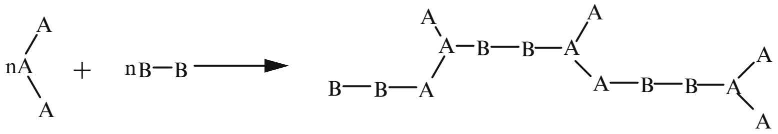
It can be shown that summation, $\sum x^2 p^{x-1} = (1+p)/(1-p)^3$. Based on that, the weight average molecular weight is:

$$\overline{M}_{\mathrm{w}} = \mathrm{M_o}(1+p)/(1-p)$$

and, the molecular weight distribution is:

$$\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}} = 1 + p$$

It is interesting that this equation tells us that at high conversion, when p approaches 1, the molecular weight distribution approaches 2. There is experimental confirmation of this. Until now this discussion was concerned with formation of linear polymers. The presence, however, of monomers with more that two functional groups results in formation of branched structures. An example is a preparation of a polyester from a dicarboxylic acid and a glycol, where the reaction mixture also contains some glycerol. Chain growth in such a polymerization is not restricted to two directions and the products are much more complex. This can be illustrated further on a trifunctional molecule condensing with a difunctional one:



Further growth, of course, is possible at every unreacted functional group and can lead to gelation. The onset of gelation can be predicted from a modified form of the Carothers equation [1]. This equation includes an *average functionality* factor that averages out the functionality of all the functional groups involved. An example is a reaction mixture of difunctional monomers with some trifunctional ones added for branching or cross-linking. The average functionality, f_{ave}, may be (2 + 2 + 2 + 3)/4 = 2.25. The Carothers equation, discussed above, states that

$$p = (N_{\mathrm{o}} - N)/N_{\mathrm{o}}$$

where N_{o} and N represent the quantities of monomer molecules present initially and at a conversion point p. The number of functional groups that have reacted at that point is $2(N_{\mathrm{o}} - N)$. In the modified equation, the number of molecules that were present initially is $N_{\mathrm{o}}f_{\mathrm{ave}}$. The equation now becomes:

$$p = \frac{2(N_{\mathrm{o}} - N)}{N_{\mathrm{o}}f_{\mathrm{ave}}}$$

N_{o}/N can be replaced by DP and the above expression becomes:

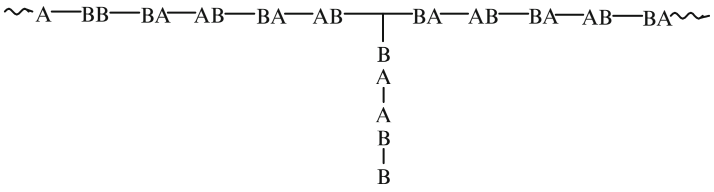
$$\bar{p} = 2/f_{\mathrm{ave}} - 2/\mathrm{DP}f_{\mathrm{ave}}$$

It is generally accepted that *gelation* occurs when the average degree of polymerization becomes infinite. At that point, the second term in the above equation becomes zero. When that occurs, the conversion term becomes p_{c}. It is the *critical reaction conversion* point:

$$p_{\mathrm{c}} = 2/f_{\mathrm{ave}}$$

Gelation, however, is less likely to be a major concern in polymerization reactions where only small quantities of tri- or multifunctional monomers are present. In the preparation of alkyds, for instance (described further in this chapter), some glycerin, which is trifunctional, is usually present.

If the amount of glycerin is small, then the product is only branched. In addition, there might be only one branch per molecule:

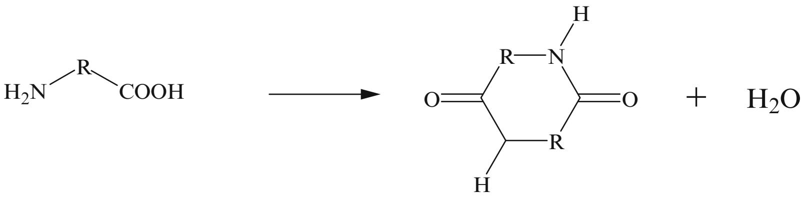


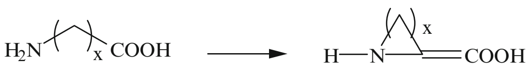
Statistical methods were developed for prediction of gelation [7]. These actually predict gelation at a lower level than does the Carothers equation shown above. As an example, we can use a reaction of three monomers, A, B, and C. We further assume that the functionality of two monomers, f_A and f_B, is equal to two, while that of f_C is greater than two. The critical reaction conversion can then be written as:

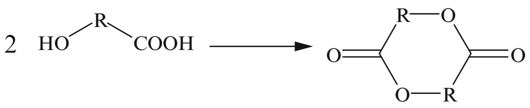
$$p_c = 1/[r + rp(f_C - 2)]^{1/2}$$

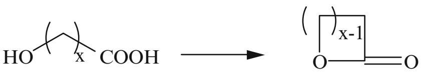
7.1.3 Ring Formation in Step-Growth Polymerizations

Step growth polymerizations can be complicated by cyclization reactions that accompany formations of linear polymers. Such ring formations can occur in reactions of monomers with either the same type of functional groups or with different ones. Following are some illustrations of cyclization reactions:







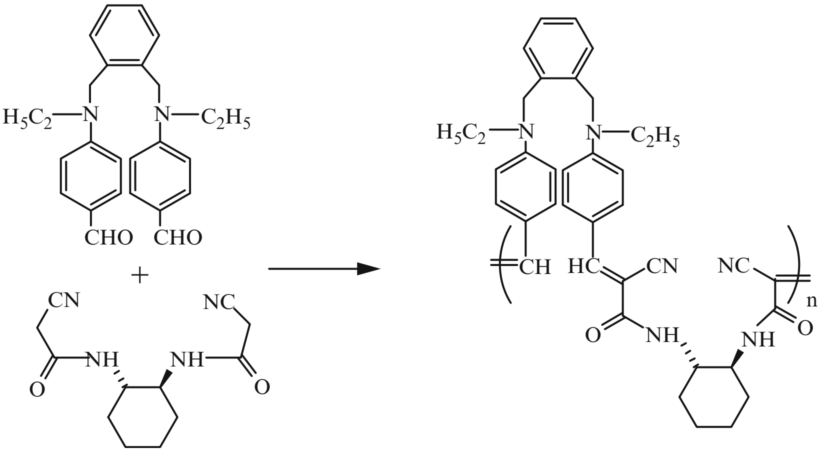


Similarly, dicarboxylic acids can cyclize into anhydrides.

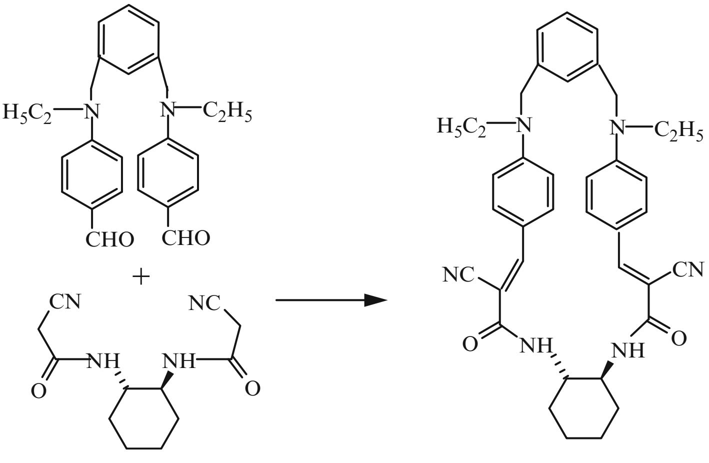
Whether ring formation is likely to take place or not depends upon the size of the ring that can form. If cyclization results in rings with strained bond angles or repulsions due to crowding, the probability of their formation is low. So, small rings, with less than five members, do not form readily. Five-membered rings, however, are essentially free from bond angle distortion and have a greater chance to form. Greater than five-membered rings are not planar and six- and seven-membered rings can also form freely, though not quite as easily as five-membered ones. Six-membered rings are more favored than seven-membered ones. Rings with eight to twelve members are relatively strain-free from bond angle distortion, but they are thermodynamically unstable. This is because substituents (hydrogens or others) are forced into positions of repulsion due to crowding. Also, there is little ring formation with eight to twelve members.

Whether cyclization will take place or not during polymerization also depends on the kinetic feasibility to cyclize. This feasibility is a function of the probability that functional end groups on a molecule will approach each other. As the size of the monomer increases, so does the size of the potential ring. An increase in the size of the monomer, however, also means an increase in the number of different configurations that the monomer molecule can assume. Very few of these configurations are such that the two ends become adjacent [4]. With fewer chances of the end groups encountering each other, there is decreased probability of ring formation. From practical considerations, ring formations are mainly a problem when five-, six-, or seven-membered rings can form. Formation of large rings with more than twelve members is seldom encountered [5].

It was reported that at least in one instance, the products of a reaction can be affected by the isomer used [244]. Thus, in the following Knoevenagel condensation, a polymer will form when an *ortho* isomer is being reacted:



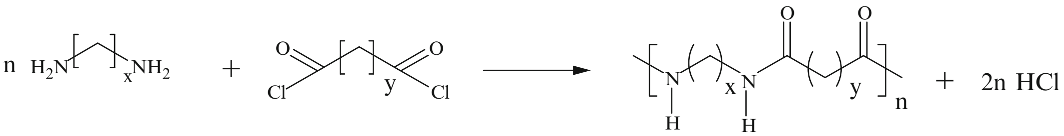
By contrast, the *meta* isomer forms only ring structures instead [242]:



7.1.4 Techniques of Polymer Preparation

Many step-growth polymerizations are carried out by mass or bulk type polymerization. This is widely done not only due to convenience, but also because it results in minimum contamination. Few step-growth reactions are highly exothermic, so thermal control is not hard to maintain. Because equilibrium considerations are very important, the reactions are usually carried out in a way that allows continuous removal of the by-product. Occasionally, the polymerizations are carried out in dispersion in some convenient carriers. Solution polymerizations are sometimes used as a way of moderating the reactions.

Step-growth polymerizations can also be carried out with certain monomers at low temperature by a technique known as ***interfacial polymerization*** or ***interfacial polycondensation*** [28]. The reactions (applicable only to fast reactions) are conducted at the interface between two immiscible liquids. Usually one of the liquids is water and the other one an organic solvent. An example may by a Schotten–Baumann polarization reaction. In such an interfacial polymerization, the diamine would be in the aqueous phase and the diacid chloride in the organic phase. The strong reactivity of acid chloride groups with amines allows the reaction to be carried out at room temperature:



Addition of a base to the aqueous phase removes the hydrochloric acid that forms and catalyzes the reaction. The choice of the organic solvent is important, because it appears that the reaction occurs on the organic side of the interface [28].

There are several important differences between interfacial polymerizations and high temperature condensations. Much higher molecular weight products form from polymerizations at the interface. This is probably due to the high speed of the reactions between the diamines that diffuse into the organic phase and the diacid chloride chain ends [28]. Exact stoichiometry is not necessary to attain high molecular weights in interfacial polycondensation. The opposite is true in high temperature polymerizations.

Interfacial polycondensation is an interesting procedure that is often used in demonstrations in polymer chemistry courses. Polyamides are prepared rapidly, in front of the class from diacid chlorides and diamines. The products are removed quickly as they form, by pulling them out as a string from the interface [47]. Polyesters can also be prepared from diacid chlorides and bisphenols. On the other hand, preparation of polyesters from glycols and diacid chlorides is usually unsuccessful due to low reactivity of the dialcohols. The diacid chlorides tend to undergo hydrolysis instead. Commercially, this procedure is so far confined mainly to preparations of polycarbonates (discussed further in this chapter).

7.2 Polyesters

The class of compounds called polyesters consists of all heterochain macromolecular compounds that possess repeat carboxylate ester groups in the backbones. This excludes all polymers with ester groups located as pendant groups, like acrylic and methacrylic polymers, poly(vinyl esters), and esters of cellulose, or starch. What remains, however, is still a large group of polymeric materials that can be subdivided into saturated and unsaturated polyesters.

7.2.1 Linear Saturated Polyesters

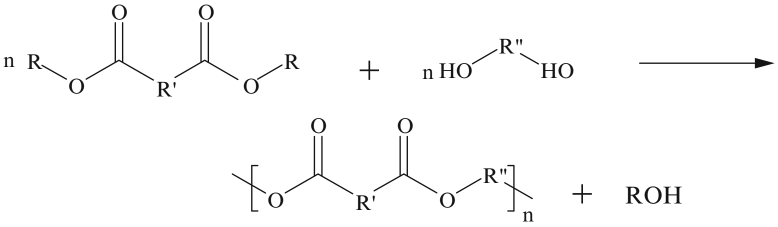
The saturated polyesters that find commercial applications are mostly linear except for some specially prepared branched polymers used in the preparation of polyurethanes. The linear polyesters became commercially important materials early in this century and still find many uses in industry. The earliest studies reported condensations of ethylene, trimethylene, hexamethylene, and decamethylene glycols with malonic, succinic, adipic, sebacic, and *ortho* phthalic acids [6]. Later studies showed that such condensations yield high molecular weight compounds [44]. Nevertheless, these polyesters exhibit poor hydrolytic stability and are generally low melting. Subsequently, however, it was found that aromatic dicarboxylic acids yield polymers with high melting points and poly(ethylene terephthalate), which melts at 265°C, is now an important commercial material.

Physical properties of linear polyesters follow the general observation of the relationships between physical properties and chemical structures of polymers (see Chap. 2). Aromatic diacids and\or glycols with aromatic rings in the structures yield polyesters with high melting points, while the aliphatic ones yield low melting solids or viscous liquids. In addition, hydrogen bonding, dipole interactions, polarizations, stiff interchain bonds, molecular symmetry or regularity, and the ability of polymeric chains to undergo close packing raise the melting points. Conversely, bulky side chains and flexible interchain bonds lower the melting points.

7.2.1.1 Synthetic Methods

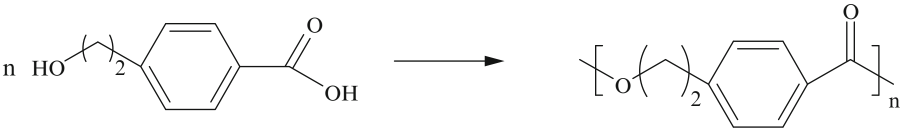
The synthetic methods that are in general use for the preparations of linear polyesters [15] can be summarized as follows:

1. Dibasic acids are reacted with glycols. Stoichiometric balance is strictly maintained. When low boiling glycols are used, however, they are often added in a slight excess and the excess gradually removed by vacuum [6] or by sweeping an inert gas over or through the reaction mixture [6, 8]. This procedure is useful with dicarboxylic acids that otherwise require high temperatures and strong catalysts. Running the reaction at high temperatures can cause the glycols to condense into ethers and the dicarboxylic acids to decompose.
2. Diesters or half esters of dicarboxylic acids or amine salts of the acids are reacted with glycols [19]:

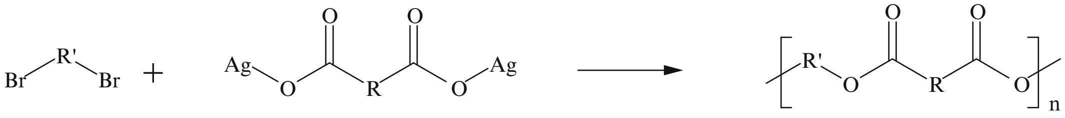


The above transesterification reaction is practical for use with high melting and poorly soluble dicarboxylic acids. In addition, less energy is needed to remove alcohol than water.

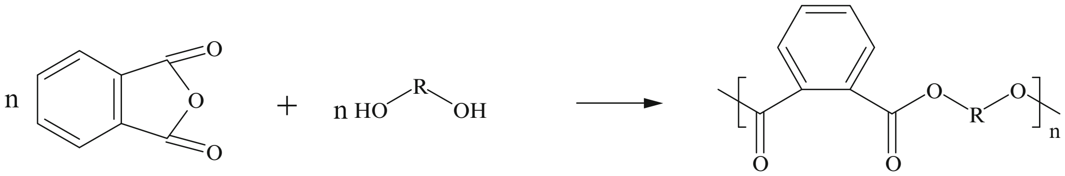
3. Hydroxy acids, like *p*-hydroxyethoxybezoic acid or ω-hydroxydecanoic acid, are capable of self-condensation to form polyesters [10]:



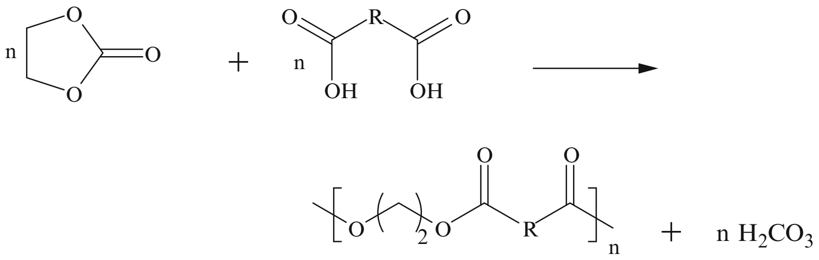
4. Although not practical commercially, polyesters can be prepared in the laboratory by reacting aliphatic dibromides with silver salts of dibasic acids [6]:



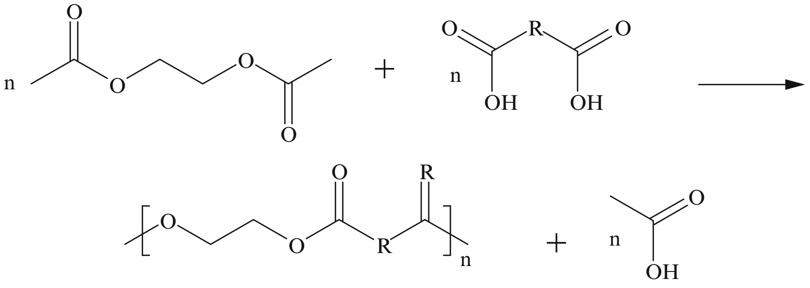
5. Polyesters also form from reactions of dicarboxylic acid anhydrides with glycols [10]:



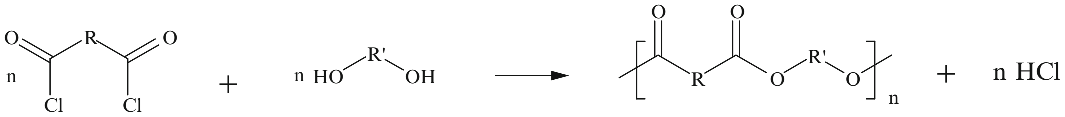
6. Glycol carbonates undergo ester interchange reactions with dibasic acids [11]:



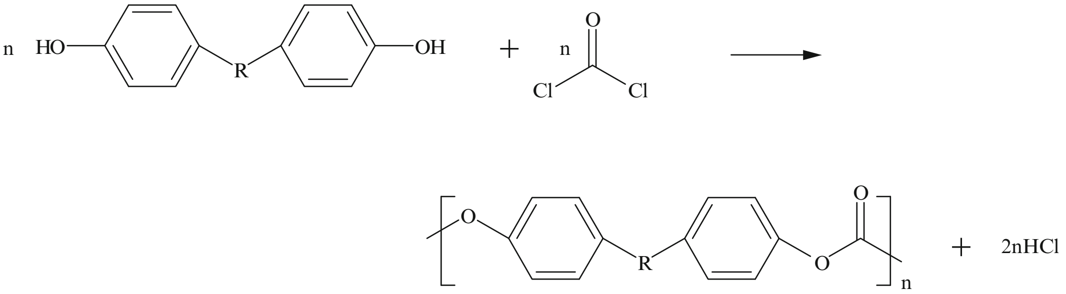
7. Ester interchange reactions between glycol acetates [12, 13] or diphenol diacetates [12] and dicarboxylic acids:



8. Acid chlorides react with diphenols to form polyesters. The reaction is quite efficient when scavenger of HCl is added to the aqueous phase. Such scavengers can be tertiary amines [15]:

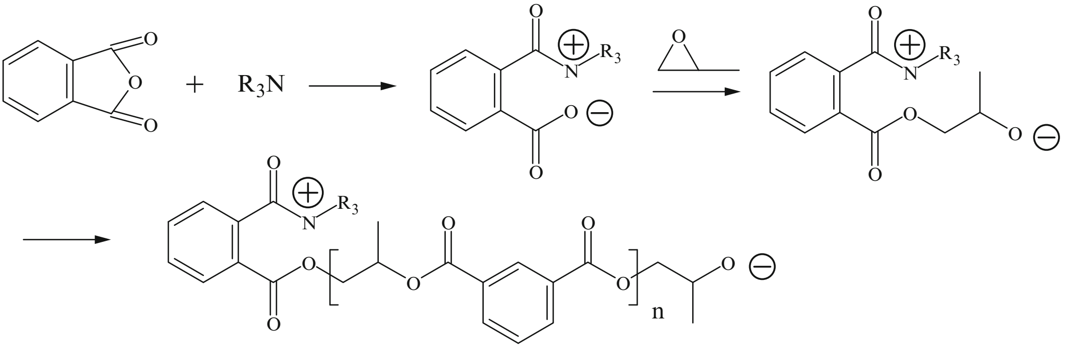


When in place of dicarboxylic acid chlorides phosgene is used, polycarbonates form:

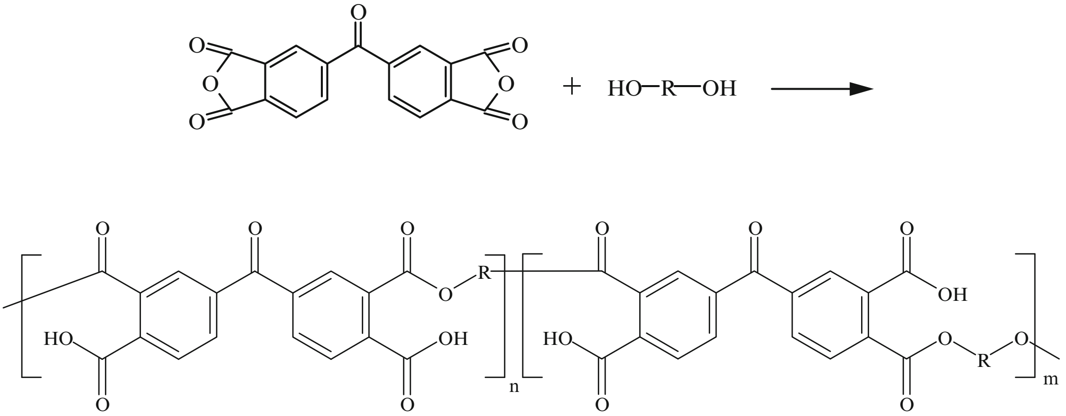


9. Polyesters also form in ring opening polymerizations of lactones. This is discussed in Chap. 5.

Many modifications of the above-described reactions are known. For instance, poly(propylene phthalate) can be prepared from phthalic anhydride and propylene oxide [14]. The reaction is catalyzed by tertiary amines that probably form carboxylate ion intermediates:

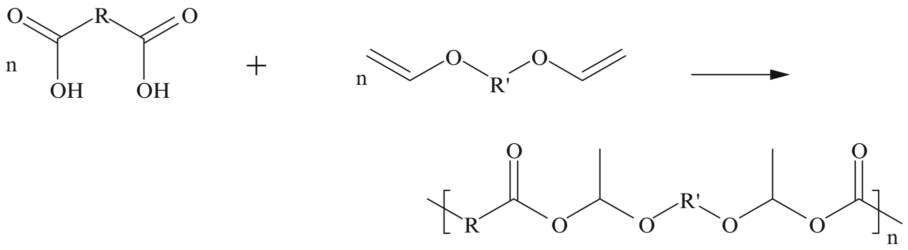


This produces a low molecular weight polyester. A modification is a reaction of a dianhydride with a glycol:

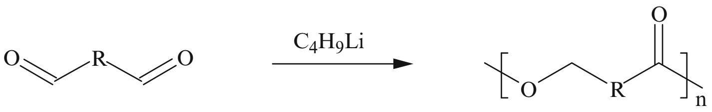


In all esterification reactions, catalysts increase the speed of condensations. Such catalysts are either acids or bases.

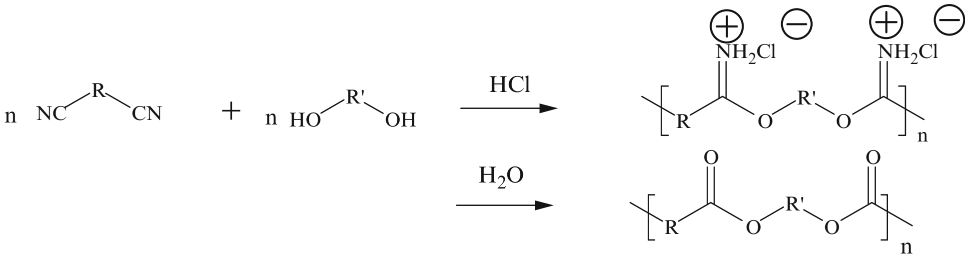
Beyond the above, there are many other polyester syntheses that can be found in the literature, but are not in common use. For instance, polyesters form from additions of carboxylic acids to divinyl ethers [29]:



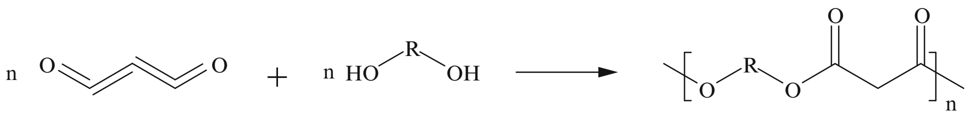
Polyesters also form by the Tischenko reaction from dialdehydes [26, 27]. The intramolecular hydride transfer reaction is typically catalyzed by bases:



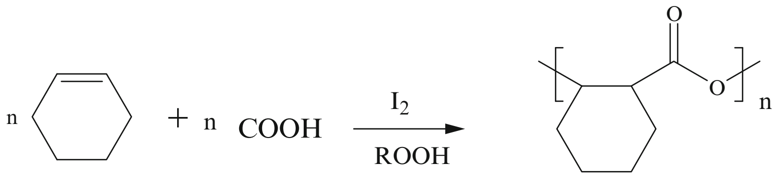
Another reported procedure consists of condensations of nitriles with glycols. The resultant poly (iminoether hydroxide)s hydrolyze to polyesters [32].



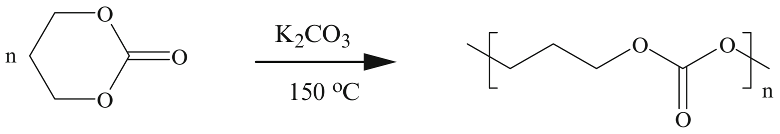
Carbon suboxide condenses with glycols to form polyesters [26]:



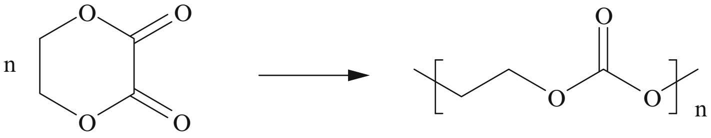
Also, an alternating free-radical addition copolymerization of cyclohexene and formic acid, perhaps via charge transfer, donor–acceptor complexes, yields polyesters [30]:



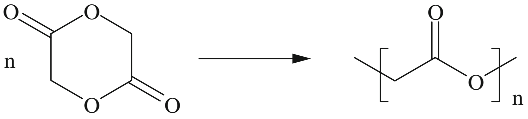
Cyclic carbonates, oxalates, and glycolates polymerize by ring opening polymerizations to yield polyesters. An example is a conversion of a cyclic carbonate into a low molecular weight polymer (about 4,000) [39, 40]:



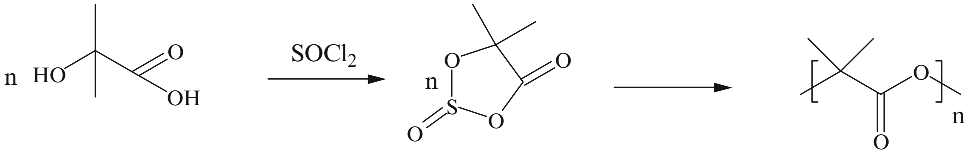
Another example is a ring opening polymerization of an oxalate [39]. Again, only low molecular weight polymers result:



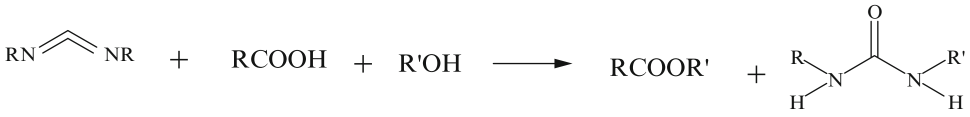
Lactides, on the other hand, when subjected to ring opening polymerization with Lewis acids yield high molecular weight polymers [41]:



Also, α-hydroxycarboxylic acids can polymerize to high molecular weight polymers through formation of anhydrosulfides [42]:



In addition, it was reported [49] that polyesterification reactions are possible at room temperature. High molecular weight polyesters form directly from carboxylic acids and phenols. These solution polymerization reactions proceed under mild conditions, near neutral pH. Equimolar mixtures of acids and alcohols condense as the reactions are being driven by additions of water across carbodiimide groups. Substituted ureas form as by-products:

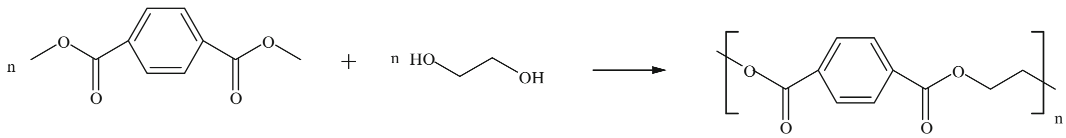


The reaction is useful in preparations of isoregic ordered chains with translational polar symmetry. It can also be applied in polymerizations of functional or chiral monomers.

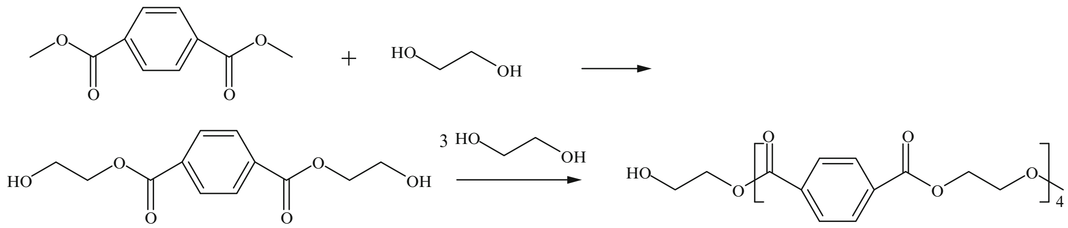
7.2.1.2 Commercial Linear Saturated Polyesters

Many linear aliphatic polyesters are produced commercially. They are relatively low in molecular weight, less than 10,000. The main use of these materials is as plasticizers for poly(vinyl chloride) polymers and copolymers. Such polyesters are usually formed from dicarboxylic acids and glycols. Often, monocarboxylic acids or monohydroxy compounds are added towards the end of the reaction, in small quantities, to control molecular weight and to cap the reactive end groups. The condensation reactions are carried out at 200–250°C in an inert atmosphere. To obtain a molecular weight of about 1,000, these reactions are run for only several hours. For higher molecular weights, however, the glycols are added in excess and the initial products heated under vacuum (about 1 mmHg) for several hours.

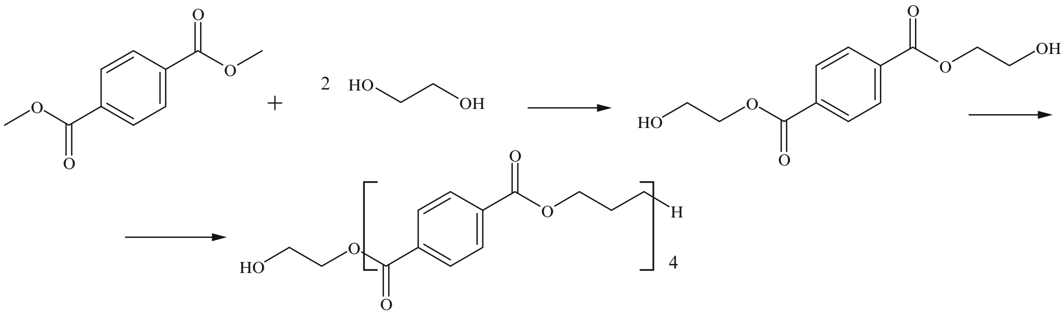
Among the high molecular weight aliphatic-aromatic polyesters, the highest commercial volume material is poly(ethylene terephthalate). Most of it is prepared from dimethylene terephthalate and ethylene glycol by a transesterification reaction:



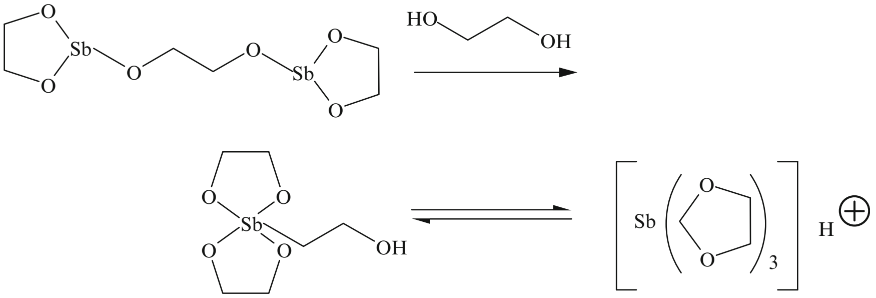
Often the reaction is carried out in two steps. An excess of two moles of ethylene glycol is used and the first stage of the reaction is carried out at 150–210°C to form bis(2-hydroxyethyl)terephthalate, a small amount of an oligomer, and methanol, which is removed:



In the second stage, the temperature is maintained at 270–285°C and the reaction is carried out under vacuum at about 1 mmHg. The bis(2-hydroxyethyl)terephthalate undergoes a transesterification reaction and the excess glycol is removed:



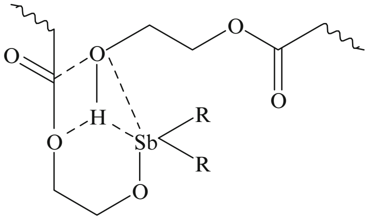
In the process, ethanol forms and is removed. Various metal oxide or acetate catalysts are employed in the first stage. These are antimony, barium, calcium, cobalt, lead, manganese, titanium, or zinc oxides or acetates. Carbonates, alcoholates, and alkanoates can also be used. Based on disclosures in the patent literature, it appears that antimony compounds, particularly the trioxide, dominate the field of catalysts for the second stage of this reaction [16]. The exact mechanism by which the antimony compounds act as catalysts for the syntheses of polyesters is still being investigated. It was shown that bis(2-hydroxyethyl)-terephthalate competes successfully with oligomer end groups for Sb_2O_3 and that a complex of this compound with the metal oxide is unreactive in these polymerizations [17]. In addition, during polymerizations under vacuum, there is an increase in metal surfaces of antimony oxide [18]. It was suggested that a reaction of antimony trioxide with ethylene glycol results in formation of antimony glycolates with a ligand number of 3 [19, 20]:



A study of antimony glycolates as effective catalysts for preparation of poly(ethylene terephthalate) with varying number of hydroxyethoxy ligands rated them in the following decreasing order of effectiveness [20]:

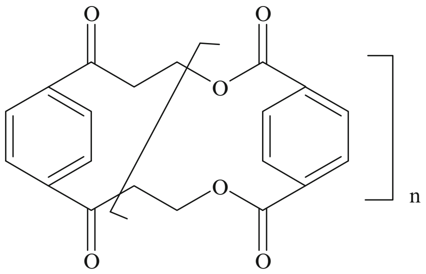
$$5 = 3>2>1 \gg 0$$

This led to a suggestion by Maerov [20] that a key step in condensation may involve a chemical reaction that ties up a hydroxyl chain end with the catalyst molecule. Introduction of a second hydroxyethoxy chain end is followed by the right electronic bond shift:



The role of antimony is to establish a favorable spatial configuration for the transition state [20]. An earlier study, however, resulted in a conclusion that antimony's activity is inversely proportional to the hydroxyl group concentration [21].

Based on model reactions for the preparation of poly(ethylene terephthalate) by ester interchange, the optimum molar ratio of ethylene glycol to dimethyl terephthalate is 2.4 to 1. This ratio allows complete removal of methanol [22]. The overall polyesterification reaction is third order [22, 23]. In addition, high molecular weight polymerizations of poly(ethylene terephthalate) invariably produce some cyclic oligomers as by-products [24, 25]. Eight different cyclic species were identified in one commercial polymer:

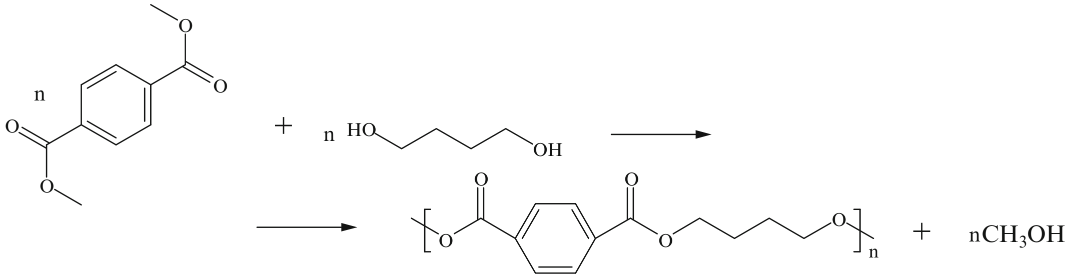


The most important side reaction, however, is formation of diethylene glycol. It becomes included in the polymer as a di(oxyethylene)oxy link. Commercial polymerizations are carried out until molecular weights of about 20,000 are reached, for use in fibers, and higher ones, for use in injection moldings or extrusions. These materials may contain up to 2–4 mole percent of di(oxyethylene)oxy units [54]. Presence of such units influences the degree of whiteness of the polyesters and the melting temperature.

A process was developed [54] to reduce the presence of di(oxyethylene)oxy units in poly(ethylene terephthalate). The condensation reactions are still carried out in two steps. In the first one, or during the period of precondensation, the material is prepared in the melt as described previously. In second step, however, the reaction is carried out below the melting temperature. This still yields high molecular weight polymers. The products, however, are low in di(oxyethylene)oxy linkages.

There has been continued interest in developing a process for direct esterification of terephthalic acid with ethylene glycol. It does not appear, however, that this is currently practiced on commercial scale in the U.S. In Japan, a process was commercialized where terephthalic acid is reacted with two moles of ethylene oxide to form the dihydroxy ester in situ, as the starting material. One mole of ethylene glycol is then removed under vacuum in the subsequent condensation process. Also it was reported [25] that the polymer can be prepared by direct esterification at room temperature in the presence of picryl chloride. The reaction can also be performed at about 120°C in the presence of diphenyl chloro-phosphate or toluenesulfonyl chloride [25]. This is done in solution, where pyridine is either the solvent or the cosolvent. Pyridine acts as a scavenger for HCl, which is a by-product of the reaction and, perhaps, also as an activator (by converting the acid into a reactive ester intermediate).

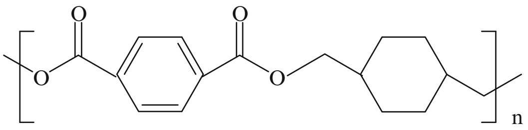
Another commercially important high molecular weight polyester is poly(butylene terephthalate), also called poly(tetramethylene terephthalate). The polymer is prepared by a catalyzed ester interchange of dimethyl terephthalate and 1,4-butane diol:



This synthesis is also carried out in two stages. In stage one, an excess of the diol is reacted with dimethyl terephthalate (about 1.3:1) to insure complete removal of methanol. Zinc acetate is favored as a catalyst for this reaction. A prepolymer mixture of bis(hydroxybutyl)terephthalate and higher oligomers forms. Stage two is conducted in vacuum at 1 mmHg and high enough temperature (usually at least 60°C above the melting temperature of the polyester) to remove excess diol and reach high molecular weight. Zinc oxide is favored as the catalyst for this stage.

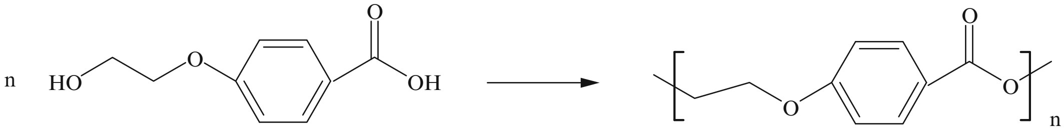
Prolonged heating of the reaction mixture at excessive temperatures results in formation of large proportions of tetrahydrofuran. This is objectionable because it affects the properties of the product. It also results in lower molecular weight polyesters.

A polyester from terephthalic acid and 1,2-dimethylol cyclohexane is produced mainly for use in fibers. This polymer is also formed from dimethyl terephthalate and the diol by a transesterification reaction. The material has the following structure:



The polymer is stiffer than poly(ethylene terephthalate) and higher melting.

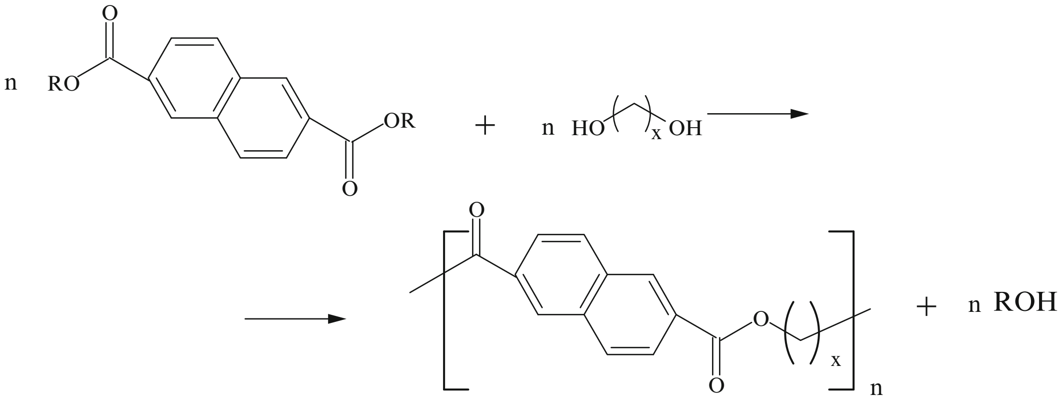
A polyester is being manufactured in Japan from a methyl ester of *p*-2-hydroxyethoxybenzoic acid by transesterification:



The product is used as a fiber.

During the last 8 or 10 years, there has been a considerable effort to introduce a new potentially high volume polyester, poly(trimethylene terephthalate) [24], into the market. The polyester is sold under a commercial trade name as "Corterra" and as a fiber by the trade name "Sorona."

Polyesters based on 2,6-disubstituted naphthalene have gained commercial importance in recent years due to their higher tensile strength, higher modulus, and good mechanical properties. These polyesters offer an additional advantage over poly(ethylene terephthalate) and poly(butylene terephthalate) by having higher first and second transition temperatures. Polyesters based on naphthalene are typically prepared by either solution polymerization or by ester interchange in the melt.

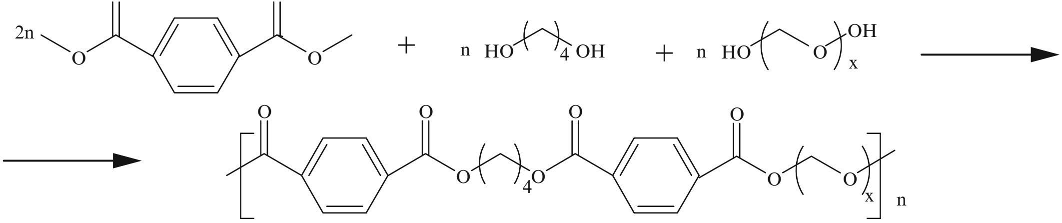


where $x = 2,4$

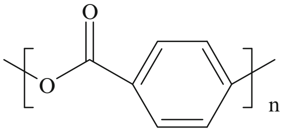
7.2.1.3 Copolyesters

Mixed dicarboxylic acids are usually used to form copolyesters. For instance, terephthalic and isophthalic acids are reacted together with 1,4-dimethylol cyclohexane to form copolyester. The product is amorphous and transparent. Another copolyester is manufactured from terephthalic, isophthalic, and an aliphatic dicarboxylic acid like adipic with either 1,4 butanediol or 1,6-hexanediol. The aliphatic dicarboxylic acid is used in minor quantities. Many such copolyesters are used as high-strength adhesives.

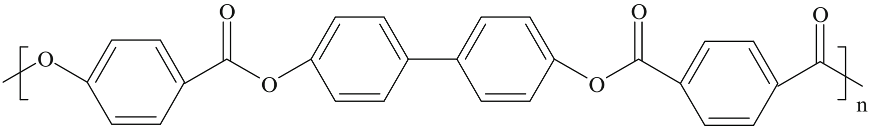
In addition, there are thermoplastic polyester elastomers. These are produced by equilibrium melt transesterification of dimethyl terephthalate, 1,4-butanediol, and a poly(tetramethylene ether) glycol (molecular weight about 1,000). Because equilibrium conditions exist in the melt, the products are random copolymers:



Wholly aromatic polyesters are produced for high temperature applications. The materials must also have good abrasion resistance. One such commercial polyester is prepared from *p*-hydroxybenzoic acid:

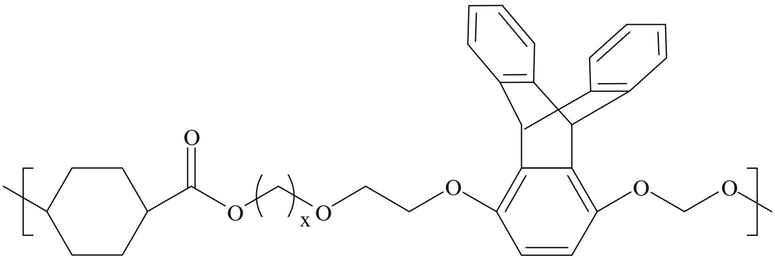


Another one is a copolyester prepared from *p*-hydroxybenzoic acid, *p*,*p*′-biphenol, and terephthalic or isophthalic acids:



The above shown polyester does not melt and decomposes at 550°C.

Turner et al. [38] reported preparation of triptysene containing polyesters. These polyesters were illustrated as follows:

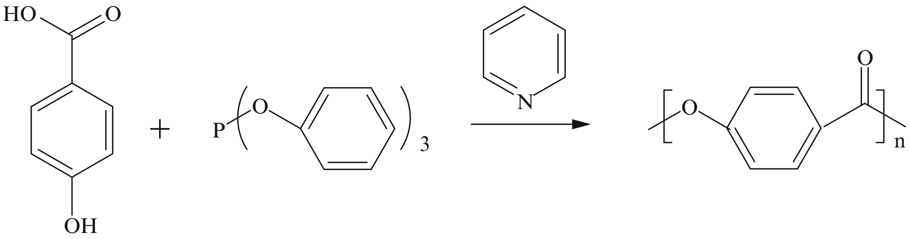


where $x = 2,4$, or 6.

The polyester was prepared by melt-phase synthesis by a transesterification reaction. Higher thermal stability was claimed for the polyesters containing triptysene than the analogous polyesters without it.

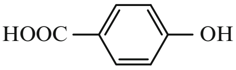
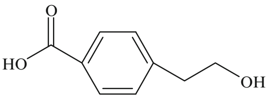
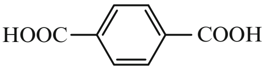
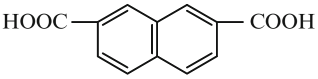
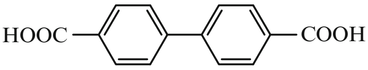
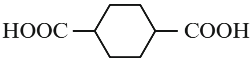
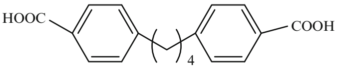
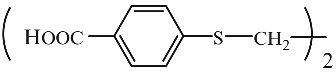
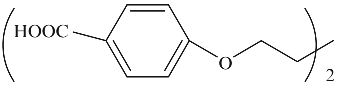
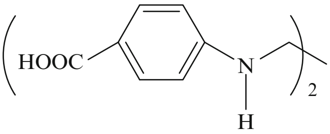
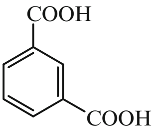
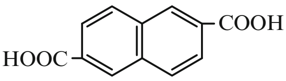
The properties of various polyesters were summarized by Wilfong [15]. Table 7.1 presents T_m and T_g values of some polyesters based on information from Wilfong and other sources in the literature.

Among new methods of forming polyesters is a preparation of completely aromatic polyesters by direct condensation of hydroxyaromatic acids (like hydroxybenzoic) with the aid of triphenylphosphorous compounds or dichlorophenylphosphine [38]:



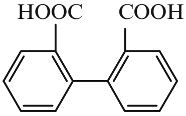
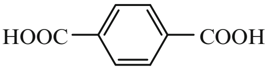
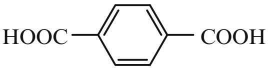
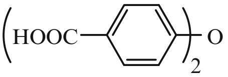
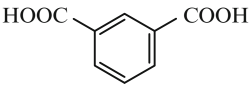
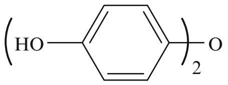
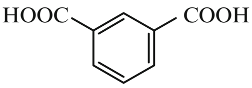
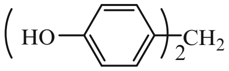
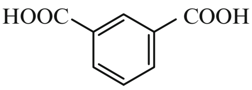
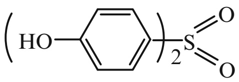
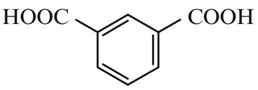
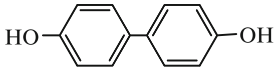
Hexachlorotriphosphatriazine can also be used to attain direct polycondensations of hydroxybenzoic acid [43].

Table 7.1 Approximate melting points of polyesters

Dicarboxylic acid	Glycol	T_g (°C)	T_m (°C)
HOOCCOOH	$HOCH_2CH_2OH$	–	172
HOOCCOOH	$HOCH_2CH_2CH_2OH$	–	89
$HOOCH_2CH_2COOH$	$HOCH_2CH_2OH$	–	108
$HOOCH_2CH_2COOH$	$HOCH_2CH_2CH_2OH$	–	52
$HOOC(CH_2)_4COOH$	$HOCH_2CH_2OH$	–	50
$HOOC(CH_2)_4COOH$	$HOCH_2CH_2CH_2OH$	–	46
$HOOC(CH_2)_8COOH$	$HOCH_2CH_2OH$	–	79–80
$HOOC(CH_2)_8COOH$	$HOCH_2CH_2CH_2OH$	–	58
		–	>350 decomp
		–	188
	$HOCH_2CH_2OH$	69	265–284
	$HOCH_2CH_2OH$	119	270
	$HOCH_2CH_2OH$	–	355
	$HOCH_2CH_2OH$	–	*Trans* 120 *cis* < 30
	$HOCH_2CH_2OH$	–	170
	$HOCH_2CH_2OH$	–	200
	$HOCH_2CH_2OH$	–	252
	$HOCH_2CH_2OH$	–	273
	$HOCH_2CH_2OH$	–	143
	$HOCH_2CH_2OH$	113	260

(continued)

Table 7.1 (continued)

Dicarboxylic acid	Glycol	T_g (°C)	T_m (°C)
	$HOCH_2CH_2OH$	–	132
	$HOCH_2CH_2CH_2OH$	<80	226–232
	$HO{-}({-}CH_2{-})_6{-}OH$	–	154–161
	$HO{-}({-}CH_2{-})_8{-}OH$	<45	129–132
	$HO{-}({-}CH_2{-})_{10}{-}OH$	<25	130–138
	$HOCH_2CH_2OH$	–	152
		173	283
		150	348
		279	330
		164	315

From various sources in the literature

7.2.2 *Linear Unsaturated Polyesters*

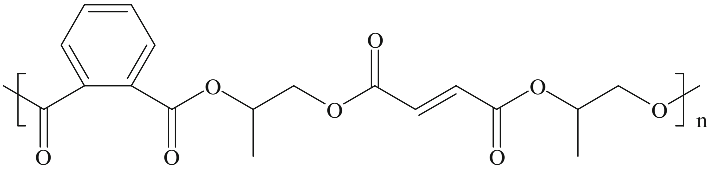
The materials in this group are linear copolyesters. One of the dicarboxylic acids is an aliphatic unsaturated diacid. The unsaturation is introduced into the polymer backbone for the purpose of subsequent cross-linking. Unsaturated polyester technology was developed for use in glass fiber laminates, thermosetting molding compositions, casting resins, and solventless lacquers.

Propylene glycol is often used as the diol. To a lesser extent are also used other glycols, like diethylene glycol, for greater flexibility, or neopentyl glycol for a somewhat better thermal resistance. Bisphenol A (2,2 bis(4-hydroxyphenyl) propane) is used when better chemical resistance is needed. Use of mixed diols is common. Many unsaturated dicarboxylic acids can be used, but maleic (as an anhydride) or fumaric acids are the most common. Chloro maleic or chloro fumaric acids are also employed.

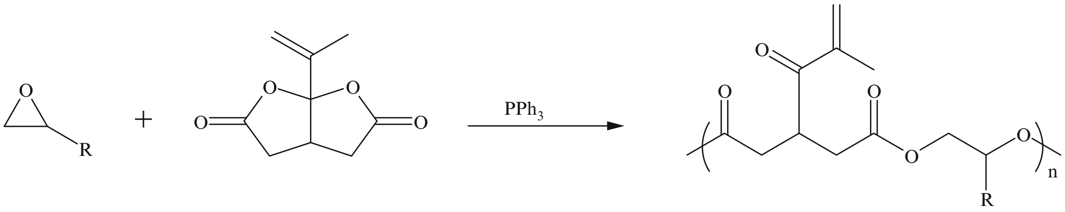
The saturated dicarboxylic acids act as modifiers. While aliphatic dicarboxylic acids can be used, the most common one is *ortho* phthalic acid (added to the reaction mixture as an anhydride). The acid improves compatibility with styrene that is polymerized in the presence of the polyester to form hard, rigid, cross-linked materials. Other modifiers are used to obtain special properties. When a flexible product is needed, adipic or sebacic acids may be used instead. For better heat resistance, *endo*-methylene tetrahydrophthalic anhydride (nadic anhydride) may be utilized. Flame retardency is achieved by using chlorinated dicarboxylic acids, like tetrachlorophthalic.

Styrene is the most common monomer used in cross-linking unsaturated polyesters. When special properties are required, other monomers like methyl methacrylate may be employed. Sometimes this is done in combination with styrene. Diallyl phthalate and triallyl cyanurate form better heat-resistant products.

An example of a typical batch preparation of a polyester is one where 1.2 moles of propylene glycol, 0.67 moles of maleic anhydride, and 0.33 moles of phthalic anhydride are combined. Propylene glycol is used in excess to compensate for loss during the reaction. The condensation at 150–200°C lasts for 6–16 h, with constant removal of water, the by-product. An aromatic solvent, like toluene or xylene, is often added to the reaction mixtures to facilitate water removal by azeotropic distillation. Esterification catalysts, like toluene sulfonic acid, reduce the reaction time. In addition, the reactions are blanketed by inert gases, like nitrogen or carbon dioxide, to prevent discoloration from oxygen at high temperatures. When molecular weights of 1,000–2,000 are reached, the products are cooled to 90°C and blended with vinyl monomers. Often the blends are mixtures of equal weights of the polyesters and the monomers. The structure of the above-described unsaturated polyester can be illustrated as follows:



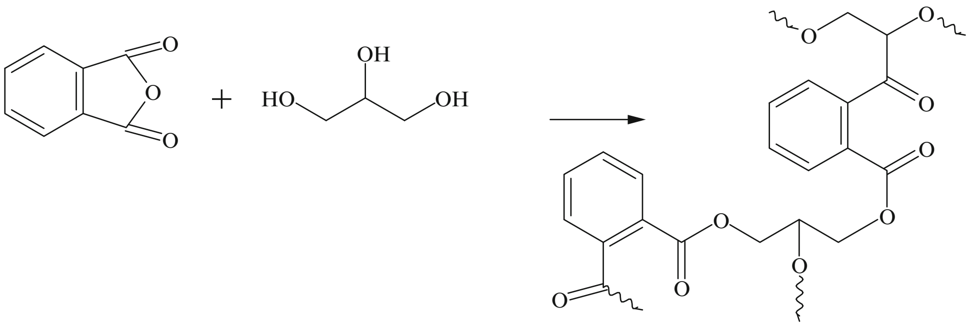
It is interesting that unsaturated polyesters can actually be prepared by anionic alternating copolymerization of an epoxide and bicyclic bis(γ-butyrolactone) bearing an isopropenyl group [34]. The reaction was illustrated as follows:



If the reaction is carried for a prolonged period of time, an insoluble, cross-linked product results.

7.2.3 Network Polyesters for Surface Coatings

The original polyesters for coatings were prepared from phthalic anhydride and glycerol and were referred to as ***glyptals*** or ***glyptal resins***:



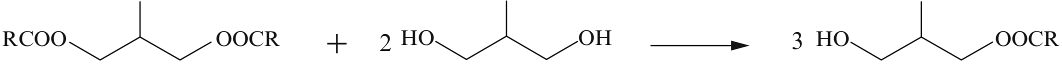
The products from above polyesterifications are brittle materials. They are, therefore, modified with oils, either drying or nondrying. Such oil-modified resins bear the names of ***alkyds***. While glycerol is widely used, other polyhydroxy compounds (polyols) are also utilized. These may be trimethylolpropane, pentaerythritol, sorbitol, or others. Phthalic anhydride is usually used in alkyd preparations. Other dicarboxylic compounds, however, may also be included for modification of properties. Common modifiers might be isophthalic, adipic, or sebacic acids, or maleic anhydride. In addition, many other acid modifiers are described in the patent literature.

The oils in alkyd resins are usually of vegetable origin. They are classified by the type and amount of residual unsaturation into drying, semidrying, and nondrying oils. The drying oils contain most of residual unsaturation, while the nondrying ones contain mostly saturated fatty acids.

Alkyds are also classified by the quantity of modifying oil that they contain into *short*, ***medium***, or *long* oil alkyds. Short oil alkyds contain 30–50% oil and are usually baked to obtain a hard dry surface. Medium oil (50–65%) and long oil (65–75%) alkyds will air dry upon addition of metal dryers.

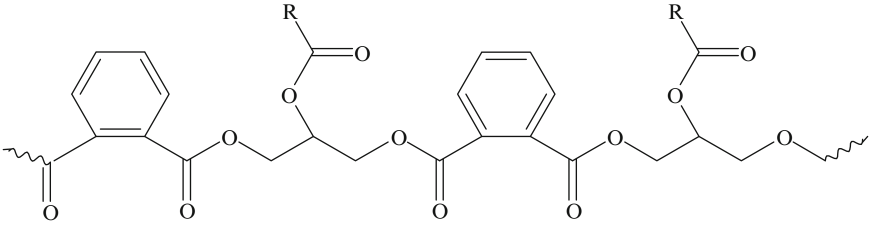
There are two main methods for preparation of alkyd resins. In the first one, called ***fatty acid process***, a free fatty acid is coesterified directly with the dibasic acid and the polyol at 200–240°C. The reaction may be carried out without a solvent by first heating in an inert atmosphere. At the end, an inert gas may be blown into the resin from the bottom of the reaction kettle to remove water and unreacted materials. As a modification of this, a small quantity of a solvent may be used to remove water of esterification continuously by azeotropic distillation with the aid of moisture traps.

In the second method, known as the *alcoholysis process*, the drying oil is heated with the glycerol in the first stage of the reaction, at about 240°C. This is usually done in the presence of a transesterification basic catalyst to form monoglycerides



After the first stage is complete, phthalic anhydride, with or without another dibasic acid, is added and a copolyesterification is carried out in the same manner as in the first stage of the reaction.

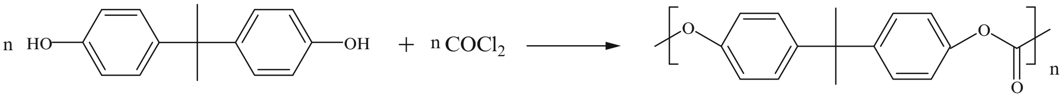
The conditions under which the reaction is carried out and the rate at which the temperature is raised during the condensation affect the molecular weight distribution of the final product. In addition, the monoglyceride content of the original reaction mixture determines the microgel content of the alkyd and the dynamic properties of the dried film [31]. The finished alkyd resin can be illustrated as follows:



7.2.4 Polycarbonates

A special group of polyesters of carbonic acid are known as ***polycarbonates***. The first polycarbonates were prepared as early as 1898 by Einhorn by reacting phosgene with hydroquinone and with resorcinol [33]. These materials lack desirable properties and remain laboratory curiosities. During the fifties, however, new polymers were developed from 4,4′-dihydroxydiphenyl alkanes. These polycarbonates have high melting points and good thermal and hydrolytic stability. Nevertheless, to date only one polycarbonate has achieved significant commercial importance. It is based on 2,2′-bis(4-hydroxyphenyl)propane.

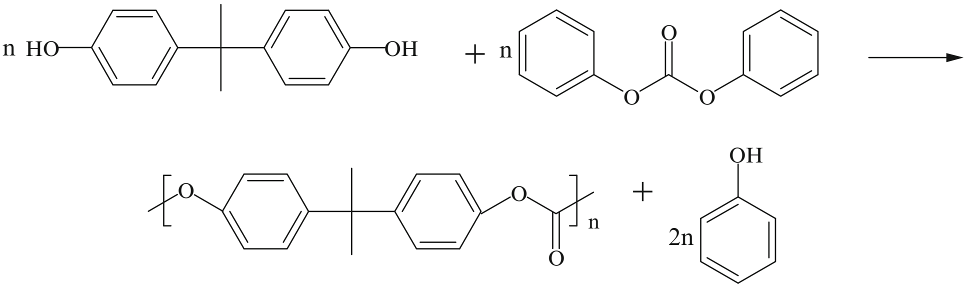
There are two main methods for preparing polycarbonates, one is by a direct reaction of phosgene with the diphenol and the other one by an ester interchange. The direct phosgenation is a form of a Schotten–Baumann reaction that is carried out in the presence of a base:



The reaction may be carried out in the presence of pyridine that acts as a catalyst and as an HCl scavenger. Often a chlorinated solvent is used as a diluent for the pyridine. Phosgene is bubbled through a solution of the diphenol at 25–35°C. The pyridine hydrochloride precipitates out and after washing the pyridine solution with dilute HCl and water, the polymer is precipitated with a nonsolvent.

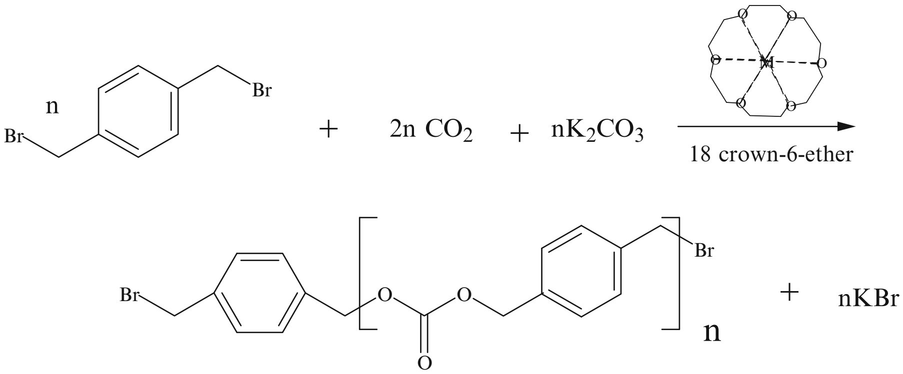
An interfacial polymerization procedure is also employed in direct phosgenation. A caustic solution of the diphenol is dispersed in an organic chlorinated solvent containing small quantities of a tertiary amine. Phosgene is bubbled through the reaction mixture at 25°C. When the reaction is complete, the organic phase contains the polymer. It is separated and the product isolated as above.

The ester interchange method is carried out between the diphenol and diphenyl carbonate:

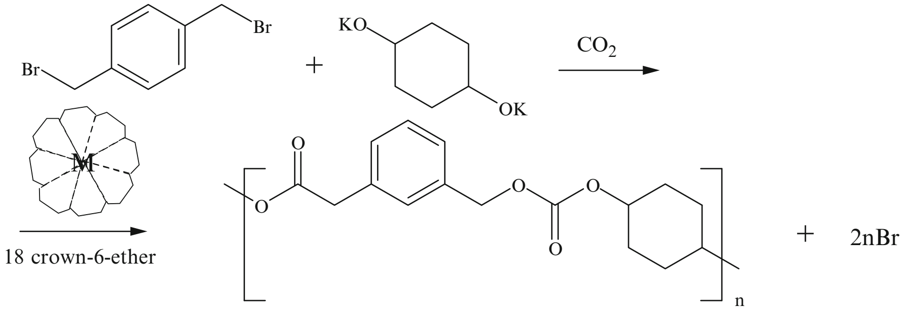


To obtain high molecular weights by this method, almost complete removal of the phenol is required. The reaction is carried out with typical basic catalysts, like lithium hydride, zinc oxide, or antimony oxide under an inert atmosphere. Initial reaction temperature is 150°C. It is raised over 1 h period to 210°C, while the pressure is reduced to 20 mmHg. Reaction mixture is then heated to about 300°C for 5–6 h at 1 mmHg. Heating is stopped when desired viscosity is reached.

A synthetic route to polycarbonates was reported that uses crown ethers. Crown ethers generally form stable complexes with metal cations, and by increasing the dissociation of ion pairs, provide highly reactive, unsolvated anions. This led to direct preparations of new polycarbonates from α,ω-dibromo compounds, carbon dioxide, and potassium carbonate or salts of the diols [36] in the presence of 18-crown-6-ether:



When a potassium salt of a diol is present in the reaction mixture, mixed polyesters form [36]:



In addition to crown ethers, cryptates and polyglyme exhibit similar behavior [37].

Another direct route to polycarbonate was reported by Okuyama et al. [36]. The process consists of an oxidative carbonylation procedure. It is catalyzed with a Pd complex system. {1,1′-Di-*tert*-butyl-3,3′-methylenediiimidazolin-2,2′,dylidene}palladium dibromide and produces a highest molecular weight polymer, (M_n = 9,600, M_w = 24,000) in 80% yields.

Table 7.2 presents some T_g and T_m values of some polycarbonates picked from the literature.

7.2.5 Polyesters from Lactones

Polyesters that are obtainable by ring opening polymerization of lactones (see Chap. 5) are not produced commercially on a large scale. Judging from the patent literature, however, there is a continuing interest in these materials, particularly in Japan. Because of fairly good hydrolytic stability, polypivalyllactone is at the most advanced stages of commercial development:

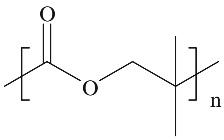
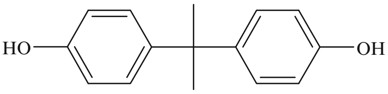
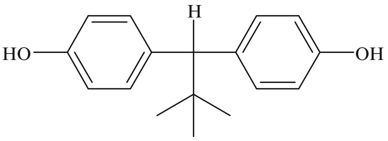
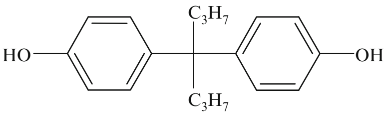
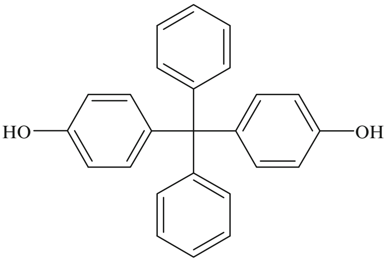
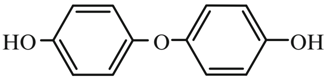
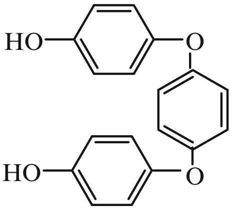
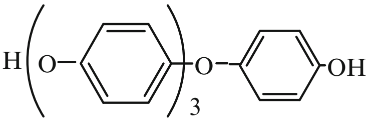
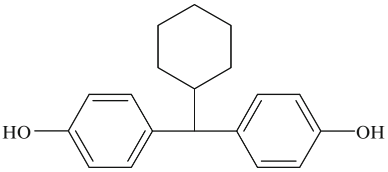
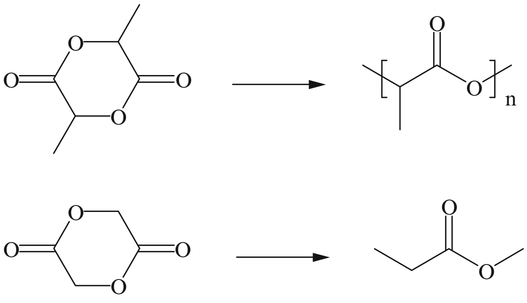


Table 7.2 Melting points of some polycarbonates

Structure of the parent diphenol	Approximately T_g (°C)	Approximately T_m (°C)
	145–150	265–270
	125–130	185–200
	145–150	170–180
	121	210–230
	–	180–210
	–	205–210
	–	250–260
	170	240–250

From various literature sources

The polymer can be spun into an elastic yarn of very fine denier. It is also claimed to exhibit good mechanical properties for molding and compares favorably with commercial polyesters and nylons. Also, polycaprolactone was reported to be used in some medical applications in biodegradable surgical sutures and postoperative support pins and splints [39]. Similar uses are also found for two other polyesters, poly(lactic acid) and poly-(glycolic acid) [40]. The two polymers form from their cyclic dimers by cationic ring opening polymerizations with the aid of Lewis acids:



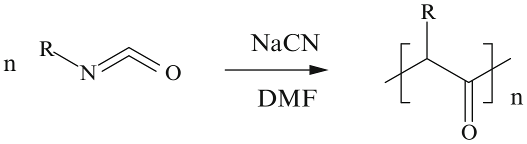
7.3 Polyamides

The family of synthetic polymeric materials with amide linkages in their backbones is large. It includes synthetic linear aliphatic polyamides, which carry the generic name of *nylon*, aromatic polyamides, and fatty polyamides used in adhesives and coatings. In addition to the synthetic materials, there is also a large family of naturally occurring polymers of α-amino acids, called *proteins*. The latter ones are discussed in Chap. 8 with the rest of the naturally occurring polymers. The nylons include polyamides produced by ring opening polymerizations of lactams and condensation products of diamines with dicarboxylic acids.

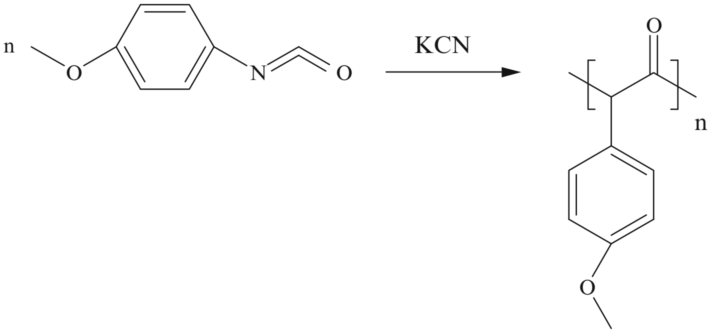
7.3.1 Nylons

The nylons are named by the number of carbon atoms in the repeat units. The materials formed by ring opening polymerizations of lactams, therefore, carry only one number in their names, like, for instance, nylon 6 that is formed from caprolactam. By the same method of nomenclature, a nylon prepared by condensing a diamine with a dicarboxylic acid, like, for example, hexamethylene diamine with adipic acid, is called nylon 6,6. It is customary for the first number to represent the number of carbons in the diamine and the second number to represent the number of carbons in the diacid. A discussion of various individual nylons follows. Not all of them are industrially important.

At present, we only know how to prepare ***Nylon 1*** by anionic polymerization of isocyanates. This reaction is discussed in Chap. 4:



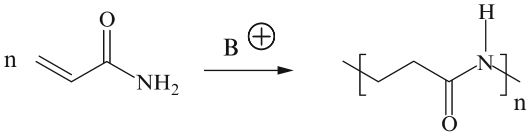
Potassium and sodium cyanide catalyze the reaction. It can be carried out between −20 and −100°C. An example is the following preparation [47]:



The resultant polymer has a molecular weight of one million. When the methyl group is replaced by butyl, the product is a tough film former, but depolymerizes in the presence of some catalysts. Many other interesting high molecular weight polymers with various substitutions can be formed by this reaction at low temperature.

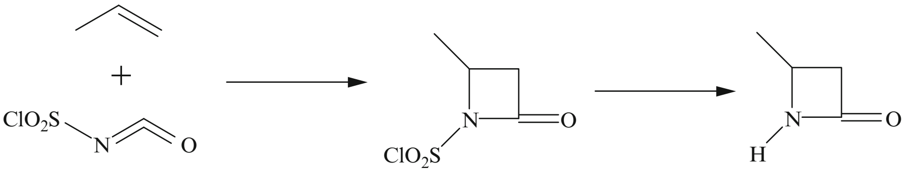
Polymerization of *N*-carboxy-α-amino acid anhydrides results in formations of ***Nylon 2***. This reaction is also discussed in Chap. 5. These polymers are mainly of interest to protein chemists in model studies of naturally occurring poly(α-amino acids).

Nylon 3 can be synthesized by intramolecular hydrogen transfer polymerization of acrylamide [48] (see Chap. 4):



The fibers from nylon 3 are reported to resemble natural silk [50]. They possess high water absorbency and good light and oxygen stability. The polymer, however, is too high melting for melt spinning, or for molding and extrusion [46]. Nylon 3 fibers can be spun, however, from special solutions containing formic acid [52].

It is difficult to synthesize β-propiolactam. A synthetic route, however, was found for substituted propiolactams like β-butyrolactams [50]. The compounds form by nucleophilic additions of carbonylsulfamoyl chloride to olefins [51]:

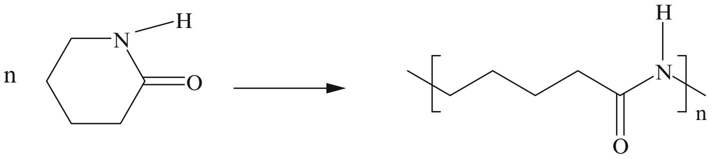


The above shown β-butyrolactam polymerizes readily by anionic mechanism, yielding a very high molecular weight polymer. This lactam preparation reaction is quite general. It can be carried out on propene, 1-butene, 1-hexene, and styrene [50]. Although substituted lactams are harder to polymerize [53], the four-membered lactams exhibit such a strong tendency toward ring opening that even substituted β-propiolactams polymerize well [50]. The rate of polymerization, however, does tend to decrease with the number of substituents.

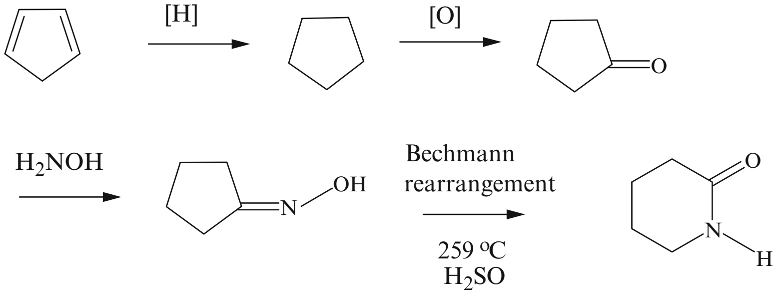
Nylon 4 or polypyrrolidone is an attractive polymer for use in fibers. The original syntheses of nylon 4 from 2-pyrrolidone were carried out by alkaline catalyzed ring opening polymerizations promoted by *N*-acylpyrrolidone [49]. The products from these reactions melt between 260 and 265°C.

They are unstable at these temperatures and cannot be melt spun. Fibers, however, were prepared by dry spinning from hydrocarbon suspensions [49]. Later, it was found that when the anionic ring opening polymerizations of 2-pyrrolidone are activated by CO_2 in place of the *N*-acyl derivative, the resultant higher molecular weight product has much better heat resistance [54]. This "new" nylon 4, reportedly, can be melt spun.

Nylon 5 or poly(α-piperidone) can be prepared by ring opening anionic polymerization of valerolactam [53]. The reaction requires very pure monomer to yield a high molecular weight polymer [53]:

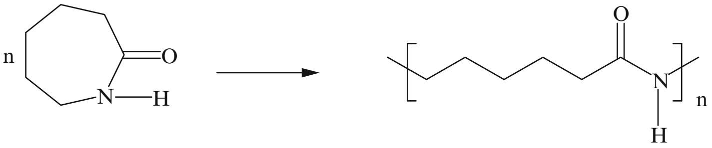


One route to valerolactam is from cyclopentadiene:



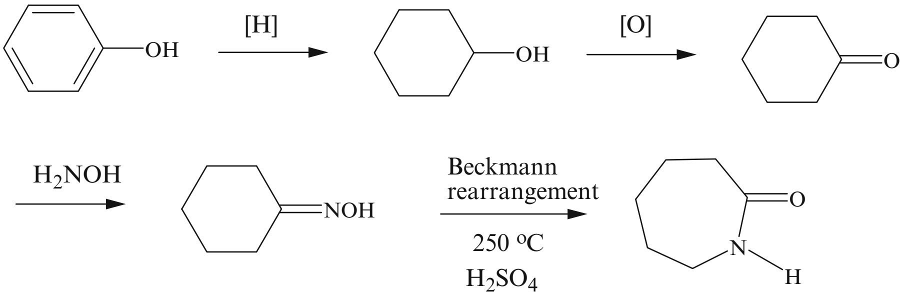
Valerolactam can also be polymerized with the aid of coordination catalysts to a high molecular weight polymer using alkali metal-$Al(C_2H_5)_3$ catalysts or alkali metal alkyl-$Al(C_2H_5)_3$ catalysts [55]. The polymerizations require **relatively long times**.

Nylon 6 is obtained via ring opening polymerization of caprolactam:

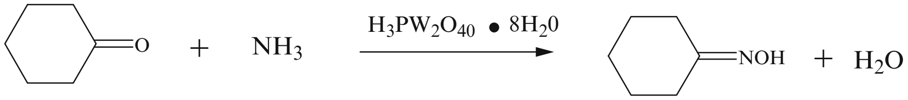


This polymer developed over the years into an important commercial material. As a result, many preparatory routes were developed for the starting material and the polymerization reaction was studied thoroughly.

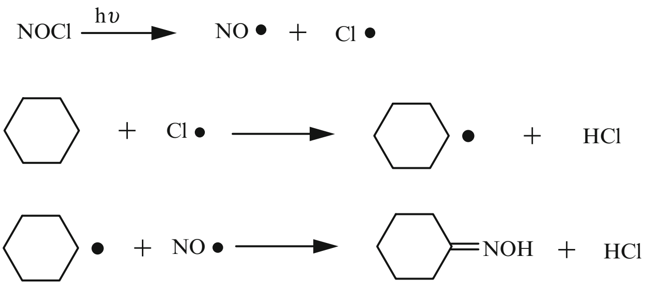
The most common starting materials for preparations of caprolactam are phenol, cyclohexane, and toluene. Some caprolactam is also made from aniline. In these synthetic processes, the key material is cyclohexanone oxime. The route based on phenol can be shown as follows:



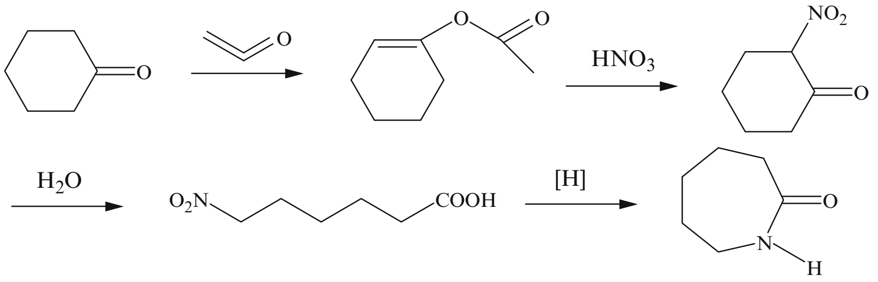
A by-product of the above reaction is ammonium sulfate. To avoid the necessity of disposing of ammonium sulfate, many caprolactam producers sought other routes to the oxime. One approach is to form it directly by reacting cyclohexanone with ammonia and hydrogen peroxide in the presence of tungstic acid catalyst [56]:



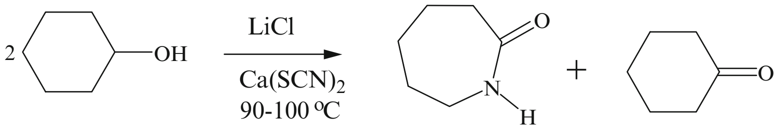
The reaction is conducted in water and the product oxime is extracted with an organic solvent. Another process is based on photo-nitrosyl chlorination. Here cyclohexane is converted in one step to cyclohexanone oxime hydrochloride [57]:



Another process uses ketene to form cyclohexene acetate [58]:

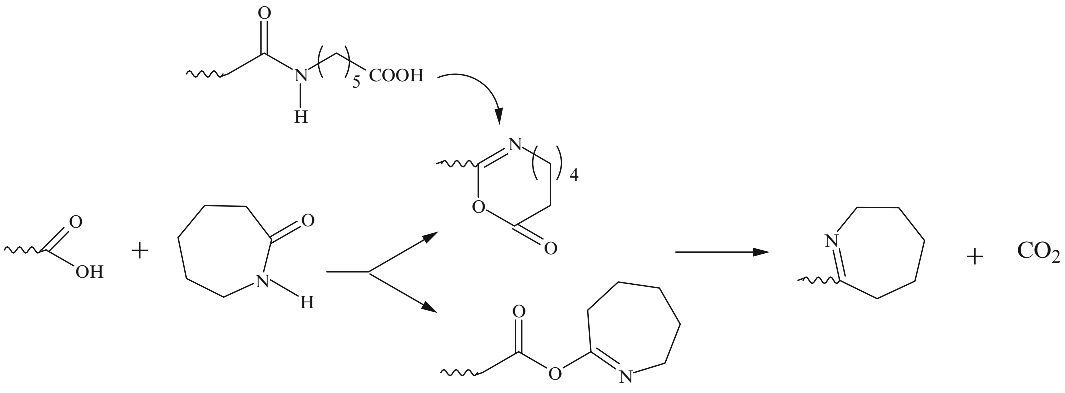


Among some more recent developments is a one-step synthesis of caprolactam from cyclohexanol [59]:

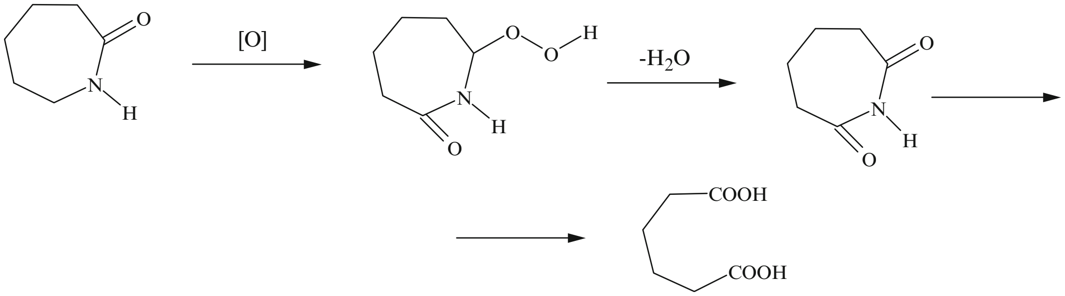


There are other processes for caprolactam syntheses as well; however, a thorough discussion of this subject belongs in books dedicated to the subject.

The mechanism of the reaction of ring opening polymerization of lactams is discussed in Chap. 5. Several important side reactions accompany this polymerization. One is formation of cyclic oligomers [58]. The cyclic oligomers, soluble in water and alcohol mixtures, range in size from cyclic dimers to cyclic nonamers [60–62]. Formation of these compounds may be governed by equilibrium [63]. The polyamide will also thermally oxidize upon prolonged exposure to heat and air. Another important side reaction is decarboxylation that occurs at high temperatures. This is a result of interaction of a carboxyl group with a molecule of caprolactam or with an amide group [58]:



Polymerizations of caprolactam should be conducted in inert atmospheres to prevent oxidative decompositions. These can result in formations of carbon monoxide, carbon dioxide, acetaldehyde, formaldehyde, and methanol. Caprolactam can even oxidize in air at temperatures between 70 and 100°C [64], according to the following scheme:



Much of nylon 6 is used in producing fibers. Polycaprolactam prepared by water catalyzed polymerizations is best suited for this purpose. It can also be used in molding, though anionically polymerized caprolactam can be used as well [65]. The polymerizations are carried out both in batch and in continuous processes. Often tubular flow reactors are employed.

A typical polymerization reaction is carried out as follows. Caprolactam, water (5–10% by weight of monomer), and acetic acid (about 0.1%) are fed into the reactor under nitrogen atmosphere. The reaction mixture is heated to about 250°C for 12 h. Internal pressure is maintained at 15 atmospheres by venting off steam. The product of polymerization is extruded as a ribbon, quenched, and chopped into chips. It consists of about 90% polymer and about 10% low molecular weight compounds and monomer. The polymer is purified by either water leaching at 85°C or by vacuum extraction of the undesirable by-products at 180°C.

Castings of nylon 6 are commonly formed in situ in molds. Here the preparation of the polymer by anionic mechanism is preferred. The catalyst systems consist of 0.1–1.0 mole percent of acetyl caprolactam and 0.15–0.5 mole percent sodium caprolactam. The reaction temperature is kept between 140 and 180°C. An exotherm can raise it as much as 50°C as the polymerization proceeds.

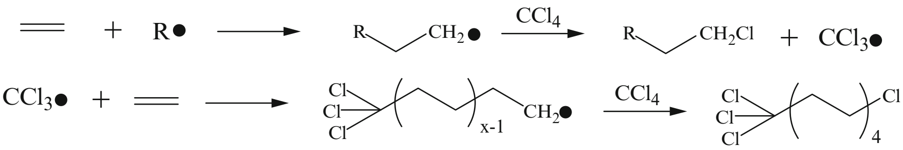
Nylon 7 and *nylon 9* are part of a process developed in Russia to form polyamides for use in fibers. The process starts with telomerization of ethylene [66]. A free-radical polymerization of ethylene is conducted in the presence of chlorine compounds that act as chain-transferring agents. The reaction is

Table 7.3 Compositions of telomers

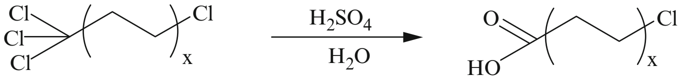
X	Fraction (%)
1	5
2	44
3	28
4	15
>4	8

From Nesmeyanov and Reundlina [66], by permission of Tetrahedral Letters, Elsevier Science, Ltd

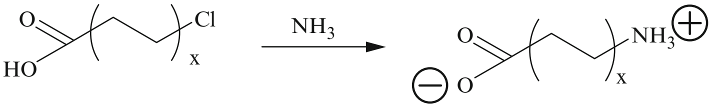
carried out at 120–200°C temperature and 400–600 atmospheres pressure. The preferred chain-transferring agents for this reaction are CCl_4 and $COCl_2$ [66]:



The resultant chloro alkanes are then hydrolyzed with sulfuric acid:

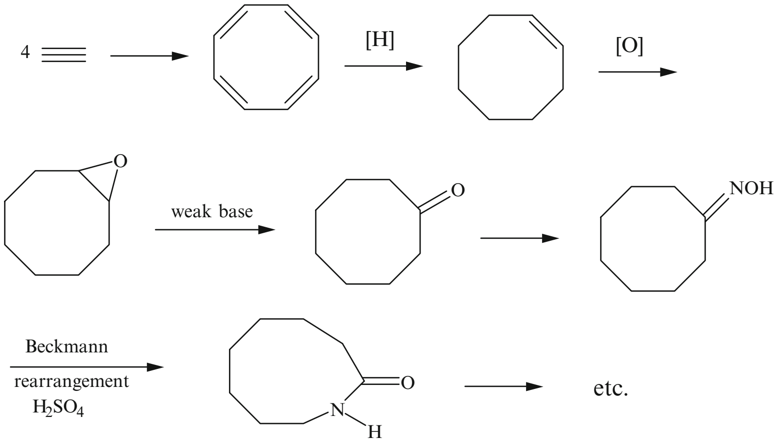


After hydrolyses, the products are treated with ammonia:

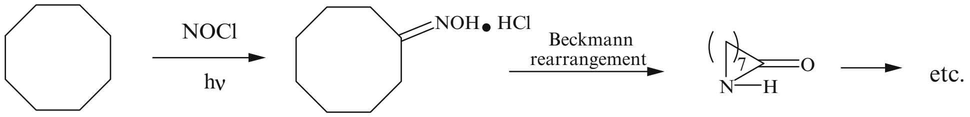


The amino acid is condensed to a lactam and subsequently polymerized. Table 7.3 shows the composition of the telomers in the above free-radical polymerization [66]. As seen from the table, the economics of producing nylon 7 by this process is not as favorable as one may wish. An advantage, however, to producing nylon 7 is that the polymer contains little monomer and can be spun without washing or extraction, as is required with nylon 6.

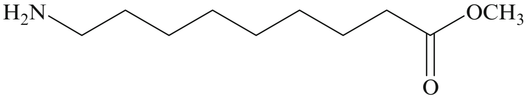
An early synthesis of *nylon 8* used cyclooctatetraene that was formed from acetylene and then converted to ***nylon 8*** as follows:



The acetylene was later replaced by butadiene for economic reasons. Butadiene is cyclodimerized, then hydrogenated to cyclooctane, and the oxime is prepared directly from cyclooctane by photonitrosation:

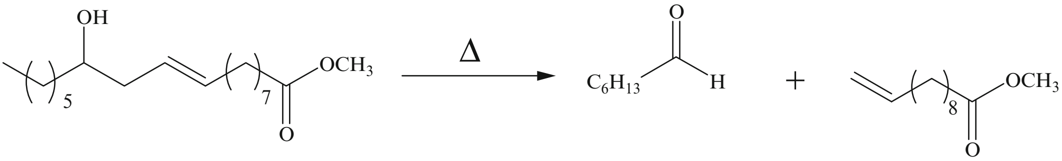


Nylon 9 or poly(ω-pelargonamide) is produced in Russia together with nylon 7, poly (aminoenanthic acid) as described above. In the U.S., Kohlhase et al. [67] developed a route to nylon 9 via ozonolysis of unsaturated fatty acids like those that can be obtained from soybean oil. The glycerol fatty acid esters of oleic, linoleic, and linolenic acids are transesterified with methanol to form methyl esters. The esters are then cleaved via ozonolysis to yield methylazelaldehyde and by-products that are removed. The purified product is reacted with ammonia and then reduced over Raney nickel to yield a methyl ester of the amino acid:

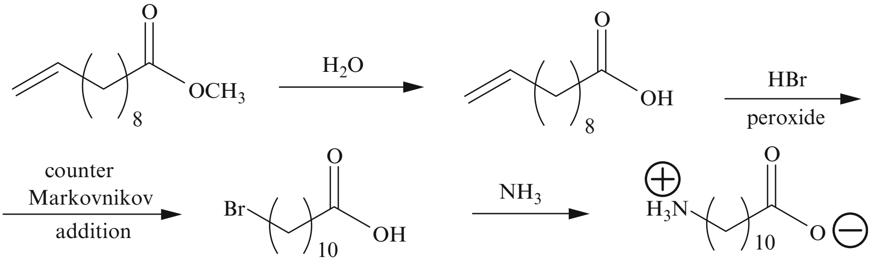


After hydrolysis and purification, the free amino acid is converted to high molecular weight polymers [68]. To date, nylon 9 has not been commercialized in the U.S., though the polymer has a high melting point of 209°C and is more flexible than nylon 6. It is also lower in water absorption.

Nylon 11 was originally synthesized in France. The monomer, ω-amino-undecanoic acid, is obtained from methyl ricinoleate that comes from castor oil. Methyl ricinoleate is first cleaved thermally to heptaldehyde and methyl undecylenate:



The ester is then hydrolyzed and converted to an amino acid:



Polycondensation is conducted in the melt under nitrogen at 215°C for several hours. The polymer is transparent in its natural form. It has high-impact resistance, low moisture absorption, and good low temperature flexibility. It is also manufactured in the U.S.

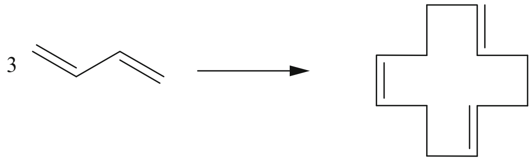
Nylon 12 is produced in U.S., Japan, and Europe with the original development coming from Europe. All current manufacturing processes of this polyamide, formed by ring opening polymerization of lauryl lactam, are based on cyclododecatriene. This ring compound can be obtained by

Table 7.4 Approximate melting points of polyamides

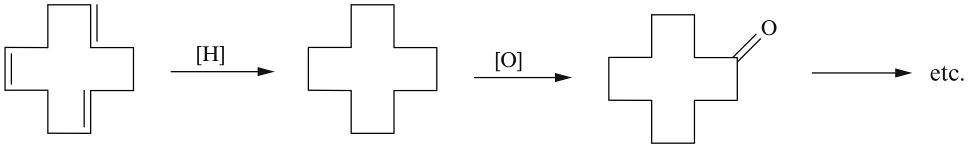
Nylon	Repeat unit	MP (°C)
3	$–(CH_2)_2–CO–NH–$	320–330
4	$–(CH_2)_3–CO–NH–$	260–265
5	$–(CH_2)_4–CO–NH–$	260
6	$–(CH_2)_5–CO–NH–$	215–220
7	$–(CH_2)_6–CO–NH–$	225–230
8	$–(CH_2)_7–CO–NH–$	195
9	$–(CH_2)_8–CO–NH–$	197–200
10	$–(CH_2)_9–CO–NH–$	173
11	$–(CH_2)_{10}–CO–NH–$	185–187
12	$–(CH_2)_{11}–CO–NH–$	180
13	$–(CH_2)_{12}–CO–NH–$	173

From various literature sources

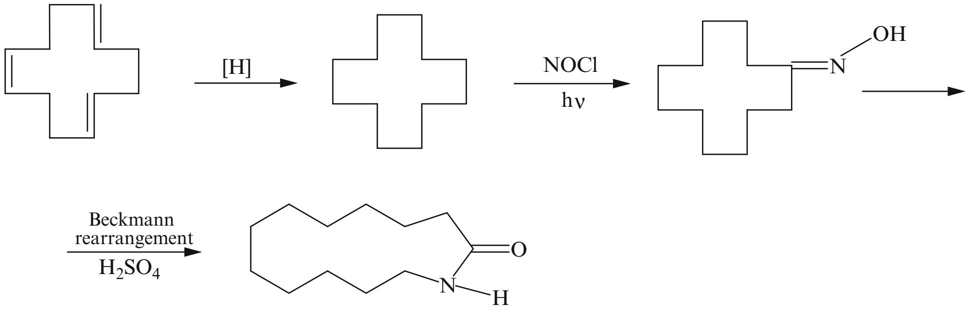
trimerization of butadiene using Ziegler–Natta type catalysts. One patent reports using polyalkyltitanate and dialkylaluminum monochloride [69]:



The cyclododecatriene is then converted to lauryl lactam by different processes. One of them consists of hydrogenation of the cyclic triene, followed by oxidation to a cyclic ketone, conversion to an oxime, and rearrangement by the Beckmann reaction to the lactam:



Another process utilizes photonitrosation:

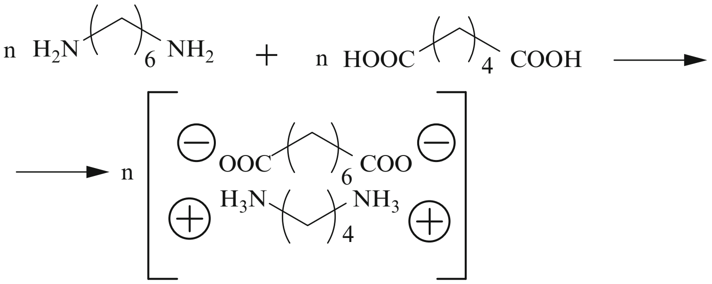


There are still other processes, but they lack industrial importance. Nylon 12, like nylon 11, exhibits low moisture absorbency, good dimensional stability, and good flexibility at low temperatures.

Preparations of other nylons were reported from time to time in the literature. For one reason or another, however, they have not developed into industrially important materials. Thus, for instance, for some time now it has been known that *nylon 13* can be prepared from erucic acid that is found in crambe and rapeseed oils. The polymer is supposed to be quite similar to nylon 11, though lower melting.

The melting points of the nylons describe above are summarized in Table 7.4.

Nylon 6,6 is a condensation product of hexamethylene diamine and adipic acid. This polyamide was originally synthesized in 1935 and first produced commercially in 1938. It is still one of the major commercial nylons produced today. Because high molecular weight is required for such polymers to possess good physical properties, it is necessary to follow exact stoichiometry of the reactants in the condensation. To achieve that, the practice is to initially form a "nylon salt," prior to the polymerization. To do this, equimolar quantities of adipic acid and hexamethylene diamine are combined in aqueous environment to form solutions of the salt. The end point is controlled electrochemically. An alternate procedure is to combine the diacid with the diamine in boiling methanol. A 1:1 adduct precipitates out, is filtered off, and dissolved in water.



A 60–75% solution of the salt in water is then fed into a reaction kettle. In a typical batch process, some acetic acid may also be added if it is desired to limit molecular weight (10,000–15,000). The temperature in the reaction kettle is raised to 220°C, and due to water and steam in the reactor, internal pressure of about 20 atmospheres develops. After 1–2 h, the temperature is raised to 270–280°C. Some steam is bled off to maintain internal pressure at 20 atmospheres. The temperature is maintained and the bleeding out of the steam is continued for 2 h. During that period, the internal pressure is gradually reduced to atmospheric. In some processes, vacuum is applied at this point to the reaction kettle if high molecular weight products are desired. When the reaction is complete, the molten polymer is ejected from the kettle by applying pressure with nitrogen or carbon dioxide.

In one continuous process, the desired conditions are maintained while the reaction mixture moves through various zones of the reactor. Tubular reactors are also often employed in continuous polymerizations.

Nylon 6.10 is prepared by the same procedure as nylon 6,6 from a salt of hexamethylene diamine and sebacic acid, while *nylon 6,9* is prepared from a salt of hexamethylene diamine and azelaic acid.

The melting points of various nylons that are formed from diamines and dicarboxylic acids are presented in Table 7.5.

One commercial polyamide is prepared by condensation of a cycloaliphatic diamine with a twelve carbon dicarboxylic acid. The diamine, bis(*p*-aminocyclohexyl)methane, is prepared from aniline:

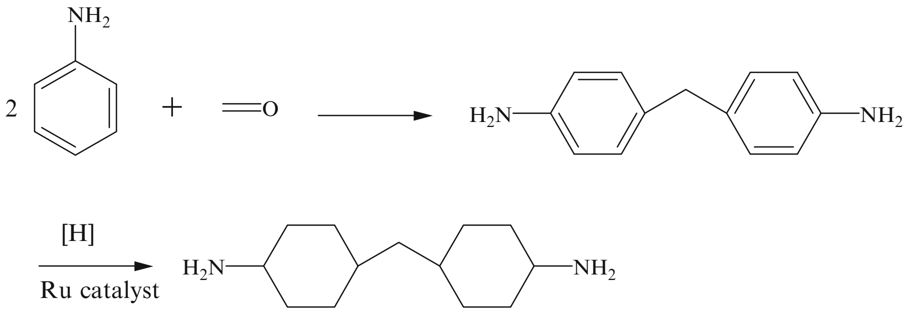
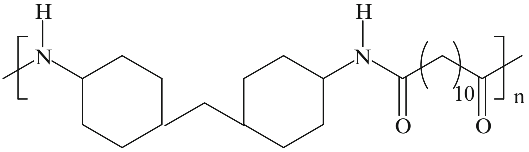


Table 7.5 Melting points of nylons

		Melting point (°C)	
Nylon	Repeat unit	Salt	Polymer
4,6	$-NH-(CH_2)_4-NH-CO-(CH_2)_4-CO-$	204	278
4,7	$-NH-(CH_2)_4-NH-CO-(CH_2)_5-CO-$	138	233
4,9	$-NH-(CH_2)_4-NH-CO-(CH_2)_7-CO-$	175	223
4,10	$-NH-(CH_2)_4-NH-CO-(CH_2)_8-CO-$		236
5,10	$-NH-(CH_2)_5-NH-CO-(CH_2)_8-CO-$	129	195
6,6	$-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-$	183	250
6,9	$-NH-(CH_2)_6-NH-CO-(CH_2)_7-CO-$		205
6,10	$-NH-(CH_2)_6-NH-CO-(CH_2)_8-CO-$	170	209
6,12	$-NH-(CH_2)_6-NH-CO-(CH_2)_{10}-CO-$		212
8,6	$-NH-(CH_2)_8-NH-CO-(CH_2)_4-CO-$	153	235
8.10	$-NH-(CH_2)_8-NH-CO-(CH_2)_8-CO-$	164	197
9,6	$-NH-(CH_2)_9-NH-CO-(CH_2)_4-CO-$	125	204–205
9,10	$-NH-(CH_2)_9-NH-CO-(CH_2)_8-CO-$	159	174–176
10,6	$-NH-(CH_2)_{10}-NH-CO-(CH_2)_4-CO-$	142	230
10,10	$-NH-(CH_2)_{10}-NH-CO-(CH_2)_8-CO-$	178	194
11,10	$-NH-(CH_2)_{11}-NH-CO-(CH_2)_8-CO-$	153	168–169
12,6	$-NH-(CH_2)_{12}-NH-CO-(CH_2)_4-CO-$	144	208–210
12,10	$-NH-(CH_2)_{12}-NH-CO-(CH_2)_8-CO-$	157	171–173
13,13	$-NH-(CH_2)_{13}-NH-CO-(CH_2)_{11}-CO-$		174

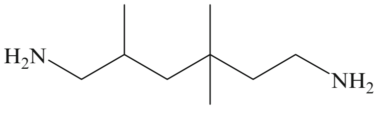
From ref [70] and other literature sources

The diamine is then condensed with dodecanedioic acid, which is obtained from cyclododecatriene. The structure of this polyamide is as follows:

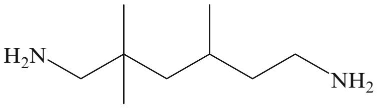


The polymer has a T_m of 280–290°C and a T_g of 120°C. It exhibits lower moisture pick up than do nylons 6 and 6,6, increased hardness and tensile strength, though lower impact strength. The bulk of this polymer is used in fiber production. The fibers, with a trade name of “Quiana,” are claimed to exhibit high luster and a silk like feel.

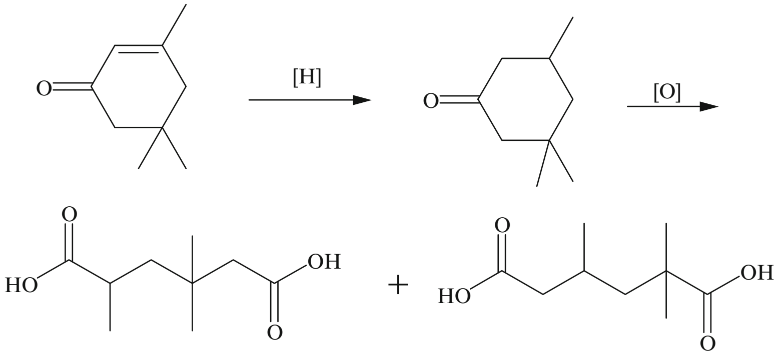
A number of ***copolyamides*** are manufactured commercially to suit various needs. One of them is a polyamide formed by condensation of trimethylhexamethylene diamine with terephthalic acid. The diamine is a mixture of 2,4,4 and 2,2,4 isomers:



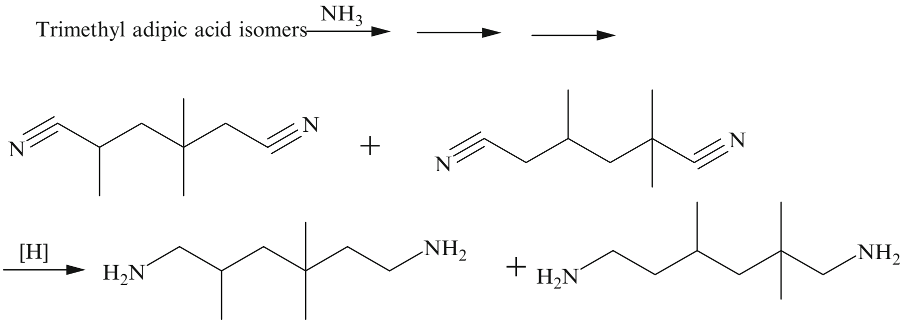
and



The mixture of the two isomers is synthesized from isophorone according to the following scheme:



The mixture of the isomers of trimethyl adipic acids is treated with ammonia, converted to amides, dehydrated to nitriles, and reduced to amines:



This polyamide is prepared somewhat differently. Salts of the diamine isomers with terephthalic acid are only partially polycondensed and the reaction is completed during extrusion [71], because the melt viscosity of the polymer is very high. The product is amorphous and exhibits greater light trasmittancy. It melts at 200°C and is sold under the trade name of Trogamid T.

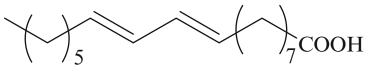
Many commercial nylon copolymers are also formed by melt mixing different nylons. Amide interchange reactions occur at melt conditions. At first block copolymers form, but prolonged heating and stirring results in formation of random copolymers. Nylon copolymers are also best prepared directly from mixed monomers.

Nylon polymers generally exhibit high-impact strength, toughness, good flexibility, and abrasion resistance. The principal structural differences between many nylons are in the length of the aliphatic segments between the amide linkages. As a result, the differences in properties depend mainly upon the amount of hydrogen bonding that is possible between the functional groups and on the amount of crystallinity. Also, due to high cohesive energy, nylons are soluble in only a few solvent. The melt viscosity of these materials, however, is generally low

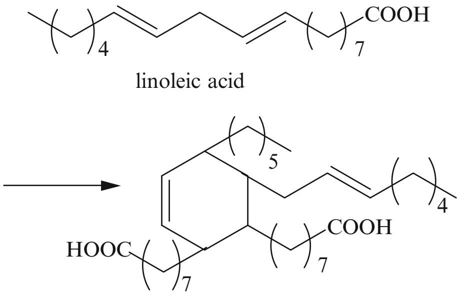
In any one series of melting points of polyamides, polymers that contain even numbers of methylene groups between amide linkages fall on a higher curve than those that contain odd ones do [72]. This is due to the crystalline arrangement of the polymeric chains [72, 73]. A zigzag planar configuration of polymers with even number of methylene linkages allows only 50% of the functional groups to form hydrogen bonds. This same configuration, however, allows polymers with odd numbers of methylene linkages to form 100% hydrogen bonding [72, 73]. Polyamides, like nylon 6,6 or nylon 6,10, arrange themselves in pleated sheets during crystallization and hydrogen bonds form between N–H group of one molecule and the C=O moieties from a neighboring one.

7.3.2 Fatty Polyamides

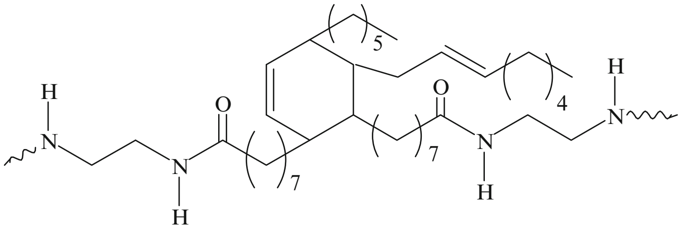
The fatty polyamides are produced by reacting di- and polyfunctional amines with polybasic acids that result from condensations of unsaturated vegetable oil acids. The most commonly used amines are ethylene diamine and diethylene triamine. The dicarboxylic acids are synthesized by heating mixtures of unsaturated vegetable fatty acids. The starting materials may come from linseed, soybean, or tung (also called China wood) oil. The fatty acids are heated for several hours at 300°C. If a catalyst is used, the heating is done at a lower temperature. After condensation, the volatile fractions are removed by vacuum. The residues, called ***dimer acids***, are then condensed with the amines. A formation of one such dimer acid from linoleic acid can be illustrated as follows:



isomerized linoleic acid



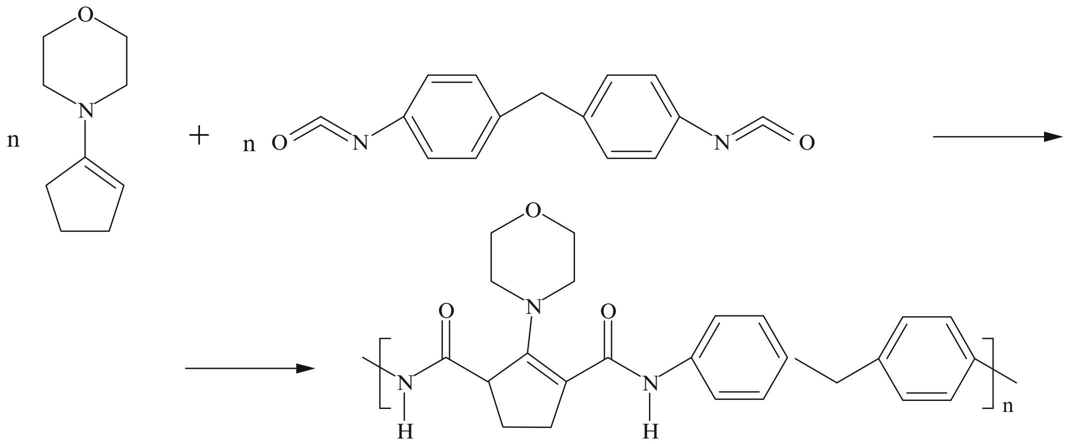
The polyamide from the above shown dimer acid condensed with a diamine, like ethylene diamine, can be illustrated as follows:



Two types of fatty polyamides are available commercially, solid and liquid. The solid polymers are mostly linear condensation products of diacids and diamines that range in molecular weights from 2,000 to 15,000. The liquid ones are highly branched, low molecular weights materials produced by condensations of the dimer acids with triamines and even higher polyamines.

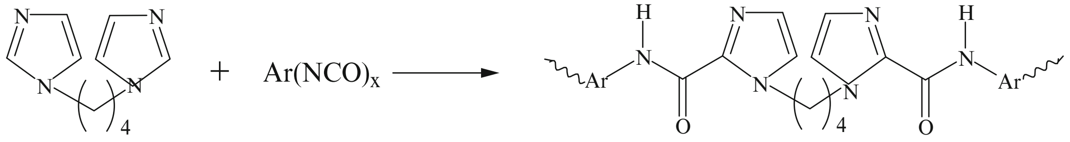
7.3.3 Special Reactions for Formation of Polyamides

There are occasional reports in the literature on use of special reactions to form polyamides. One is a synthesis via enamines. In this case, diisocyanates are condensed with cyclopentanone enamines of morpholine or of piperidine [77]:

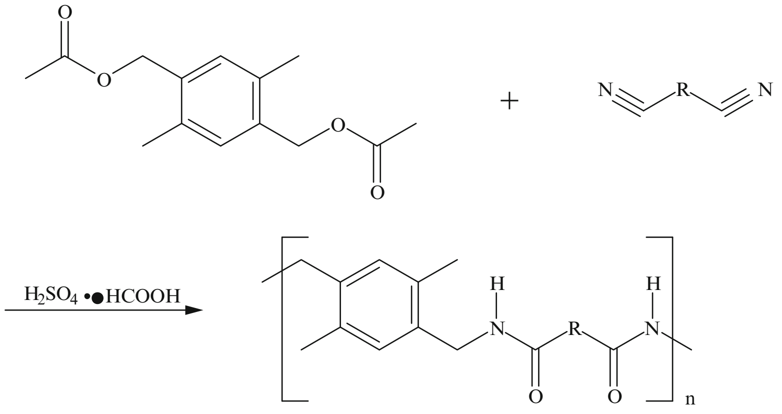


The molecular weights of the polymers decrease when the ring sizes of the ketone components increase. Excess diisocyanate yields branched and cross-linked polymers. The enamine units in the polymers can be hydrolyzed with formic acid to the corresponding ketones [77].

A similar reaction was reported from aromatic isocyanates and imidazoles, where 1,4 tetramethylene-*N*,*N*′-di imidazoles were reacted with aromatic polyisocyanates to form thermoset polyamides [45]:



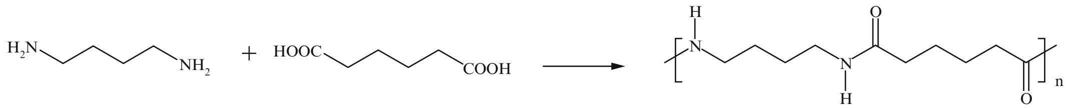
Another route to polyamides is via the Ritter reaction [78]:



When aromatic di nitriles are used, high melting polymers with good thermal stability form [78].

Direct polycondensation of various dicarboxylic acids with diamines is possible [81] under mild conditions by using a catalytic system of an enol phosphite in the presence of imidazole. One such enol phosphite is diethyl,1-methyl-3-oxo-1-butenyl phosphite. Polymers with inherent viscosities of 1–0.25 form. Among the organic bases, imidazole is most effective [84]. The reaction is applicable to both aliphatic and aromatic dicarboxylic acids and diamines.

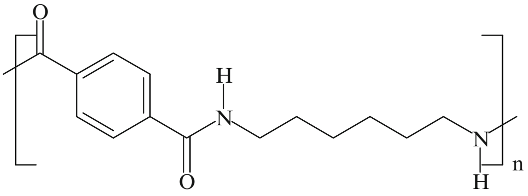
Direct polycondensation of a diamine with dicarboxylic acid was carried out in supercritical carbon dioxide in preparation of nylon 4,6 [84].



This nylon was reported to melt at 210°C.

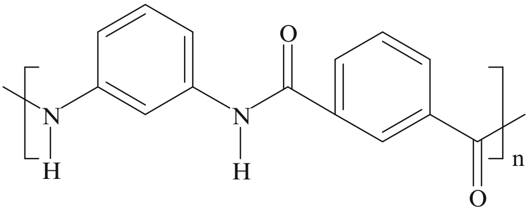
7.3.4 Aromatic Polyamides

In this section are discussed not only wholly aromatic polyamides, but also some mixed polyamides prepared from aromatic diacids and aliphatic diamines or vice versa. One such material was already described in Sect. 7.3.2. Another one, called Nylon 6T, is formed by interfacial polymerization of terephthaloyl chloride and hexamethylene diamine:

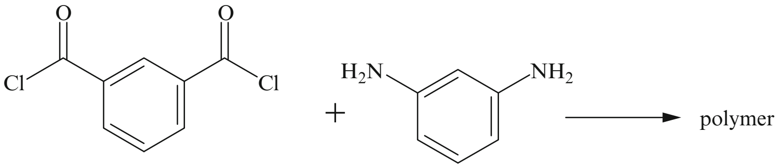


The polymer has good heat stability and the strength is unaffected by heating up to 185°C for 5 h. The polyamide melts at 370°C. When hexamethylene diamine is replaced with tetramethylene diamine, the melting point rises to 430°C. The condensation product from isophthalic acid and tetramethylene diamine melts at 250°C.

Fully aromatic polyamides form from reactions of aromatic diacid chlorides and aromatic diamines [79, 80]. An example is formation of poly(*m*-phenylene diamine isophthalamide):

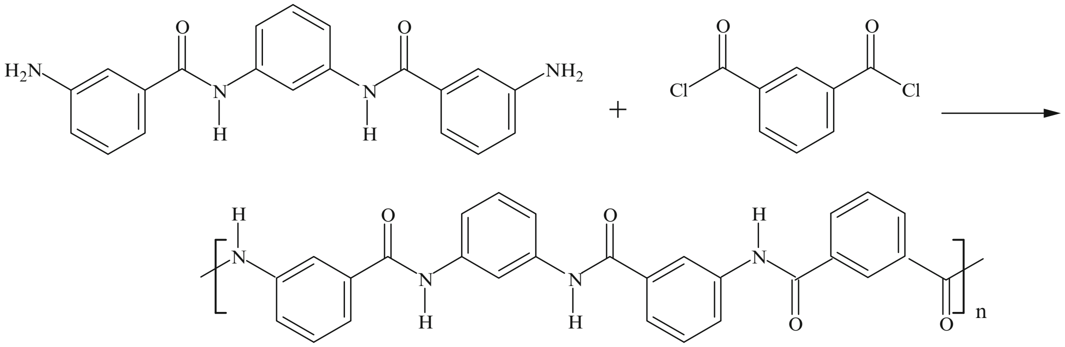


The polymer can be prepared in dimethylacetamide from isophthaloyl chloride and *m*-phenylene diamine in the presence of an acid scavenger at room temperature:



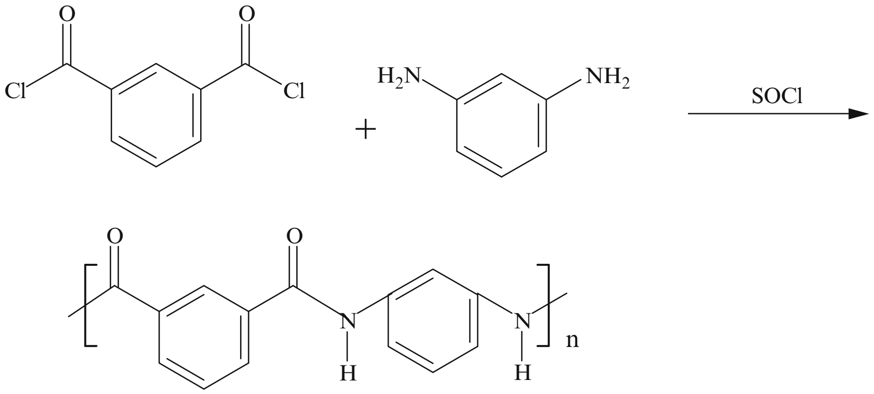
Because the polymer is soluble in dimethylacetamide containing 5% LiCl, fibers can be spun directly from solution. This polyamide melts at 371°C with degradation. It is fire-resistant. The fibers are sold under a trade name of Nomex.

Such aromatic polyamides with regular structure were reported to possess better flexibility and higher temperature resistance [74, 75]. Preparations of *ordered copolyamides* were described as follows: *N*,*N*-*m*-phenylene-bis(*m*-aminobenzamide) is formed first and then reacted with isophthaloyl chloride by interfacial condensation techniques to yield a product that melts at about 410°C:

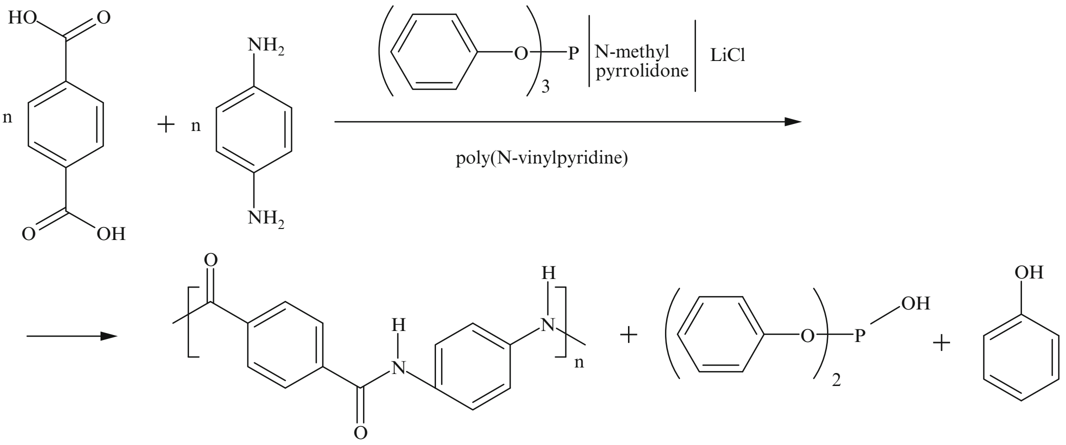


The above condensation, carried out with terephthaloyl chloride, yields a polymer that melts at 450°C. Preparations of many other wholly aromatic polyamides from aromatic diacid chlorides and aromatic diamines were reported in the literature [79, 80]. In addition, several polymers are manufactured from both fully and partially substituted (*para*) structures. They carry the trade name of HT4.

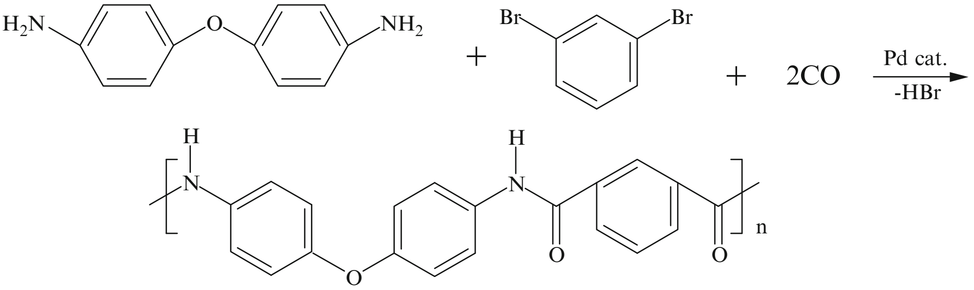
As described in the previous section, direct polycondensation of various nylon salts is possible under mild conditions in the presence of polyphosphates and organic bases [84]. This reaction, useful in forming aromatic polyamides, takes place also in the presence of thionyl chloride [84]:



Metal salts, like lithium chloride, significantly enhance reactions of carboxylic acids with amines promoted by triphenyl phosphite [82]. This allows direct polycondensation of dicarboxylic acids with diamines and self-condensation of *p*-aminobenzoic acid [82]. The presence of a solvent markedly enhances the reaction with the best results being obtained in *N*-methylpyrrolidone. High molecular weight polyamides form. Mixed solvents, like pyridine and *N*-methylpyrrolidone, can be used to form polyisophthalamides [82]. This combination of solvents, however, yields only low molecular weight polyterephthalamides. On the other hand, when the reaction is carried out in the presence of polymeric matrices of poly(ethylene oxide) or poly(4-vinylpyridine), high molecular weight polyterephthalamides form [82]:



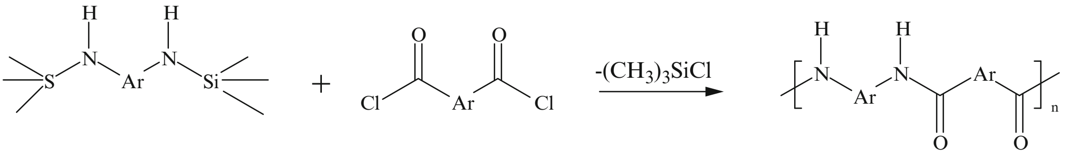
The Heck reaction was extended to carbonylation of aromatic dibromides with aromatic diamines in the presence of carbon monoxide [112]. High molecular weight aromatic polyamides form with the help of palladium catalysis:



The polymerization reaction takes place in a homogeneous dimethylacetamide solution, with catalytic amounts of $PdCl_2(PPh_3)_2$ and an HBr scavenger. The carbonylation polycondensation proceeds rapidly at 115°C and is almost complete in 1.5 h [112]. This reaction was also used to prepare many aromatic-aliphatic polyamides from corresponding aliphatic diamines with aromatic dibromides.

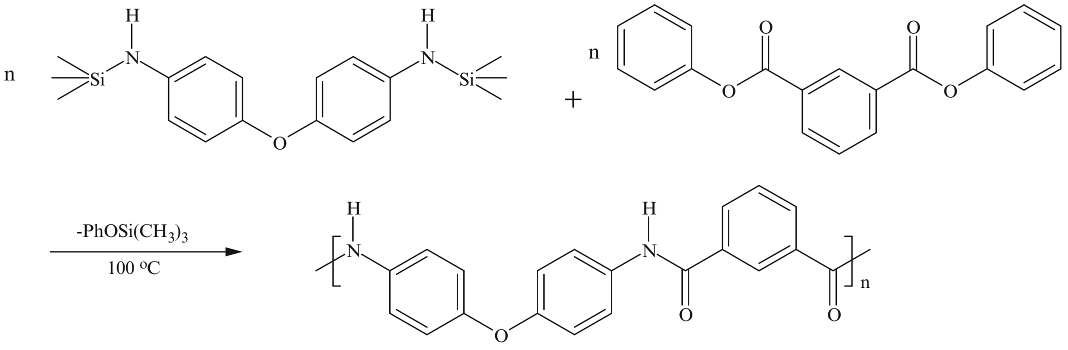
Palladium is a relatively high-priced catalyst and it would be preferable if a lower-priced nickel catalyst could be used instead. All attempts, however, to form polymers by nickel-catalyzed carbonylation polycondensations of aromatic diamines with aromatic dibromides failed to yield high molecular weight materials [112].

Trimethylsilyl-substituted amines undergo a variety of reactions with electrophiles [113]. This reaction was extended recently to preparations of high molecular weight aromatic polyamides by low temperature solution polycondensation. *N*-trimethylsilylated aromatic diamines were condensed with aromatic diacid chlorides [114] at −10°C in an amide solvent:



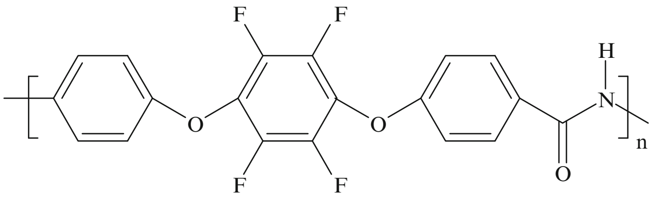
Preparations of poly-*p*-phenyleneterephthalamide by polycondensations with *N*-silylated diamine proceed more rapidly than with the parent diamine [113]. In addition, the products have higher molecular weights than similar commercial materials made from the parent diamine and sold under the trade name of Kevlar.

Silylated diamines can also condense with diphenyl esters of aromatic dicarboxylic acids [114]:

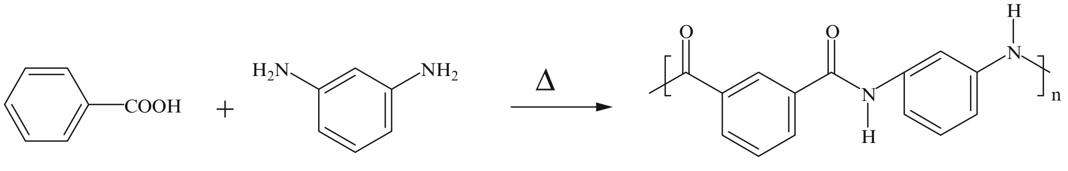


The product, above shown aromatic polyamide, was reported to be of sufficiently high molecular weight and to be a useful material [113].

An example of a specialty aromatic polyamides is a fluorinated polyamide. It was prepared in an attempt to form a polymer with superior heat stability and resistance to hydrolytic attacks [76]:



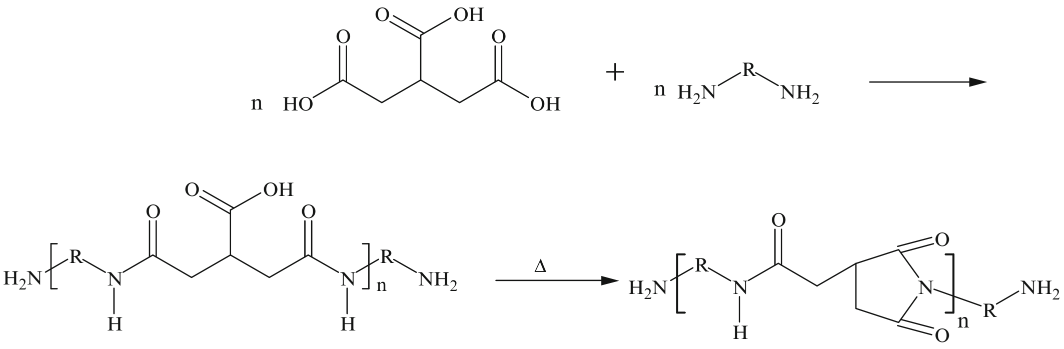
Mitsuru et al. [113] reported a direct synthesis of Nomex, an aromatic polyamide, mentioned above, by a solid state polycondensation:



The reactions were carried out at the melting state of the reactants, at first at 360°C and after oligomerization at 260°C for 1 h.

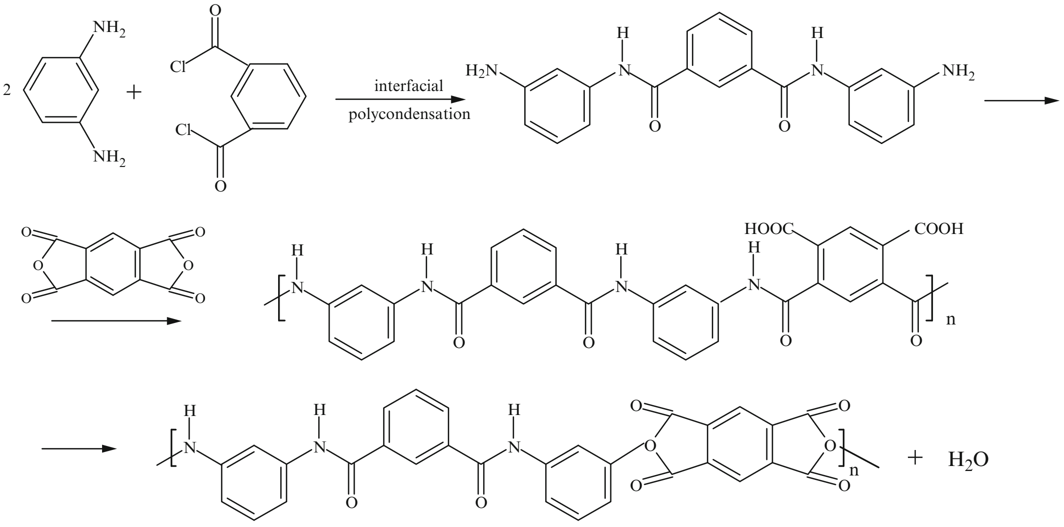
7.4 Aromatic Polyamide-Imides and Aromatic Polyester-Imides

The aromatic polyamide-imides are related to the aromatic polyamides described in the previous section. Aliphatic materials of this type were reported originally in 1947. They were formed by reacting tricarboxylic acids with diamines [83]:



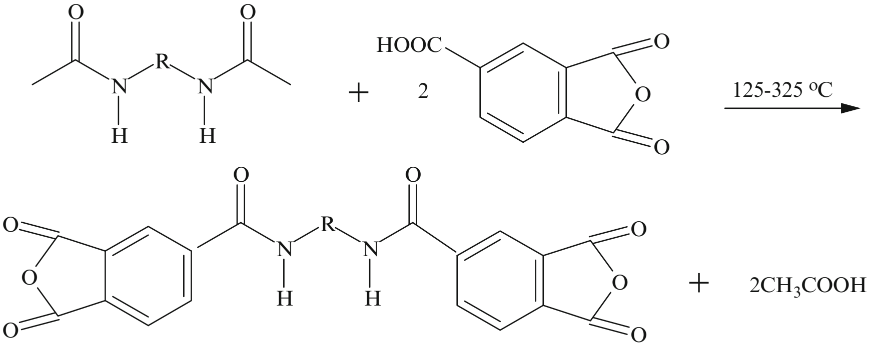
The aliphatic polyamide-imides prepared to date don't have desirable properties. When aromatic diacids are employed, however, the products exhibit good heat stability and toughness. This led to a development of a number of useful materials.

Three general methods are employed to form aromatic polyamide-imides [88]. The first one consists of an initial reaction of a mole of a diacid chloride with two moles of a diamine. The product is then reacted with a dianhydride and after that condensed to an imide:

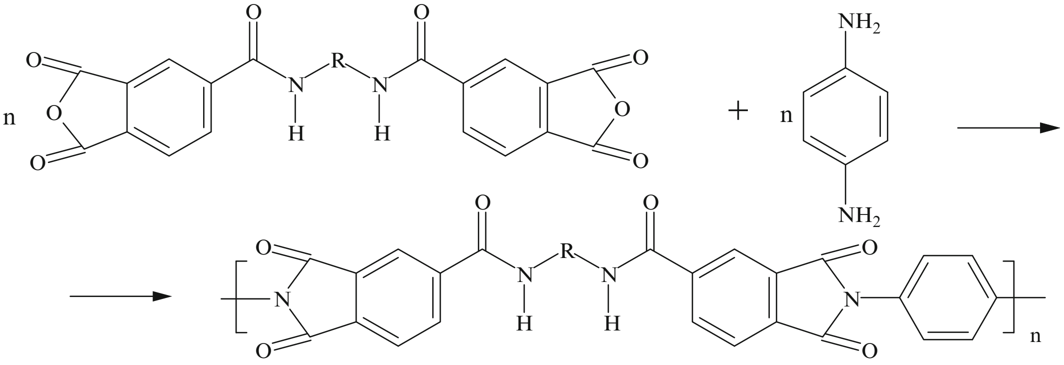


In the second method, a dianhydride is prereacted with an excess of a diamine. The product is then reacted with a diacid chloride by interfacial polymerization technique.

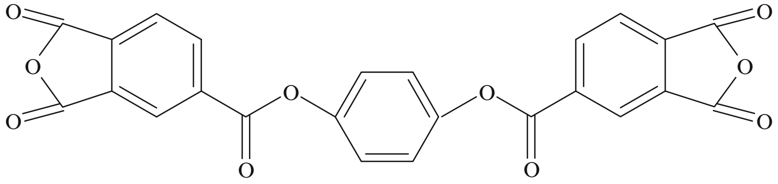
In the third method, an anhydride, like, for instance, trimellitic anhydride, is condensed with a diamine to form a preliminary condensate. An acetylated diamine can be used in this initial condensation [85]:



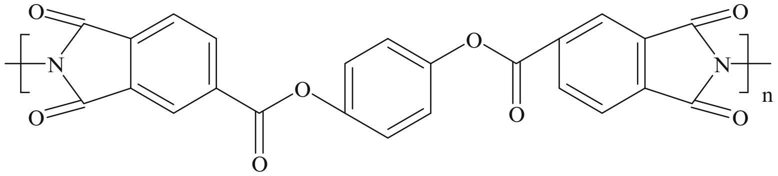
This is followed by a reaction with the same or a different diamine:



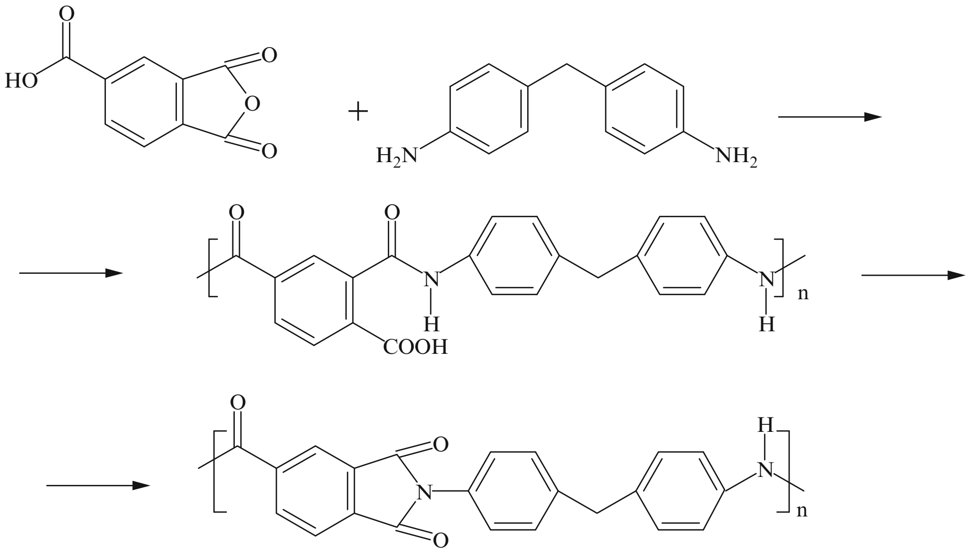
The same techniques are applied to preparations of polyester-imides. A diester can be formed first from trimellitic anhydride:



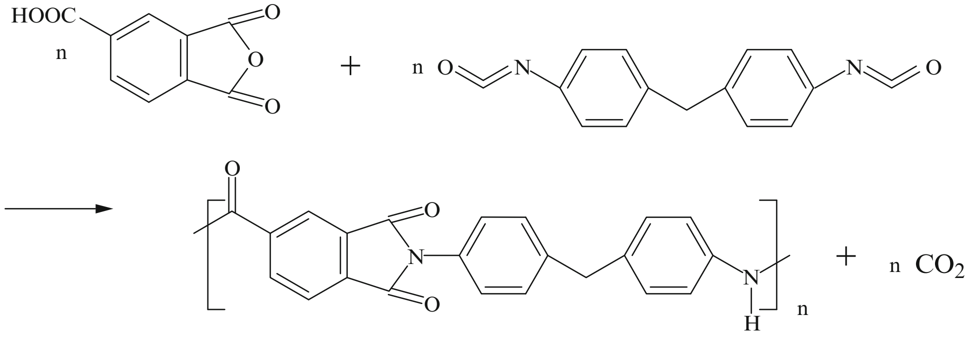
The product is then condensed with a diamine to form a polyester-imide:



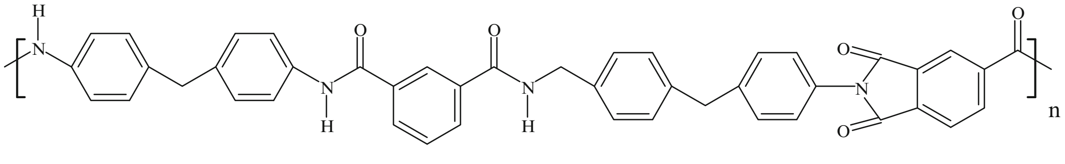
Several polyamide-imides are available commercially. Two are based on trimellitic anhydride and methylene dianiline. They are, however, prepared by two different processes. In the first one, the polymer is formed from the anhydride and a diamine:



In the second one, trimellitic anhydride is reacted with a diisocyanate:



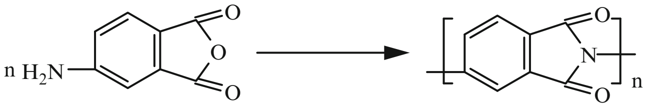
Another polyamide-imide is formed through a reaction of trimellitic anhydride, isophthalic acid, and diisocyanate. It has the following structure:



Most polyamide-imides are not as heat-resistant as are the polyimides discussed in the next section. They are, however, easier to process. The polyester-imides might be considered as "upgraded" polyesters, though properties vary, depending upon chemical structure [86].

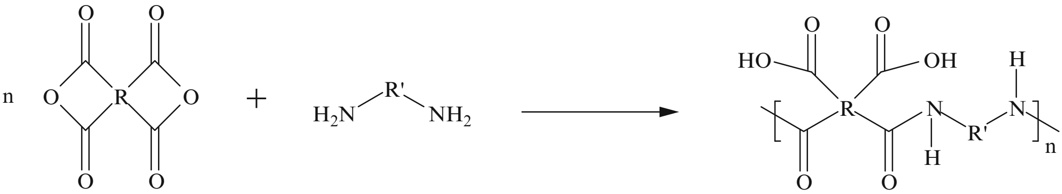
7.5 Polyimides

It is interesting that formation of a linear aromatic polyimide was observed as early as 1908 when a polyimide was formed by heating 4-aminophthalic anhydride:

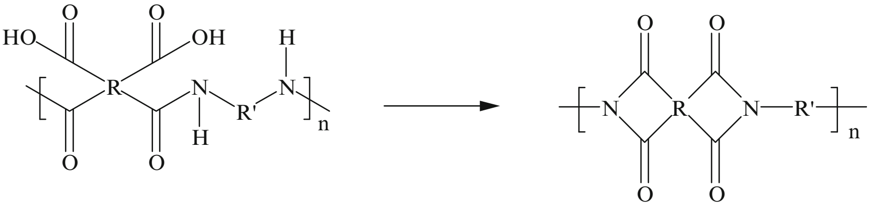


Formation of polymers, however, was at the time considered undesirable, so the material was not pursued [87]. It was learned since that an imide link is more thermally stable than an amide one and that polyimides can be very useful materials. Many polyimides were developed since. Aromatic structures in the polymeric backbone raise the melting temperatures and yield stiffer and tougher materials. Most sought-after polyimides, therefore, are products from aromatic tetra acids (or dianhydrides) and aromatic diamines.

Many commercial preparations of aromatic polyimides include a preliminary step of forming polyamic acids first [88]:



This is followed by imidation, often after the polymer has been applied to a substrate as a coating or was cast as a film:

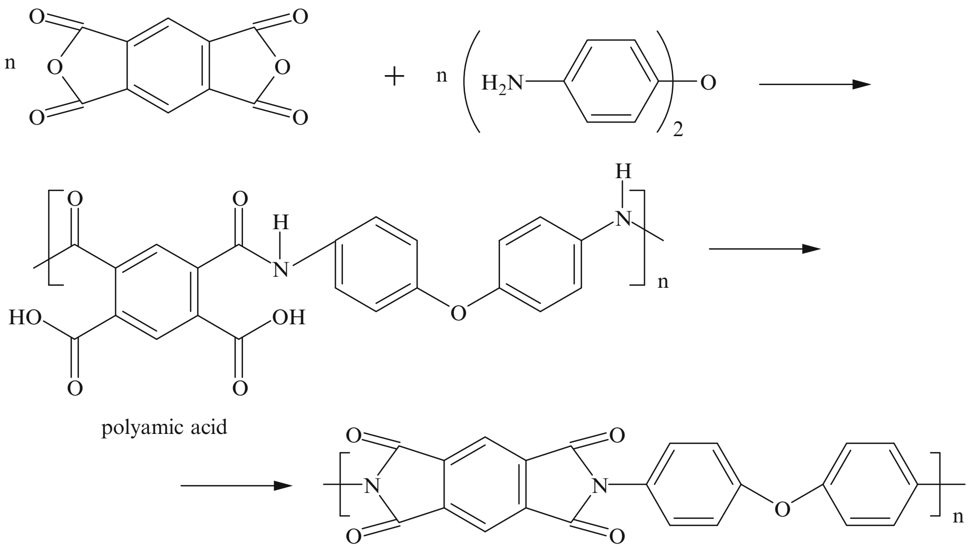


The polyamic acids are usually prepared in solution. Suitable solvents are *N*,*N*-dimethylformamide, dimethyl sulfoxide, and *n*-methyl-2-pyrrolidone. The reactions require anhydrous conditions at relatively low temperatures, like 50°C (or lower). Some, however, need high temperatures, as high as 175°C [88]. The two reagents are combined in solution. The order of addition and reagent purity can influence the molecular weight of the products that may range from 13,000 to 55,000 [88]. Some imidation accompanies the first step. It is desirable that during polyamic acid formation, the degree of imidation does not exceed 50%.

The step of conversion of polyamic acids to polyimides can take place at about 300°C in thin films. With cyclizing agents, however, it can take place at much lower temperatures [88].

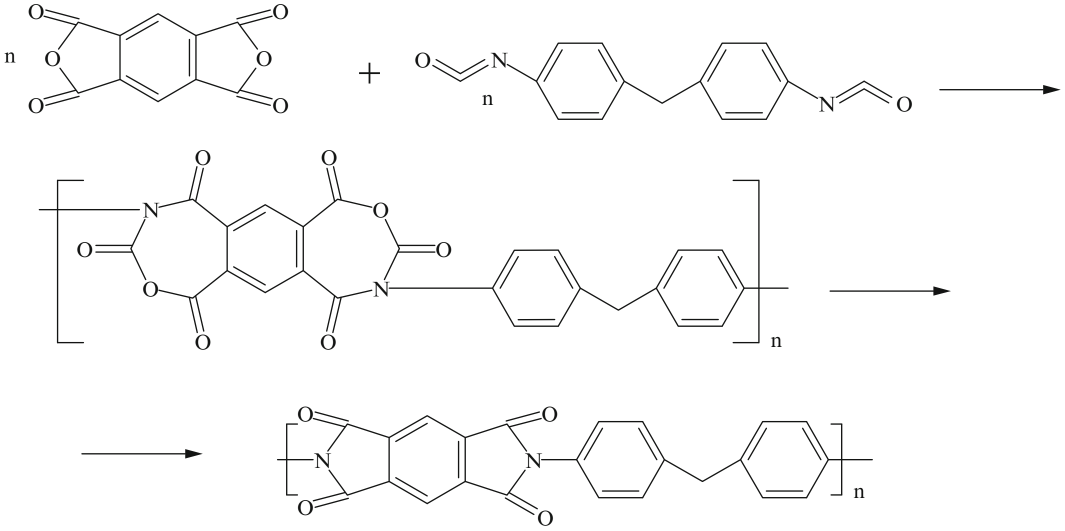
Lozano et al. reported on an improved method for forming high molecular weight polyimides [88]. They used in situ sililation of the diamines to carry out the reaction. Trimethylchlorosilane is added to the diamine solution prior to the addition of the electrophilic monomer.

Commercially, the most commonly used aromatic dianhydrides are pyromellitic dianhydride and benzophenone tetracarboxylic dianhydride. The common amines in industrial practices are *meta*-phenylene diamine, methylene dianiline, and oxy-dianiline. A typical polyimide preparation can be shown as follows:

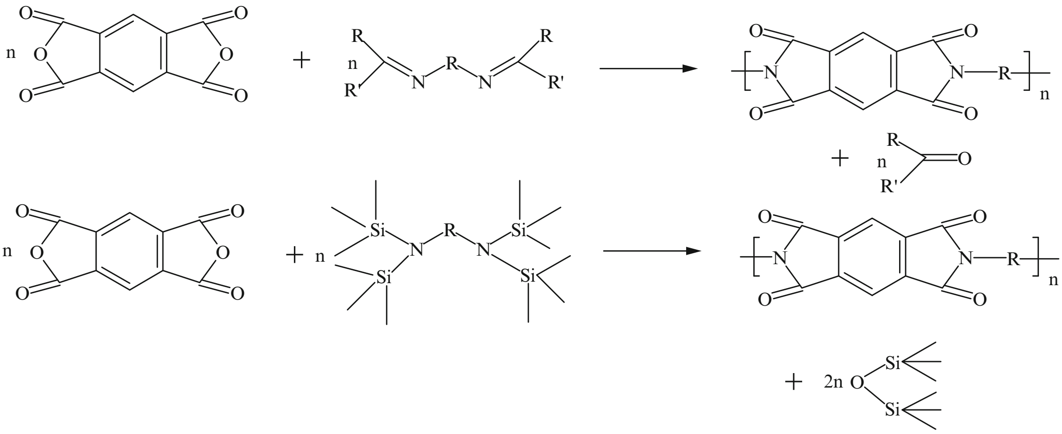


The above shown polymer melts above 600°C and is heat stable up to 500°C in an inert atmosphere. It is sold under the trade name of Kapton. A different polyether-imide sells under the trade name of Ultem.

Another route to polyimides is through reactions of diisocyanates with dianhydrides [89, 90]:

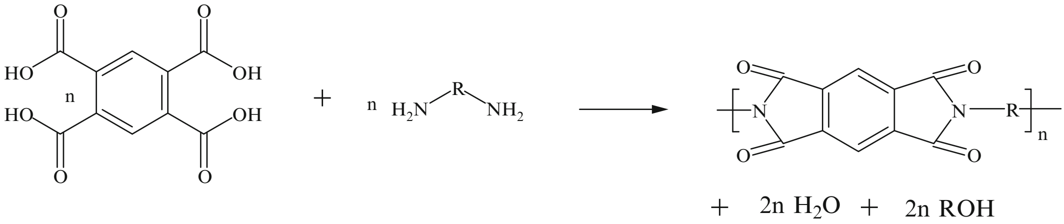


The reaction is kept between 120 and 200°C [91]. In place of isocyanates, it is also possible to use aldimines or ketimines, as well as silylated diamines.

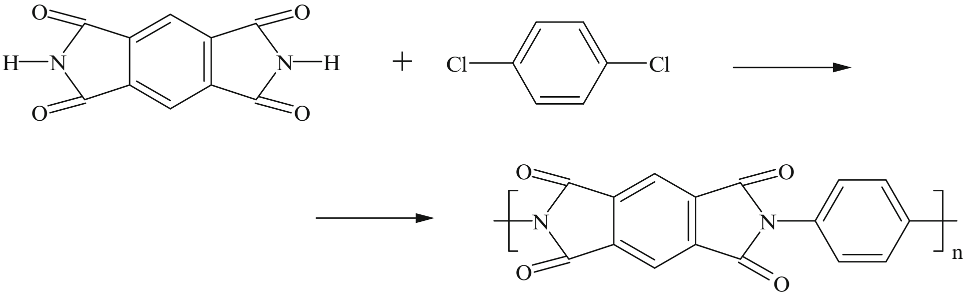


When silylated diamines are used, trimethylsilyl esters of polyamic acids are formed first and then desilylated with methanol. Due to increased solubility of silylated aromatic amines, the initial condensations and formations of polyamic acid trimethylsilyl esters can be done in various solvents, yielding high molecular weight polymers. The highest molecular weights are obtained in dimethylacetamide at 50°C. Other solvents like tetrahydrofuran and chloroform can be used as well, though they appear to yield slightly lower molecular weight products [91].

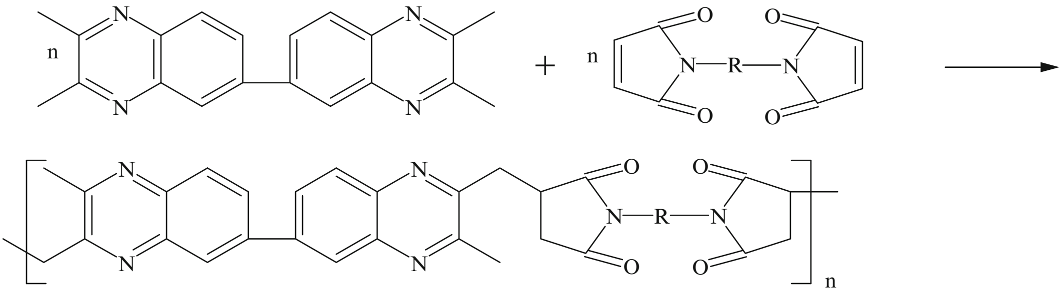
The films of the silylated precursors of polyamic acid convert directly by heat treatment to yellow, transparent, and tough films of aromatic polyimides with the elimination of trimethylsilanol [91]. Other preparations of polyimides include the use of di-half esters of tetracarboxylic acids [92]:



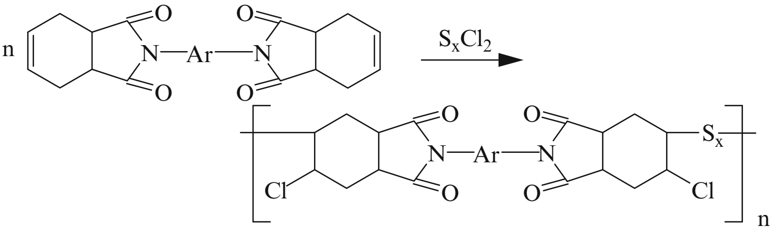
Polyimides can also be prepared by reactions of diimides with dihalides [93]:



Reactions of bis maleimides with compounds containing active hydrogens can also lead to formations of polyimides [94]:

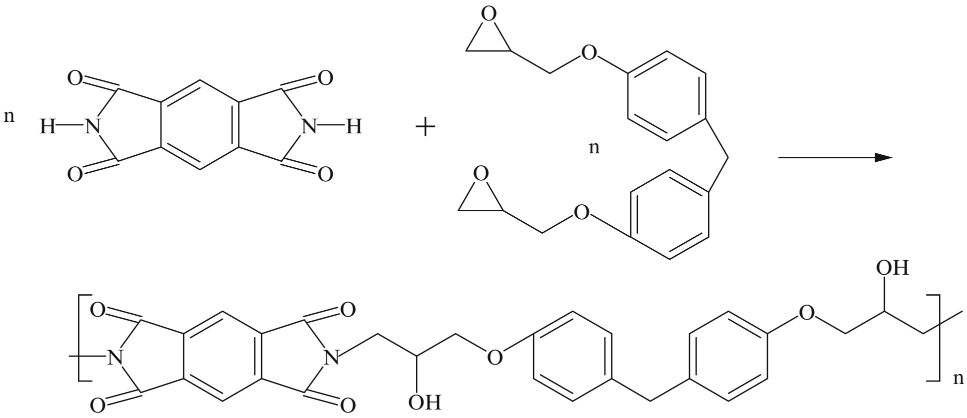


Also, unsaturated diimides can be reacted with sulfur halides to form polyimides [95]:



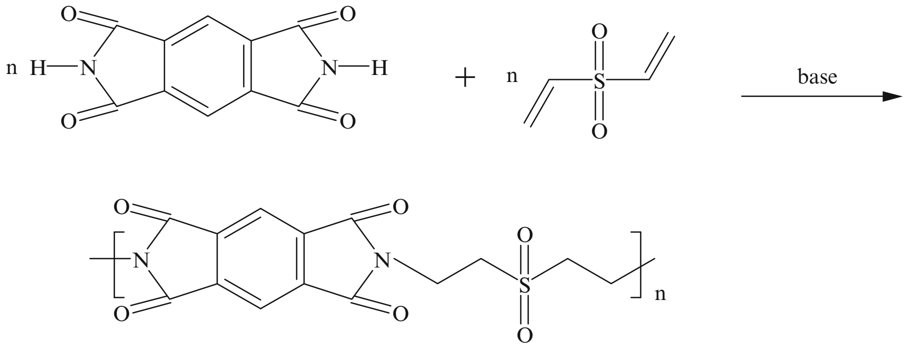
where x = 1 or 2

Diepoxides can add to pyromelitimide in the presence of a base to form polyimides with pendant hydroxyl groups [96]:

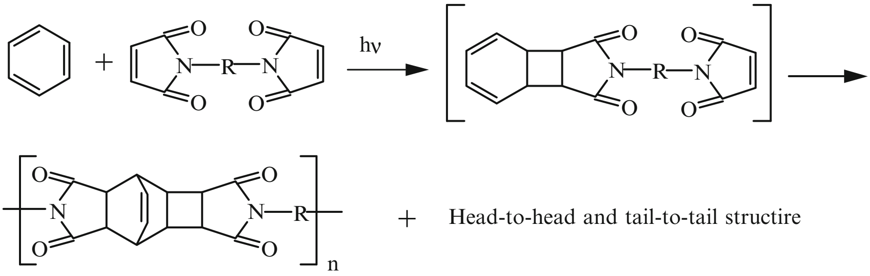


Tertiary amines and quaternary ammonium halides catalyze this reaction. Acetylation of the pendant hydroxyl groups of the product yields polymers that are soluble in solvents like dioxane and dimethylformamide.

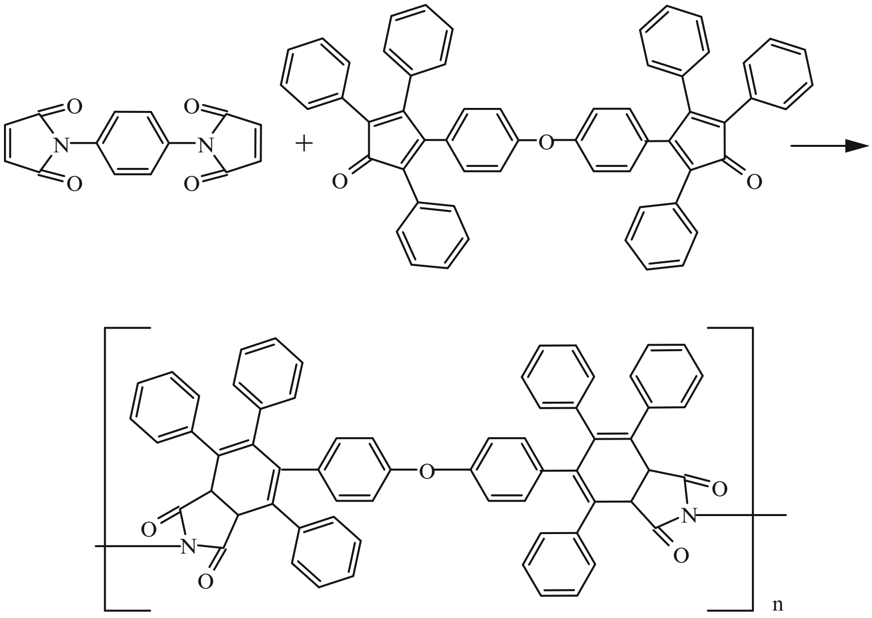
Pyromelitimide can also add to double bonds to form polyimides [97]:



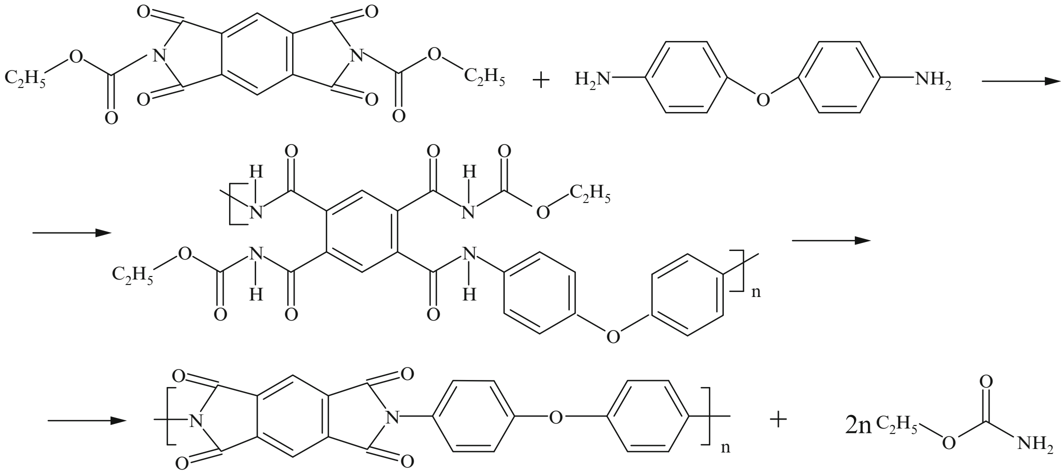
Polyimides also form by photo additions of aliphatic or aromatic bis maleimides to benzene [98]. The reactions involve 2 + 2 cycloadditions that yield homoannular diene intermediates. Diels–Alder additions follow and result in formations of the polymers:



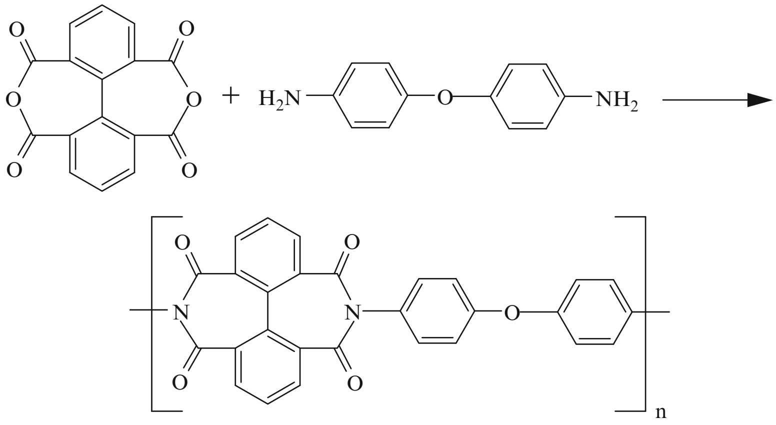
Diels–Alder reactions yield other polyimides, as, for instance, the following [99]:



Also, *N*,*N*-bis(ethoxycarbonyl) pyromelitimide condenses with diamines to yield polyimides [100]:



The first step in the above preparation takes place in solution. After casting a film, the second step takes place at 240°C under vacuum. Interesting polyimides also form from reactions of 2,2′,6,6′-biphenyltetracarboxylic acid anhydride [101] with aromatic diamines, like 4,4′-diaminodiphenyl ether:

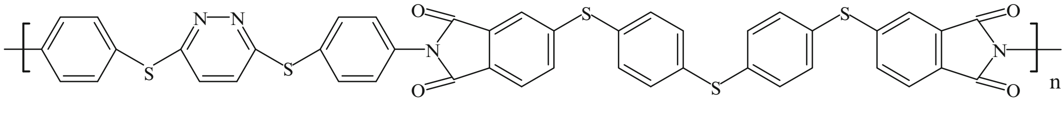


As in the previous cases, the polyamic acid forms first in solution at approximately 40°C. It is converted to the polyimide by heating in acetic anhydride at reflux for 18 h.

Heterocyclic dianhydrides, like pyrazinetetracarboxylic dianhydride, also react with diamines to form polyimides [102]. Such polymers are harder to form, however.

Two types of thermoset polyimides are currently prepared commercially. They are based on low molecular weight bis imides such as bis maleimides or bis-5-norbornene-2,3-dicarboximides. Due to unsaturations, the materials cross-link by free-radical mechanism into tight networks. Michael type additions of primary and secondary amines to the bis maleimides are often used to chain-extend them before cross-linking. This reduces the cross-linking density and the brittleness [115]. The materials are designated by the term PMR, for polymerizable monomeric reactants.

Ueda et al. [102] synthesized a polyimide from 3,6-bis-(4-aminophenylenesulfanyl)pyridazine.



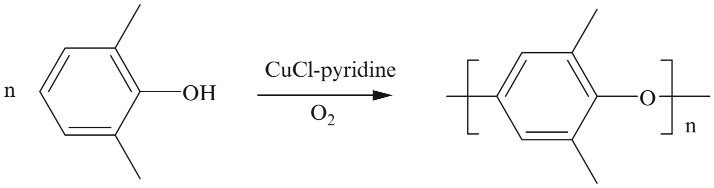
The polymer has a high refractive index, high transparency, and is aimed at optical devices.

7.6 Polyethers

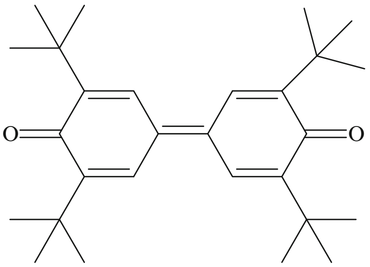
Polyethers that form by chain-growth polymerizations of carbonyl compounds and by ring opening polymerizations of cyclic ethers and acetals are discussed in Chap. 6. In this section are discussed poly(phenylene oxide)s and phenoxy resins.

7.6.1 Poly(phenylene oxide)s

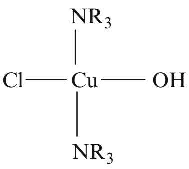
These polymers are known for good thermal stability and good mechanical properties. Commercially, these aromatic polyethers are prepared by oxidative coupling of phenols [102]. To obtain linear polymers and achieve high molecular weights, 2 and 6 positions of the phenol must be protected by substituents. This causes the aromatic rings to couple in 1,4 positions. When 2,6-dimethylphenol is used, the reaction takes place at room temperature. Oxygen is bubbled through a solution of the phenol in the presence of an amine-cuprous salt catalyst:



Phenols with halogen substituents require higher temperatures. Large substituents can lead to carbon to carbon coupling instead of carbon to oxygen:

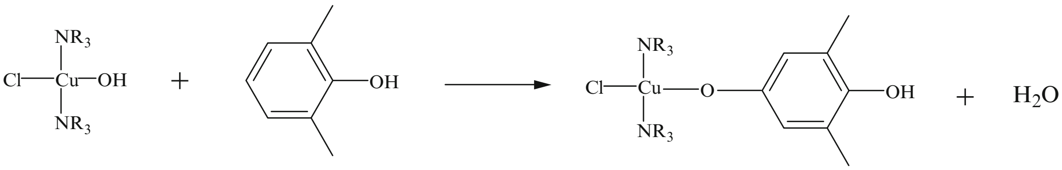


The active catalyst is believed to be a basic cupric salt that forms through oxidation of cuprous chloride followed by complexation with two molecules of the amine [102]:

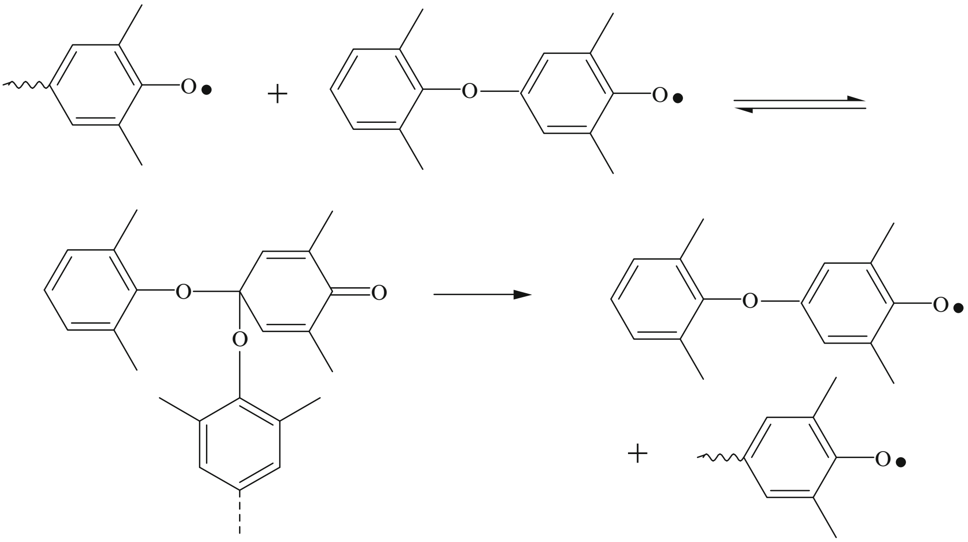


$$\mathrm{Cl{-}\overset{NR_3}{\underset{NR_3}{Cu}}{-}OH}$$

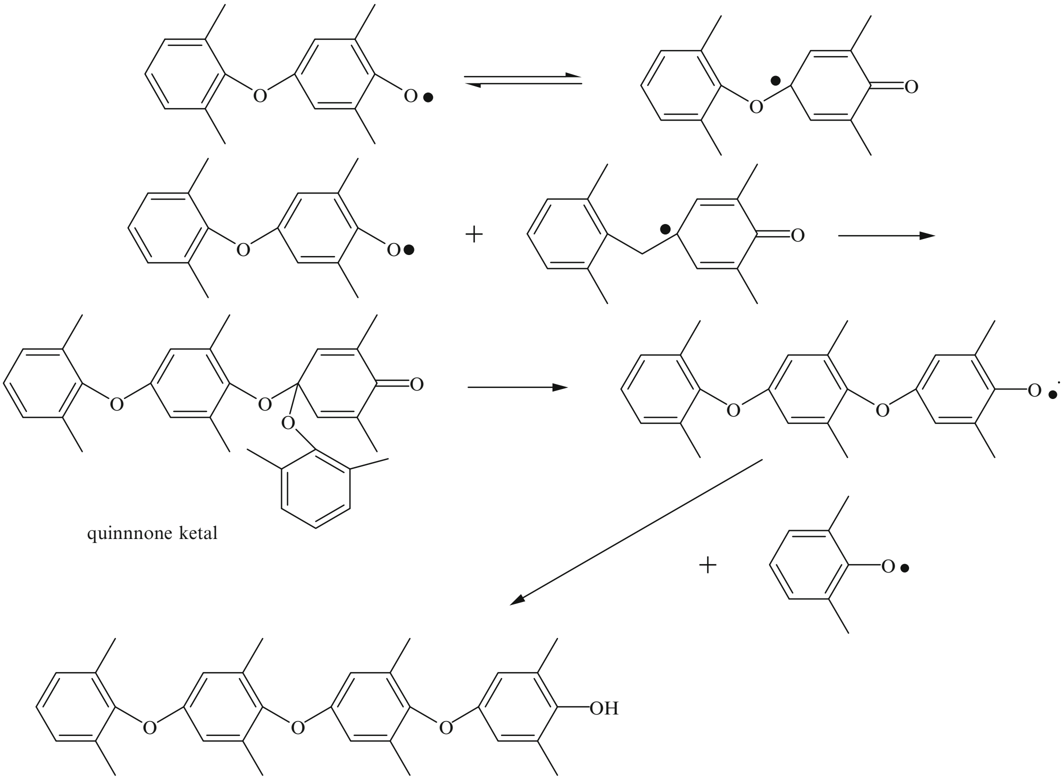
This is a step-growth polymerization involving phenoxy radicals. The polymer formation can be illustrated as follows:



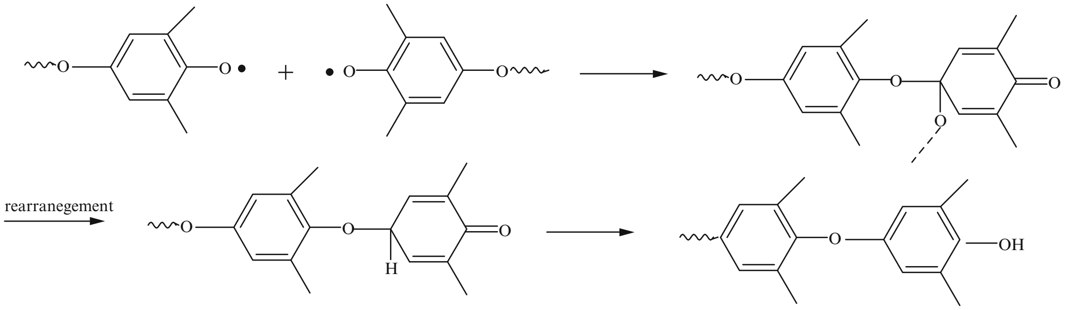
Dissociation leads to aryloxy radicals or to two new radicals that couple. Quinone ketals are formed initially. They dissociate to yield the original aryloxy radicals and then couple [102]:



Formation of aryloxy radicals as intermediates was established with ESR spectroscopy studies that showed presence of both monomeric and polymeric radicals in the reaction mixture [103]. Coupling occurs by two paths. One of them through rearrangements and the other one through redistribution. In the redistribution process, two aryloxy radicals couple to yield an unstable quinone ketal as shown above [102]. This ketal decomposes rapidly either back into the original aryloxy radicals or into two different aryloxy radicals as follows:



The redistribution process leads to production of polymers from low molecular weight radicals. It appears that this process is unlikely to take place with high molecular weight radicals because there are too many steps involved in the production of monomer radicals. Quinone ketals are the intermediates in the rearrangement. The carbonyl oxygen of a ketal is within bonding distance of the *para* position of the next succeeding benzene ring [104]. The rearrangement can, therefore, give rise to a new ketal in which the second ring carries the carbonyl oxygen. The carbonyl oxygen finally ends up on a terminal unit [104] and is reduced to OH:

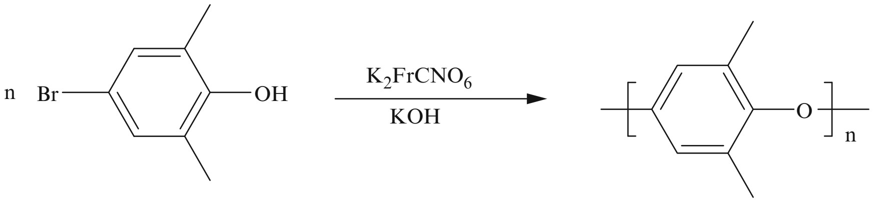


The quinone rearranges to a phenol through enolization. The product is identical to one that is obtained by direct head to tail coupling of two aryloxy radicals [102].

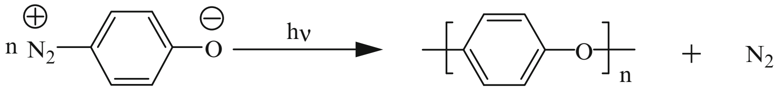
It is important to realize that both processes, redistribution and rearrangement reactions, can occur within the same polymer molecule. At any point during the rearrangement, there may be dissociation into aryloxy radicals. Also, redistribution does not have to occur by transfer of only a single unit. Rearrangement, followed by dissociation, allows any number of monomer units to be transferred in an essentially single step.

2,6-Diphenylphenol and 2,6-dimethylphenol can copolymerize by oxidative coupling [104]. If the diphenyl derivative is polymerized first and subsequently the dimethyl derivative is added to the reaction mixture, block copolymers form. If, however, the order is reversed or both phenols are polymerized together, a random copolymer results [104].

Poly(phenylene oxide)s can also be formed by oxidative displacement of bromides from 4-bromo-2,6-dimethylphenol [102, 105]. Compounds, like potassium ferricyanide, lead oxide, or silver oxide, catalyze this reaction:



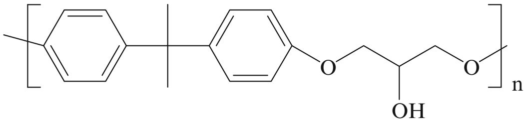
Poly(phenylene oxide)s also form through photodecomposition of benzene-1,4-diazooxides [102]:



Oxidative coupling is the only process used commercially. Although poly(phenylene oxide) is an important commercial material, there was initially a processing problem when the material was first introduced. Currently, a large portion of the polymer is sold as a blend with polystyrene (probably high-impact) to make it more attractive economically and easier to process. The ratios of poly(2,6-dimethylphenylene oxide) to polystyrene range from approximately 1:1 to 1:2 and the materials are sold under the trade name of Noryl. A fire retardant grade, containing about 5% of an additive, believed to be triphenyl phosphate, is also on the market.

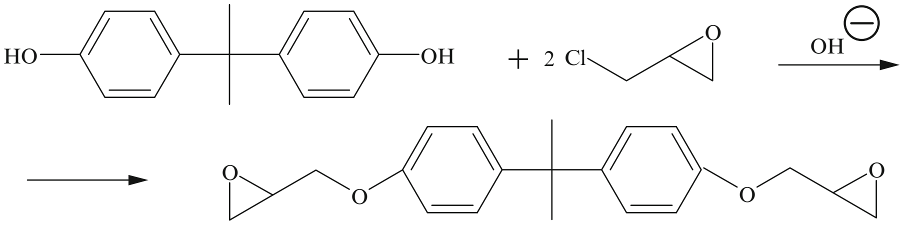
7.6.2 *Phenoxy Polymers*

These materials are part of the technology of epoxy resins that are discussed in a separate section, further in this chapter. The polymers bridge a gap between thermosetting resins and thermoplastic polymers and are used in both forms commercially [116]. An idealized picture of phenoxy polymers can be shown as follows:

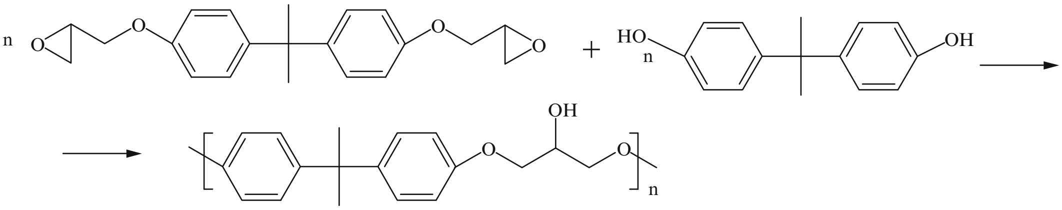


The polymer forms through caustic catalyzed condensations of diphenols with epichlorohydrin. Any diphenol or combination of diphenols can undergo this reaction. In commercial practice, however, mainly 4,4-isopropylidinediphenol, commonly called Bisphenol A, is used.

Theoretically, the phenoxy resins should form in equimolar reactions of epichlorohydrin with the diphenol. There are, however, a number of side reactions that accompany the condensation. To get around them and to obtain high molecular weight polymers, the syntheses are carried out in two steps. In the first one, an excess of epichlorohydrin is used to form diepoxide:



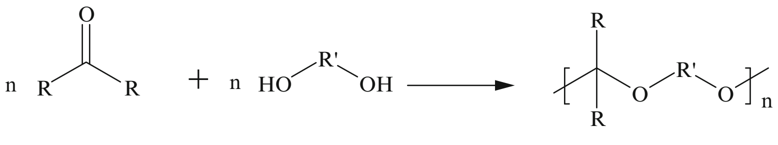
In the second step, equimolar quantities of the diepoxide are reacted with the diphenol:



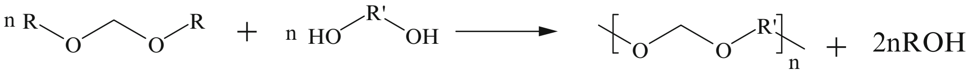
Both reactions are conducted in solution, where methyl ethyl ketone is the choice solvent. The commercial resins range in molecular weights from 15,000 to 200,000.

7.7 Polyacetals and Polyketals

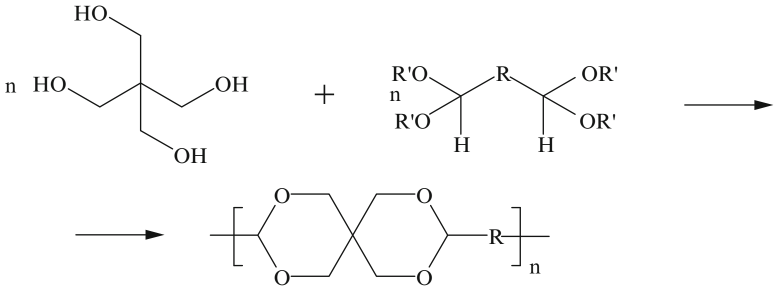
Polyacetals and polyketals are polyethers that form (1) through condensations of glycols with carbonyl compounds, (2) by exchange reactions of acetals or ketals, and (3) by additions of diols to dialkenes [109]:



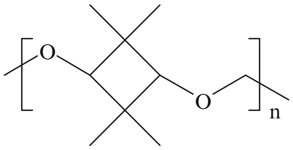
An acid-catalyzed exchange reaction of glycols and acetals yields polyacetals as follows:



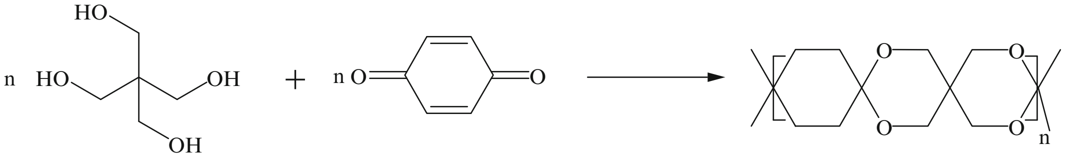
These reactions often lead to cyclic acetals that interfere with the formation of high molecular weight products. Useful polyacetals, however, can be formed from pentaerythritol and acetals of dialdehydes:



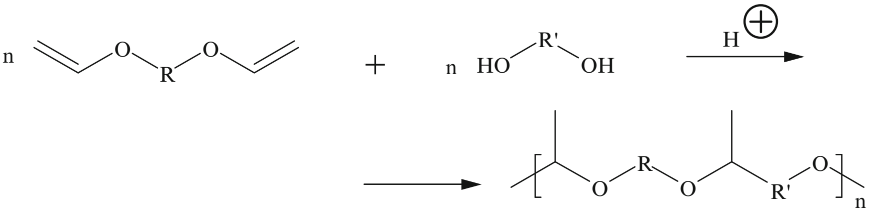
Acetals generally exhibit poor resistance to hydrolytic attack. Some, however, are much more resistant than others, depending upon the glycol. The following formal was reported to exhibit good hydrolytic stability under both acidic and basic conditions [109]:



Pentaerythritol yields spiro polymers by this reaction. The products offer superior thermal resistance [114]:



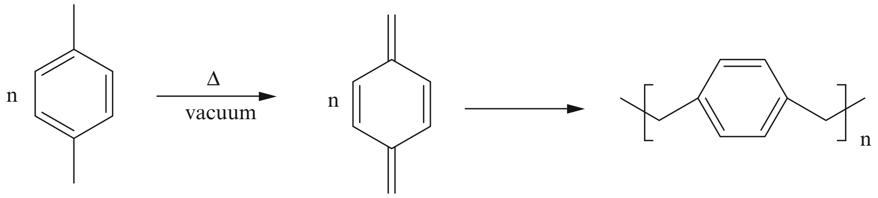
The addition of diols to dialkenes can be illustrated on addition of a glycol to a divinyl ether:



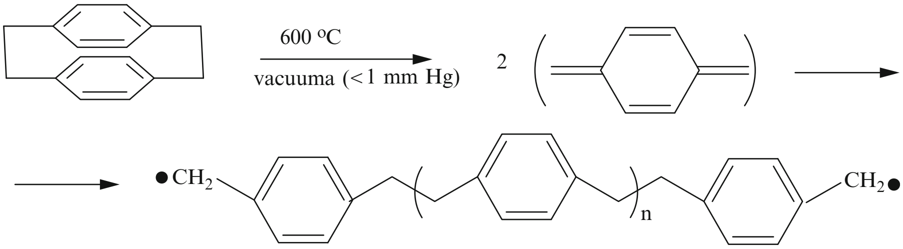
Commercially, large volume acetals are only produced by polymerizations of formaldehyde and by ring opening polymerizations of trioxane. These reactions are discussed in chapters three and four. Two such materials are manufactured in this country. One is a homopolymer of formaldehyde, polyoxymethylene. It is sold under a trade name of Delrin. The material is end-capped to prevent depolymerization by acetylating the terminal hydroxyl groups. The other one, a copolymer of formaldehyde with small quantities of a comonomer, is sold under the trade name of Celcon. Copolymerization accomplishes the same objective as end-capping. It also makes it more resistant to attacks by bases. Polyoxymethylene is highly crystalline. This is due to easy packing of the simple, polar chains. The crystallinity is estimated to be 60–77%. Polyoxymethylene is a strong material with good resistance to creep, fatigue, and abrasion.

7.8 Poly(*p*-xylylene)s

The original preparation of *p*-xylylene was carried out by vacuum pyrolysis of *p*-xylene at 900–950°C. The intermediate, *p*-xylylene polymerizes spontaneously upon condensation on cooler surfaces [106]:



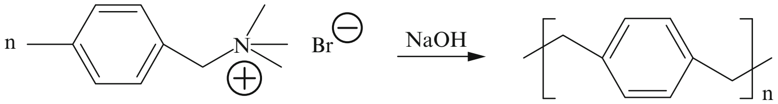
The process was improved by using di-*p*-xylylene as an intermediate [106]. This dimer converts to a polymer under milder conditions quantitatively. Both methylene bridges cleave to form *p*-xylylene, which is a reactive intermediate:



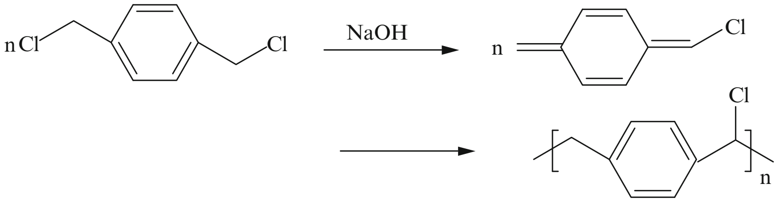
The molecular weights of these polymers were estimated to be as high as 500,000. The total process is sometimes called *transport polymerization*. Poly(*p*-xylylene) films are produced commercially. T_m of this polymer, which is crystalline, is 400°C and it carries the trade name of Perylene. Films of poly(*p*-xylylene) have only fair thermal stability and are brittle, but exhibit good chemical resistance and are very good electrical insulators. Pyrolysis of xylene in steam at 950°C yields the dimer intermediate. The yield is reported to be 15% [88].

It is possible to form substituted poly(*p*-xylylene)s by starting with substituted structures. Among the compounds that were reported were chlorinated and brominated compounds as well as some containing alkyl, cyano, acetyl, and carboxymethyl derivatives. When the di-*p*-xylylenes are unsymmetrically substituted, two homogeneous polymers form during pyrolysis because the two condense with spontaneous polymerization at two different temperatures [88].

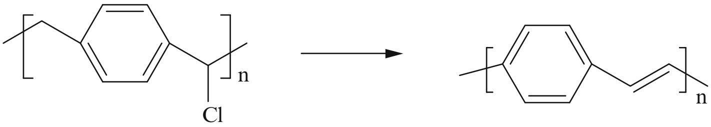
Poly(*p*-xylylene)s can also be prepared by other reactions. Among them is the condensation of trimethyl(*p*-methylbenzyl) ammonium halide in the presence of a base [47]:



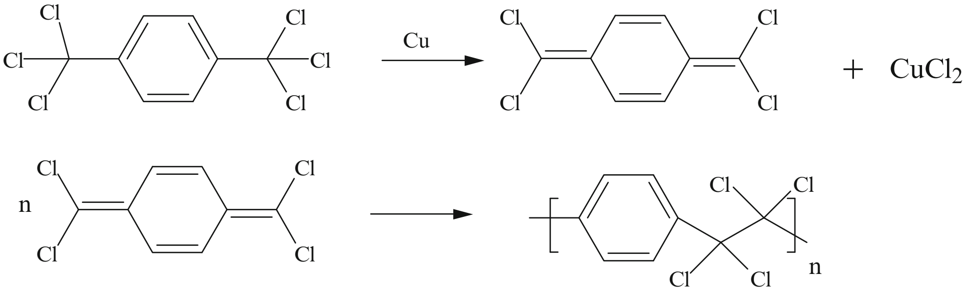
A route to a halogen-substituted polymer is through a reaction of di halo-*p*-xylylenes with caustic. It results in 1,6 elimination of HCl and formation of a chlorine-substituted poly(*p*-xylylene) [47]:



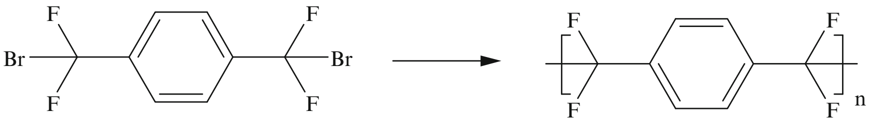
With excess caustic, however, all chlorine is removed and presumably an all-conjugated poly (phenylene vinylene) polymer forms [47]:



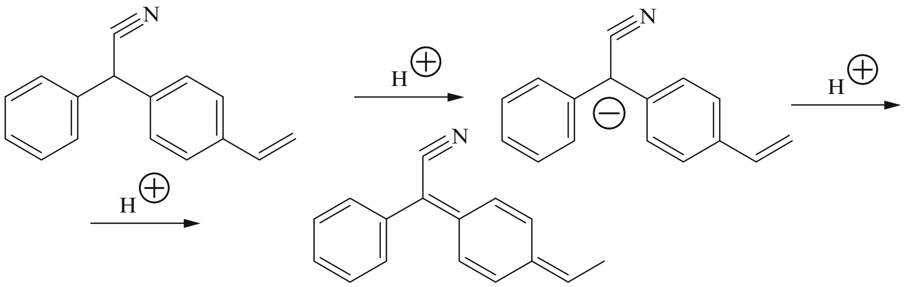
p-Bis(trichloromethyl) benzene can be pyrolyzed over copper gauze at 300–600°C temperatures to form α,α,α′,α′-tetrabromo-*p*-xylylene. This monomer polymerizes at temperatures just below 140°C [107]:



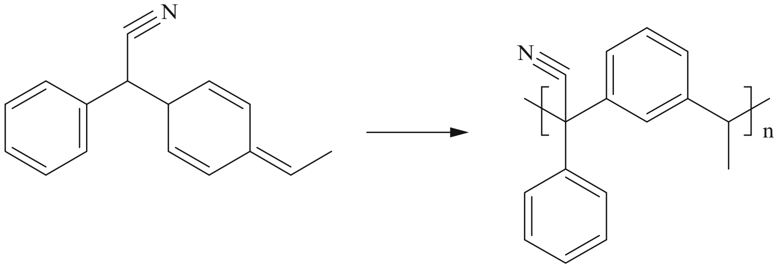
p-Xylylene polymers also form electrolytically [88] in dioxane-water solution with mercury or lead cathodes and carbon rod anodes. During the reaction, a quinone dimethide intermediate probably forms [88]. Many substituted polymers also form by this reaction [88]. Following is an example of one of them:



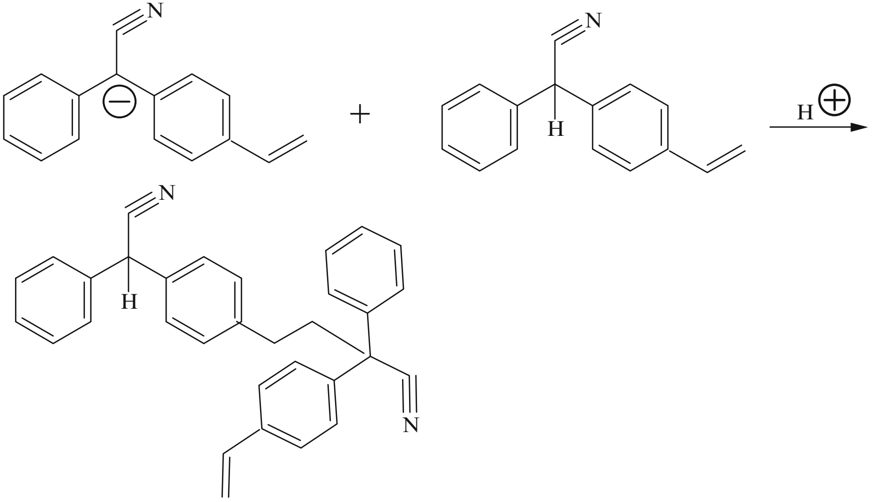
Another interesting synthesis is through an equilibration reaction of suitably substituted styrenes to *p*-xylylenes that spontaneously polymerize to linear polymers [108]. A suitable substituent can be a *p*-cyanophenylmethyl group. Such compounds undergo complete ionization and rearrange in the presence of a strong base:



The *p*-xylylene intermediate then polymerizes:



There are, however, competing side reactions, such as dimerization [108]:

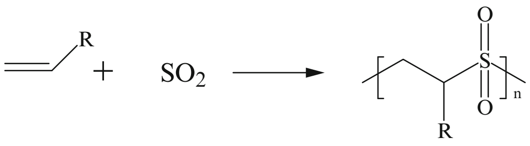


7.9 Sulfur-Containing Polymers

Industrially important sulfur-containing polymers are polysulfones and polysulfides. The materials differ considerably in properties and in use.

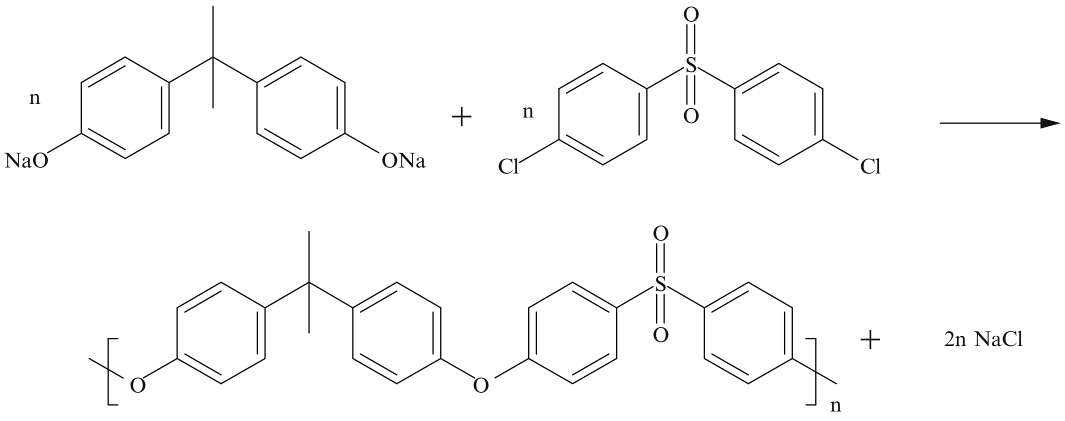
7.9.1 Polysulfones

These materials are an important group of engineering plastics. Aliphatic polysulfones were first synthesized at the end of the nineteenth century [109]. That synthesis was based on reactions of SO_2 with olefins:



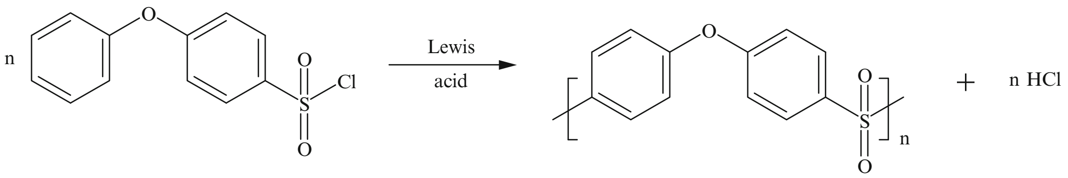
Aliphatic sulfones, however, lack good thermal stability and are not commercially important. Aromatic sulfones, on the other hand, have many desirable physical properties. They are clear, rigid, tough materials, with a high T_g. Several aromatic sulfones are prepared commercially.

The original preparation of aromatic polysulfones was described in 1958 [110]. This was followed by investigations of many different structures of polysulfones. One current commercial material is a condensation product of 2,2′ bis(hydroxyphenyl) propane with 4,4′-bis(chlorophenyl) sulfone. It forms by a Williamson synthesis, because the reactivity of the halogens is enhanced by the sulfone groups [47]:

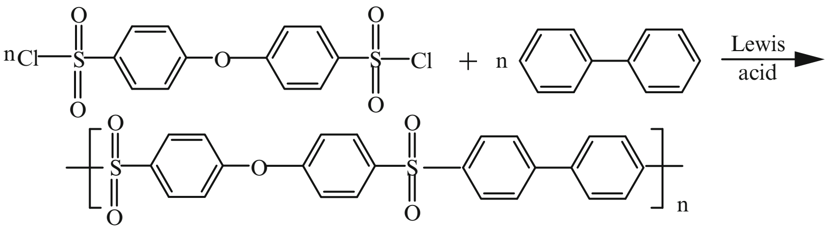


The condensation takes place at 160°C in an inert atmosphere and in some suitable solvents, like chlorobenzene. Commercially, polymers are available in molecular weight ranges from 20,000 to 40,000. Much higher molecular weight materials, however, form readily.

Aromatic polysulfones also form by the Friedel–Craft reaction [111], as for instance:

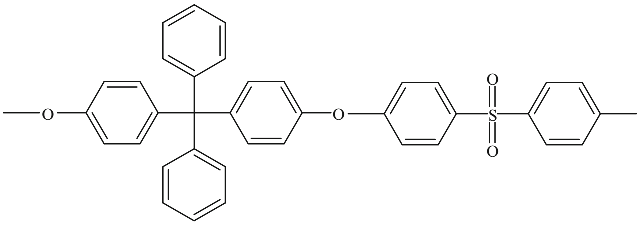
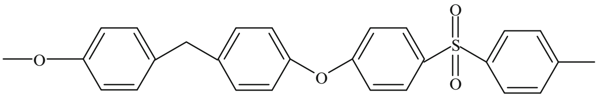
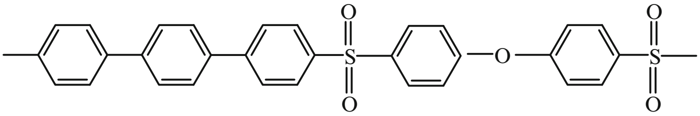
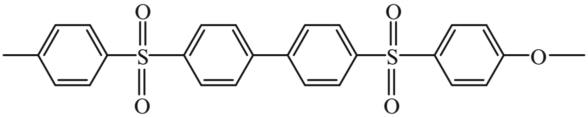
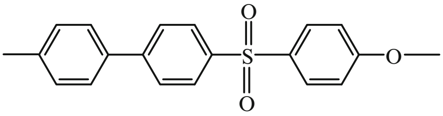
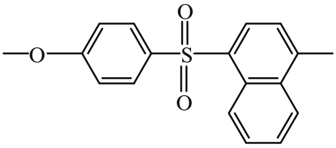


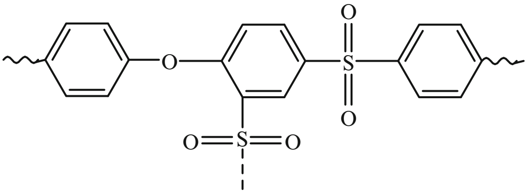
or



The reaction takes place at 80–250°C in a solution or in the melt. Lewis acid catalysts are used in concentrations of 0.1–1.0 mole percent. Cross-linking through polysubstitution does not appear to be a problem. Some chain branching, however, does occur because *ortho* substitution is possible:

Table 7.6 Relative T_g values of some aromatic polysulfones [121]

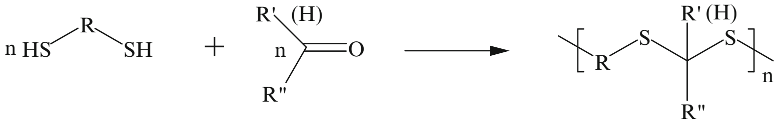
Polymer repeat unit	T_g (°C)
	220
	180
	290
	280
	265
	230



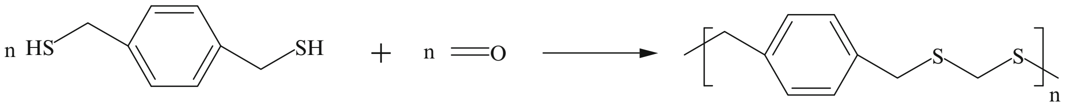
It is estimated, however, that the *ortho* substitution amounts to not more than 5–10%. Removal of the catalyst after the reaction is tedious. Table 7.6 presents the T_g values of some aromatic polysulfones.

7.9.2 Polythiols and Polymercaptans

These polymers form from reactions of di thiols with aldehydes or ketones:

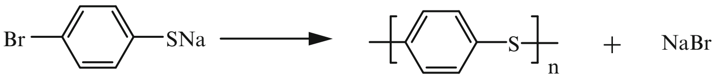


This reaction is used commercially to prepare an aromatic polymercaptan from *p*-bis (mecaptomethyl)benzene:

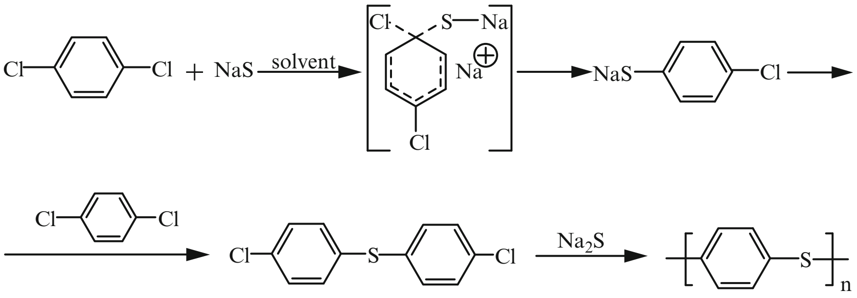


The polymer melts at 150°C and can be spun into fibers [109].

Another polymercaptan, poly(phenylene sulfide), can be prepared by several routes. This polymer forms from sodium *p*-bromothiophenol at 250–305°C [109]. It has good thermal resistance and melts at 287°C.



It also forms by a reaction of dichlorobenzene with sodium sulfide [110]. To date, the exact mechanism of this polymerization, which is carried out commercially in *N*-methylpyrrolidone solution, has not been fully established. Recent evidence indicates that in this solvent, an ionic, step growth S_NAr mechanism predominates [110]:



The polymer possesses a broad, high melting point and a glass transition temperature of ≈85°C.

An important characteristic of poly(phenylene sulfide) is its ability to undergo changes upon heating [110]. This change is complex and not completely understood. It appears to involve varying degrees of oxidation, cross-linking, and chain scission. When heated from 315 to 415°C, the polymer melts, thickens, gels, and eventually solidifies to a dark infusible solid. This curing phenomenon makes the polymer useful in many applications that range from coatings (powder or slurry) to molding (by injection, compression, or sintering). Poly(phenylene sulfide) also becomes highly conductive electrically when a dopant is added. Conducting polymers are discussed in Chap. 8.

Elastomers, based on *poly*(*alkylene sulfide*)*s*, are still another group of sulfur-containing polymers. They can be represented by a general structural formula of:

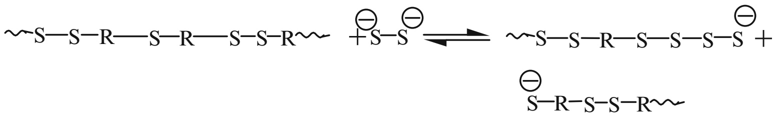
$$-[-\mathrm{R}-\mathrm{S}_x-]_n- \quad \text{where } x = 2-4$$

The most widely used methods of preparation are based on reactions of sodium polysulfides with alkyl dichlorides [110]:

$$n\mathrm{Cl}-\mathrm{R}-\mathrm{Cl} + \mathrm{Na_2S}_x \rightarrow -[-\mathrm{R}-\mathrm{S}_{x}-]_{n}- + 2n\mathrm{NaCl}$$

These reactions are usually carried out in dispersions. An aqueous sodium polysulfide containing a surfactant, like alkyl aryl sulfonate, sodium hydroxide, and magnesium chloride, is heated to 80°C.

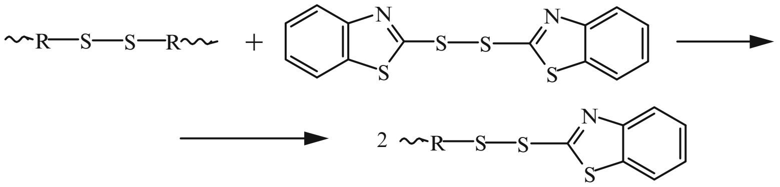
The magnesium chloride forms magnesium hydroxide and acts as a nucleating agent. Bis(2-chloroethyl) formal is then added over 2 h with stirring and external cooling of the exothermic reaction to about 90°C. After addition, this temperature and stirring are usually maintained for additional 2 h to complete the process. The product contains a distribution of polysulfide groups. The polysulfide anions can interchange continuously:



$$\sim S-S-R-S-R-S-S-R\sim + {}^{\ominus}S-S^{\ominus} \rightleftharpoons \sim S-S-R-S-S-S-S^{\ominus} + {}^{\ominus}S-R-S-S-R\sim$$

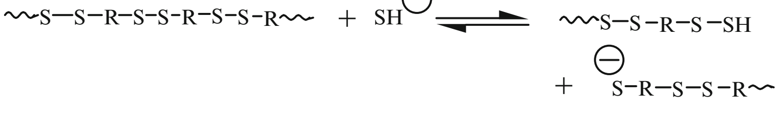
This allows building up the molecular weights of the polymers by additions of excess polysulfide. Also, low molecular weight fractions can be washed out. By such manipulations, molecular weights of 500,000 are readily achieved. It is interesting that in this particular step-growth polymerization, in order to obtain high molecular weights, strict stoichiometry is not only not required, but one of the components is deliberately added in excess.

Several different grades of poly(alkyl sulfide)s are available commercially. One form, hydroxyl-terminated, is formed by coagulating the formed polymer from the aqueous dispersion with sulfuric acid. The terminal halogens hydrolyze in the process to hydroxyl groups. For easier processing, these elastomers are usually reacted with disulfide like benzothiazyl disulfide. This reduces the molecular weight through chain cleavage:



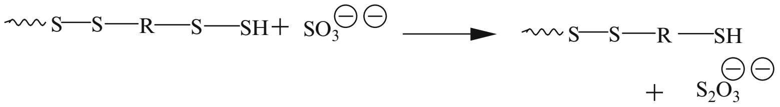
The elastomers are then chain-extended again with metal oxides, like zinc oxide, that couple the terminal hydroxy groups. The same thing can also be done by using diisocyanates.

Another group consists of thiol-terminated, low molecular weight polymers. They form from heating alkyl sulfides in aqueous dispersion of sodium bisulphite and sodium sulfite for about an hour at 80°C. This results in mercaptide and thiothiol terminal groups:



$$\sim S-S-R-S-S-R-S-S-R\sim + SH^{\ominus} \rightleftharpoons \sim S-S-R-S-SH + {}^{\ominus}S-R-S-S-R\sim$$

The sulfite ion prevents the reversal of the equilibrium by splitting of the sulfur from the thiothiol:



$$\sim S-S-R-S-SH + SO_3^{\ominus\ominus} \longrightarrow \sim S-S-R-SH + S_2O_3^{\ominus\ominus}$$

These polymers cross-link by oxidative coupling of the mercaptide groups:

$$\sim SH + [O] + HS\sim \longrightarrow \sim S-S\sim + H_2O$$

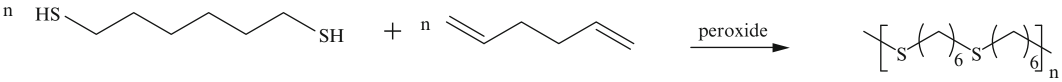
and by reactions with metal peroxides like lead peroxide. They also react with epoxy resins.

Poly(alkylene sulfide)s are exceptionally oil-resistant elastomers. They also exhibit good resistance to solvents and to weathering. On the other hand, these elastomers lack the strength of synthetic rubbers and possess an unpleasant odor.

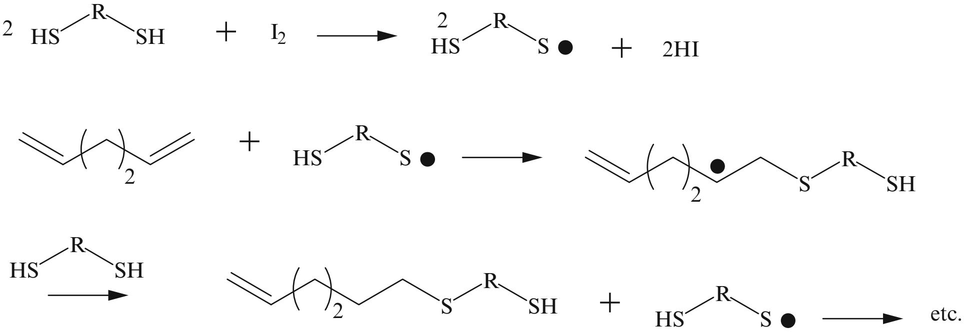
Aliphatic polysulfides also form from reactions of di thiols with alkyl dihalides. High molecular weight polymers, however, are hard to form [109]:

$$n\ \mathrm{NaS{-}R{-}SNa} + n\ \mathrm{Br{-}R'{-}Br} \longrightarrow \left[\mathrm{S{-}R{-}S{-}R'}\right]_n + 2N\ \mathrm{NaBr}$$

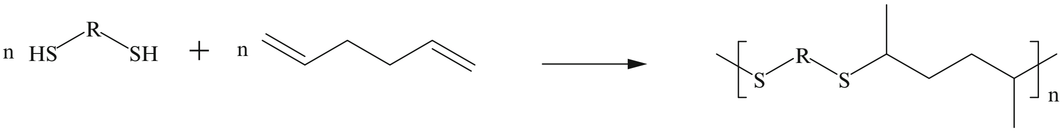
Similar polymers form through addition of di thiols to diolefins [109]. The reaction can take place either by a free-radical mechanism or by an ionic one. A free-radical mechanism requires presence of peroxides to achieve counter Markownikoff additions across the double bonds:



It is a step-growth polymerization process. The additions to the double bonds involve a series of hydrogen exchange reactions [108]:

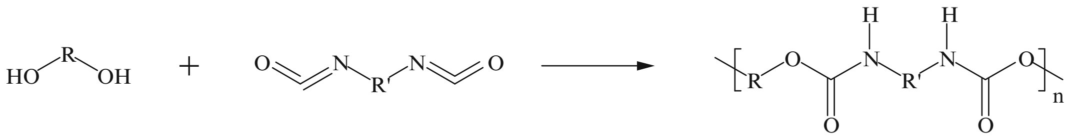


When additions take place by ionic mechanisms, they are catalyzed by either acids or bases. These additions follow the Markownikoff rule:

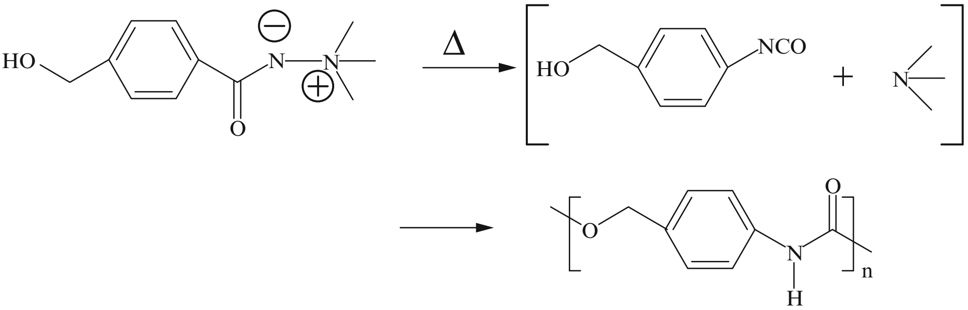


7.10 Polyurethanes

The polyurethanes [126, 132] are sometimes also called “isocyanate polymers.” They are characterized by the urethane linkage. Other functional groups, however, may be present in the polymer as well. The urethane linkages can be produced in polymers by several different routes. Among these, the most common ones are through reactions of the isocyanate groups with compounds bearing hydroxyl groups. Such compounds may be glycols, dihydroxy-terminated polyethers or polyesters, and others. Difunctional reactants will produce linear polyurethanes:



A special method for the preparation of polyurethane polymers was reported [245]. In this new procedure, use is made of "latent" aminimide monomers that are stable and not reactive under normal storage conditions. An example is a monomer, an aminimide, like 1,1,1-trimethylamine 2-(4-hydroxymethylbenzoyl)-imide that undergoes self-polyaddition above 150°C to yield the polyurethane [245]:



The above monomer can be prepared by reacting methyl *para*-hydroxymethyl-benzoate with I,l,l-trimethylhydrazinium *p*-toluene sulfonate, catalyzed by sodium methoxide. At 170°C, 90% of this monomer converts to polymer in 5 h [245].

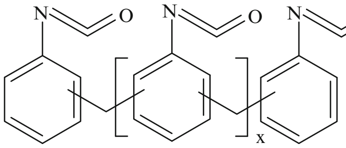
7.10.1 Preparations of Polyfunctional Isocyanates

Polyfunctional isocyanates can be formed in many ways [122]. Commercially, the most important one is through reactions of phosgene with amines or amine salts. Other reactions, however, like that of carbon monoxide with nitro compounds are also utilized. Additions of isocyanic acid to olefins are also gaining prominence.

7.10.2 Commercial Polyisocyanates

Two types of diisocyanates are employed in polymer preparations, aromatic and aliphatic ones. The most commonly used aromatic diisocyanates are toluene diisocyanate and 4,4′-diphenylmethane diisocyanate. Commercial toluene diisocyanate often comes as a mixture of 2,4 and 2,6 isomers in ratios of 80/20 or 65/35. When the reaction takes place at room temperature, the four position is 8–10 times more reactive than two. At elevated temperatures, however, this difference in reactivity decreases, and at 100°C the reactivity of the isocyanate groups in both positions is approximately equal.

Phosgenation of aniline-formaldehyde condensates yields isocyanates with a functionality that averages 2.6–2.8. The structure of the product can be shown as follows:



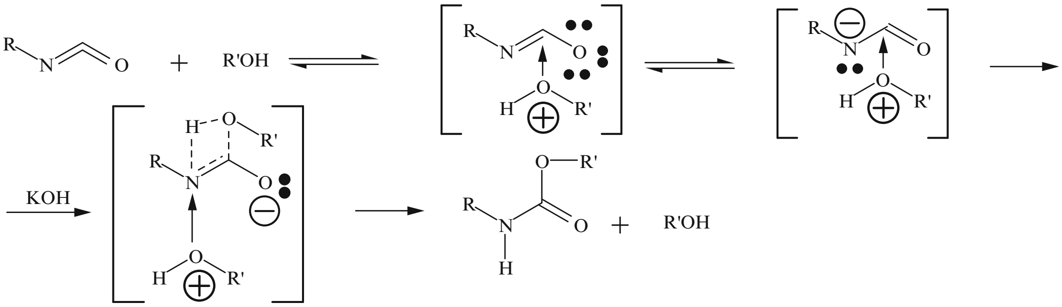
where, x =2 or 3

Among other aromatic diisocyanates that are in commercial use are *p*-phenylene diisocyanate, *m*-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3′-dimethyl-4,4′-bisphenylene diisocyanate, 4,4′-bis(2-methylisocyanophenyl)-methane, and 4,4′-bis(2-methoxyisocyanophenyl) methane.

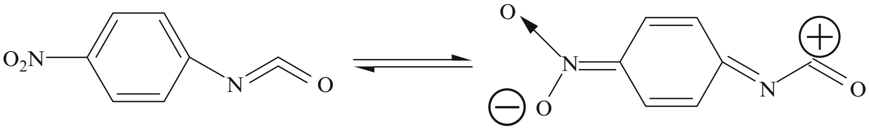
The common aliphatic diisocyanates are hexamethylene diisocyanate, hydrogenated (H_{12}) 4,4′-dipenylmethane diisocyanate, isophorone diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, and 2,4,4-trimethylhexamethylene diisocyanate. Other aliphatic diisocyanates that are commercially used are lysine diisocyanate, methylcyclohexyl diisocyanate, isopropylidine bis-(4-cyclohexyl isocyanate), and tetramethylene diisocyanate. Many additional polyfunctional isocyanates are described in the literature.

7.10.3 Chemical Reactions of the Isocyanates

These reactions can be divided into two categories. They are additions to compounds with active hydrogens and self-condensation. The reactions are well described in organic chemistry textbooks, so there is little reason to describe them here. It is noteworthy, though, that the uncatalyzed reactions of isocyanates with various active hydrogen compounds are probably broadly similar. Among them, the most investigated reactions are the ones of alcohols with isocyanates [123]:



Electron withdrawing substituents increase the positive charge on the isocyanate carbon and move the negative charge further away from the site for the reaction:



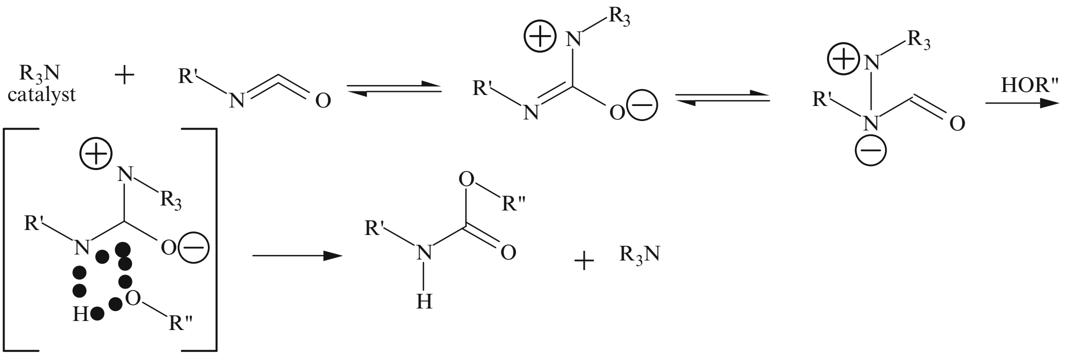
This makes an attack by an electron donor easier and yields a faster reaction. Electron donating groups, therefore, have an opposite effect.

Table 7.7 Relative effects of catalysts on reactivity of phenylisocyanate [126, 127, 132]

Catalyst	Relative rates of reactions with *n*-butyl alcohol
None	1.0
N-Methyl morpholine	4.0
Triethyl amine	8.6
Triethylene diamine	120.0
Tributyltin acetate	30,000
Dibutyltin diacetate	60,000

7.10.4 The Effect of Catalysts

Catalysts exert strong influence on the rates of reactions of isocyanates with active hydrogen compounds. Most widely used ones are tertiary amines and metal salts, particularly tin compounds. The mechanism of catalysis by tertiary amines is believed [124–126] to proceed according to the following scheme:



The catalytic activity of the tertiary amines generally parallels their base strength, except when steric hindrance is pronounced. Tin compounds exert much stronger catalytic effects on the reactions than do tertiary amines. This is illustrated in Table 7.7. The mechanism of catalysis by metal salts is believed to operate as follows [128]:

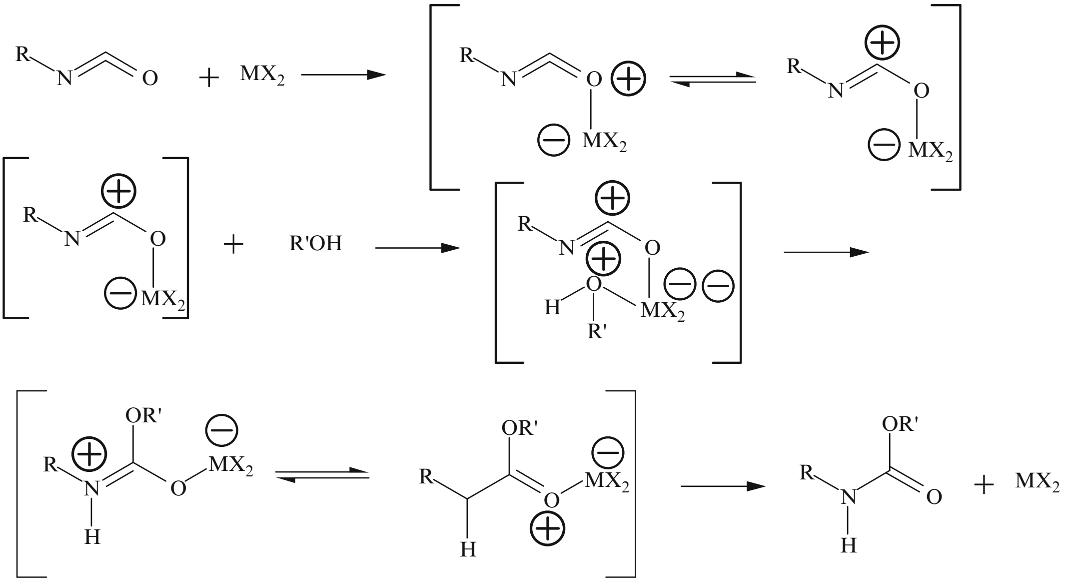


Table 7.8 T_m values of some fiber-forming polyurethanes [126, 132]

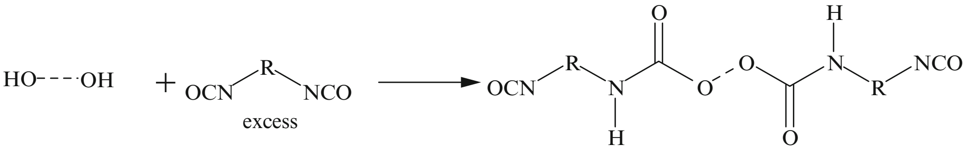
Diisocyanate	Glycol	T_m (°C)
$OCN(CH_2)_4NCO$	$HO(CH_2)_4OH$	190
$OCN(CH_2)_4NCO$	$HO(CH_2)_6OH$	180
$OCN(CH_2)_4NCO$	$HO(CH_2)_{10}OH$	170
$OCN(CH_2)_5NCO$	$HO(CH_2)_4OH$	159
$OCN(CH_2)_6NCO$	$HO(CH_2)_4OH$	183
$OCN(CH_2)_6NCO$	$HO(CH_2)_5OH$	159
$OCN(CH_2)_8NCO$	$HO(CH_2)_4OH$	160
$OCN(CH_2)_8NCO$	$HO(CH_2)_6OH$	153

Table 7.9 The effect of molar ratios on the molecular weight of the product [134–136]

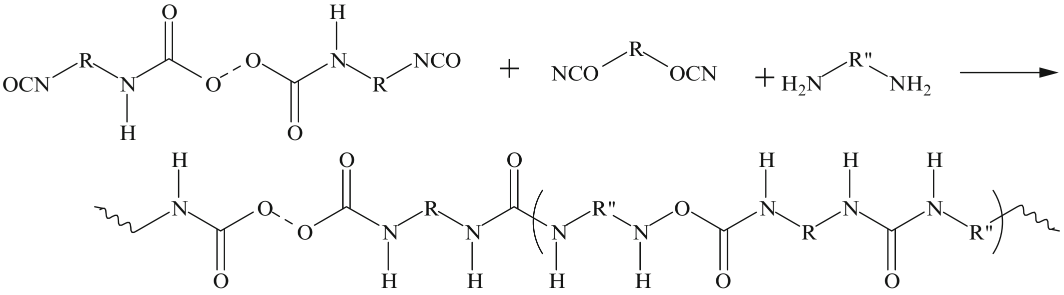
Ratio of epichlorohydrin to phenol	Molecular weight
10.0:1	370
2.0:1	451
1.4:1	791
1.33:1	802
1.25:1	1,133
1.2:1	1,420

7.10.5 Polyurethane Fibers

Originally, the main interest in polyurethanes was in preparation of fibers. They tend to resemble aliphatic polyamides, though these fibers are harder to dye, are wiry, and hard to handle. The common preparatory procedure is to add continuously the diisocyanate to the glycol while letting the temperature rise slowly to 200°C. The reaction is exothermic and excess heat must be removed. An inert nitrogen atmosphere is maintained over the reaction mixture. Table 7.8 lists T_m values of some aliphatic polyurethanes. Today, there is much less interest in polyurethane fibers. One polyurethane fiber that was commercialized sometime between 1960 and 1965 is a unique elastomeric material for expandable textiles. It is an alternating block copolymer of "soft" and "hard" segments. The "soft" segments form from hydroxyl-terminated aliphatic polyethers or polyesters of molecular weight between 1,000 and 4,000. They are linked with "hard" segments by urethane linkages. The "hard" segments form from aromatic diisocyanates and aliphatic or aromatic diamines. Hydrazine or hydrazine derivatives are sometimes used as chain extenders in place of the diamines. A preparation can be described as follows. Macro glycols are reacted first with an excess of the diisocyanate:



The reaction mixture is then chain-extended with a diamine:

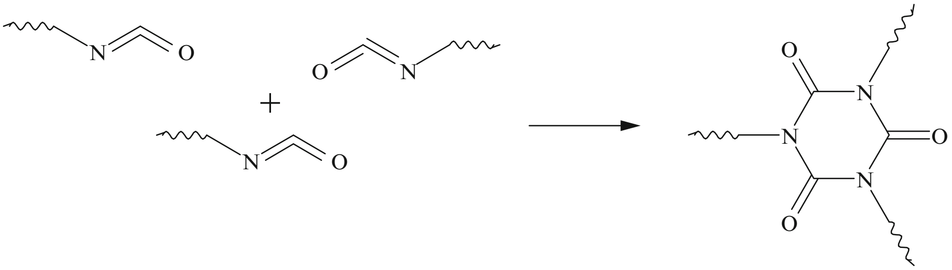


The prepolymers are spun into fibers and subsequently cross-linked, or cross-linked while they are being spun, to obtain resilient elastomeric fibers.

7.10.6 Polyurethane Elastomers

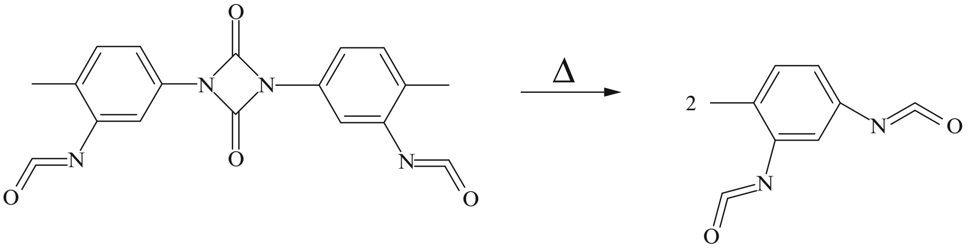
Solid elastomers can be divided into three categories, namely cast, millable, and thermoplastic ones. The cast elastomers are formed by casting liquid reaction mixtures of low molecular weight prepolymers into heated molds where they cross-link and convert to high molecular weight materials. Slightly branched polyesters are combined first with diisocyanates, like toluene diisocyanate, to form the prepolymers and degassed in a vacuum at elevated temperature (about 70°C). The reaction mixtures are then poured into molds and heated for several hours at about 110°C to form solid elastomers. These elastomers are soft and resilient, but they lack good mechanical strength.

Elastomers with better mechanical strength form from linear, hydroxyl-terminated polyesters or polyethers. These macro glycols are also prereacted first with the diisocyanates, similarly to the procedure used for expandable fibers. The products, however, are mixed with low molecular weight glycols or diamines and then heated in molds at 110°C for 24 h. Slightly less than stoichiometric amounts of glycols or diamines are used so that the polymers are terminated with isocyanate groups. These terminal isocyanate groups react in the mold with urethane hydrogens to form allophanate cross-links. Trimerization of the isocyanate groups might also take place, though this usually requires a catalyst to form at temperatures below 130°C:



The concentrations of the allophanate links vary with the time of cure [129]. Also, if the cross-linking reactions are conducted in inert nitrogen atmospheres, very little scission of cross-links takes place and a network structure forms during the cure. In open air, however, the scissions of cross-links are extensive [129] and the products have poorer physical properties.

A drawback to the cast elastomers is limited shelf life and a need to store them in the absence of moisture. As a result, millable elastomers were developed. These are produced by first forming hydroxy-terminated linear polyurethanes through reactions of linear aliphatic polyesters or polyethers with diisocyanates. The prepolymers are rubbers or gums that can be compounded on rubber mills with other ingredients and cross-linked. Cross-linking is accomplished by adding either more diisocyanates, or sulfur, or peroxides. Diisocyanates dimers that dissociate at about 150°C are often used:



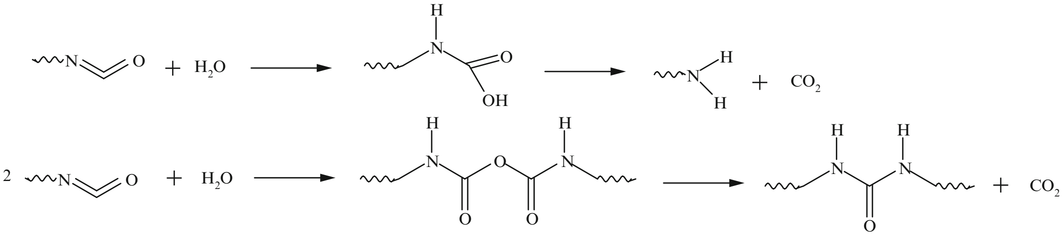
Unsaturated prepolymers cross-link with peroxides or sulfur. This unsaturation can be present in the backbone or in the pendant groups. Vulcanization or cross-linking of elastomers with sulfur or peroxides is discussed in Chap. 8.

Thermoplastic elastomers exhibit physical properties that are similar to those of cast and millable elastomers at ambient temperatures. These materials, however, are not cross-linked and flow at elevated temperatures. They are fabricated like other thermoplastic polymers, are high in molecular weight, and are hydroxyl-terminated. Such polymers form from linear hydroxyl-terminated polyester or polyethers that are condensed with diisocyanates and glycols. Strict stoichiometry must be maintained to achieve high molecular weights.

A structure study was carried out on a model compound of one elastomer [130] prepared with 4,4′-diphenylmethane diisocyanate and butanediol hard segments. It was shown that the chains are probably linked together in stacks through C=O···H–N hydrogen bonds between the urethane groups. This bonding stabilizes the overall structure in both directions, perpendicular to the chain axis. Such an arrangement of the molecules was also proposed earlier [131].

7.10.7 Polyurethane Foams

These foams are chemically very similar to other polyurethane materials, except that gas evolutions during the reactions take place simultaneously with chain lengthening and cross-linking. This results in formation of cellular structures. The degree of cross-linking determines to a great extent the rigidity of the foam. In addition, linear or only slightly branched polymers produce flexible foams, while more highly branched polymers form rigid ones. The foaming is caused by liberation of CO_2 from reactions between added water and isocyanate groups:



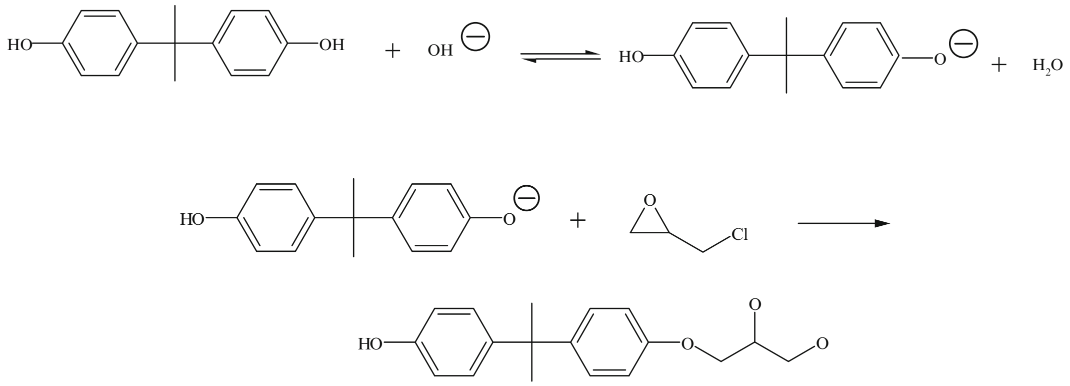
In addition, in many industrial practices, additional carbon dioxide or Freon gas (a major source of environmental pollution) may be introduced into the system as it cures. For rigid foams, a low boiling liquid may be added to form additional bubbles. Appropriate catalysts and foam stabilizers or surfactants are added to control foam formation, cell size, and cure. The catalysts are either tin compounds or tertiary amines. The surfactants that are necessary to control the cell size are usually based on siloxanes.

7.11 Epoxy Resins

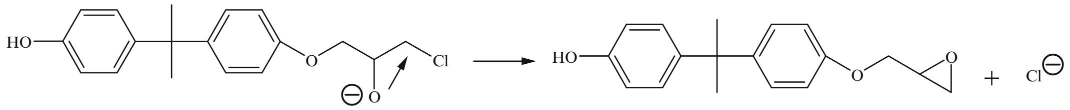
These resins comprise a general class of cross-linkable, low molecular weight materials with epirane rings as the main functional group [134, 135]. It does not include polyethers formed through ring opening polymerizations of ethylene and propylene oxides.

7.11.1 Preparation of Commercial Epoxy Resins

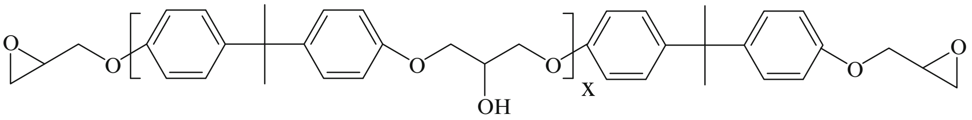
The earliest developed commercial epoxy resins were diglycidyl ethers of 4,4′-isopropylidine-diphenol (Bisphenol A) formed by reacting epichlorohydrin with the diphenol. The reaction sequences involve formations of alkoxide ions, followed by nucleophilic additions to the least hindered carbons [134]:



This is followed by ring closures through internal displacement of chloride ions:



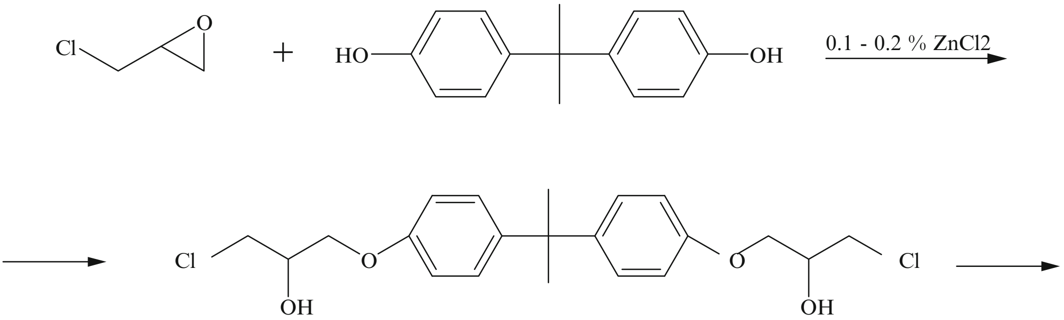
As explained in the discussion on phenoxy resins, a reaction of two moles of epichlorohydrin with one mole of the diphenol yields higher molecular weight by-products and only 10% of the diether:

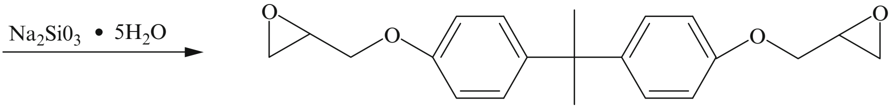


where $x = 1–10$

To obtain high yields of the diether, the quantities of epichlorohydrin in the reaction mixtures must be doubled or tripled [131]. This can result in yields as high as 70%. Another advantage of a large excess of epichlorohydrin in the reaction mixtures is that it serves as a solvent [134].

A different route to the diglycidyl ethers is via Friedel–Craft reactions [135]:





The higher molecular weight resins that form in the presence of caustic result from reactions of glycidyl ethers with phenoxy anions:

The number of repeat units in the above resin is determined by the molar ratios of the reactants. This is illustrated in Table 6.9.

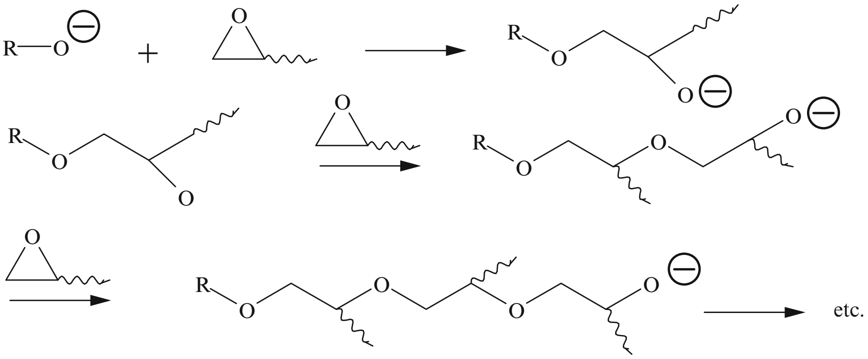
7.11.2 The Cross-linking Reactions

Diglycidyl ethers of Bisphenol A cannot be cross-linked through heating alone. Chemical cross-linking agents must be added. Most commonly used compounds are tertiary amines, polyfunctional amines, and acid anhydrides. Lewis acid, phenols, and compounds like dicyandiamide, however, are also used.

The reactions between tertiary amines and epoxy groups result in formations of quaternary bases:

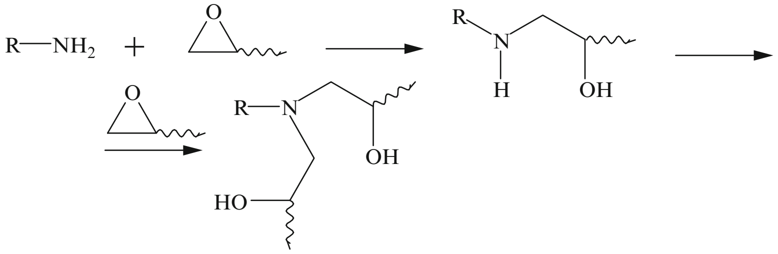
The product reacts with hydroxyl compounds to form anions:

The anions in turn initiate polymerizations of the epoxy groups:

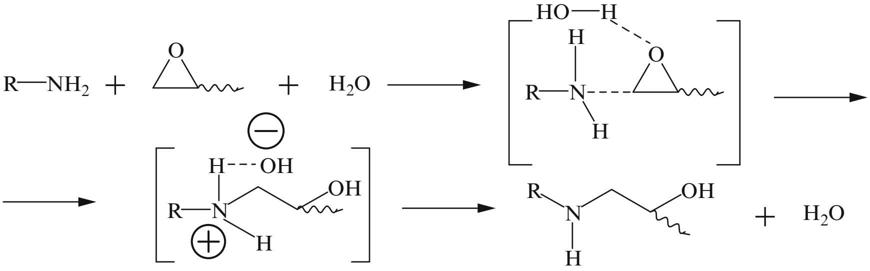


Because the monomer is a diepoxide, a three-dimensional lattice results. A similar three-dimensional product forms from reactions with other cross-linking materials, like boron trifluoride-etherate, boron trichloride-amine complexes, and imidazole derivatives. All these compounds initiate polymerizations of the epirane ring.

Cross-linking of the epoxy resins with primary and secondary amines is somewhat different because they react by nucleophilic addition to the epirane ring:



A considerable amount of evidence suggests that this reaction is accelerated by proton donors. Such donors may be water, phenols, or alcohols [136]:

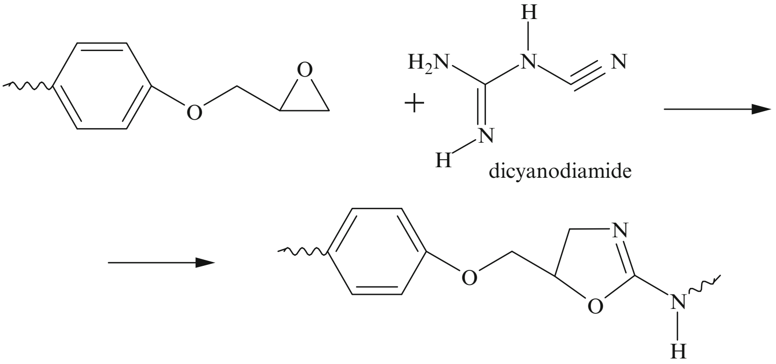


Epoxy resins can also be cured with the aid of ionic liquids [136]. The cross-linking reaction takes place at elevated temperatures

Highly idealized pictures of reaction products from Bisphenol A diglycidyl ethers with diamines can be found in the literature [137]. In actuality, the products are probably more complex. They are certainly complex when reactions involve higher molecular weight epoxy resins.

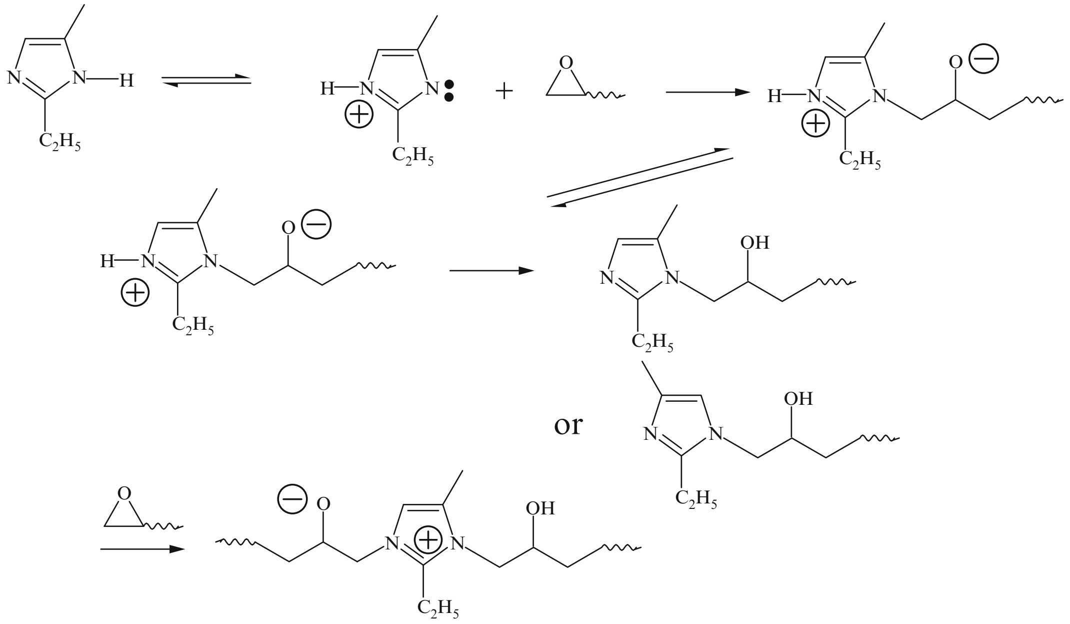
Many different aliphatic and aromatic polyamines are available for cross-linking epoxy resins. Some of these are ethylenediamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, and many others. Among the aromatic polyamine are *p*-phenylene diamine, *m*-phenylene diamine, 4,4′-diaminodiphenyl-methane, and diaminodiphenylsulfone.

A special cross-linking agent for epoxy resins is dicyanodiamide, also referred to by its trade name as cyanoguanidine. It is used for high temperature cures and it is believed that the compound condenses with the epirane structures to form 2-aminooxazoline derivatives [137]:

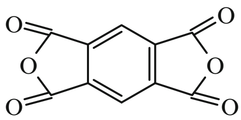


Earlier, however, it was speculated that guanidyl urea forms [140].

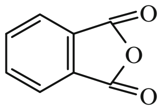
The curing mechanism of epoxy resins with imidazole was investigated. The following mechanism was proposed [137]:



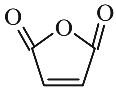
Many cyclic acid anhydrides are used industrially for cross-linking epoxy resins. These are mono and polyanhydrides. Following are some typical commercially used anhydrides:



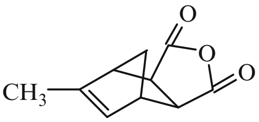
pyromellitic dianhydride



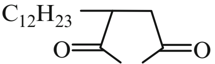
phthalic anhydride



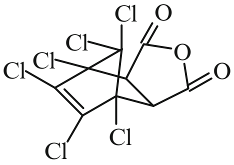
maleic anhydride



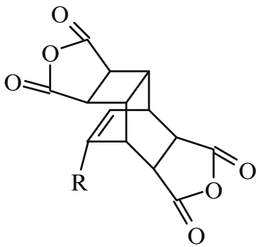
methylbicyclo [2,2,1]hept-5-ene-2,3-dicarboxylic acid anhydride



dodecylsuccinic anhydride

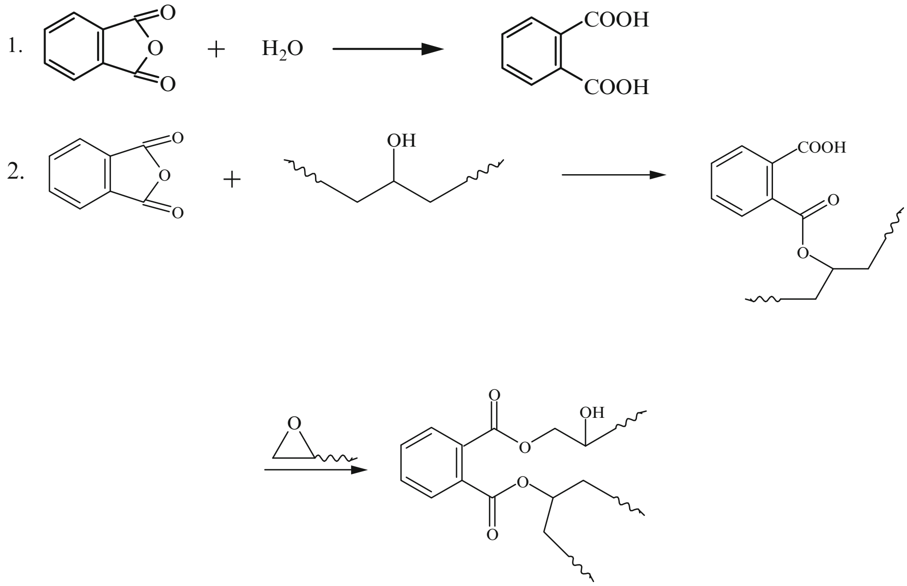


chlorendic anhydride

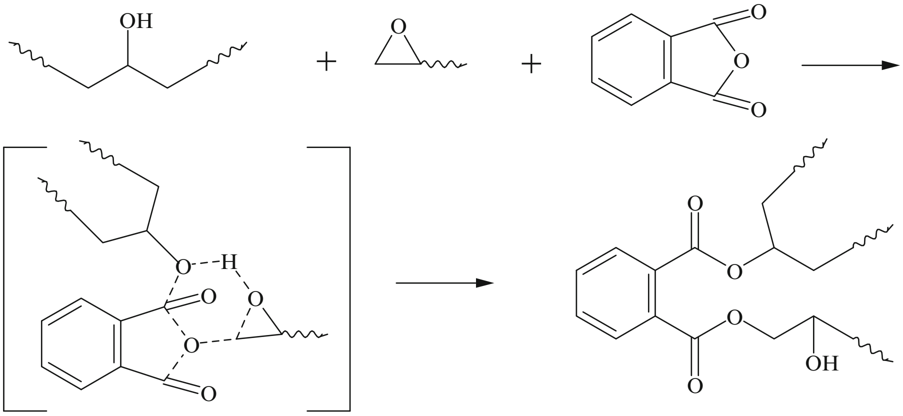


photoadduct of alkylbenzene and maleic anhydride[138]

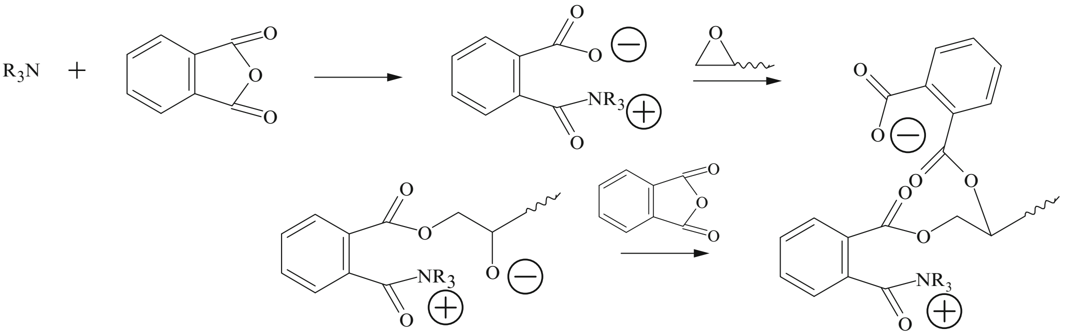
The anhydrides react with traces of moisture or with pendant hydroxyl groups first. This opens the anhydride groups and frees the carboxylic acids for reactions with the epoxy rings:



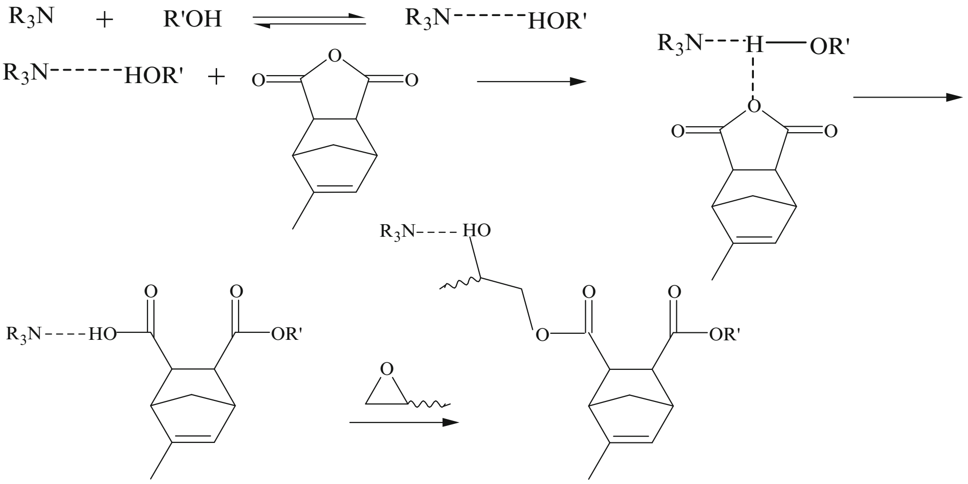
When only epoxy and hydroxyl groups are present, very little reaction takes place even at elevated temperatures, as high as 200°C. Proton donors, however, catalyze the reaction [139]. When anhydrides are present in the reaction mixtures, diesters form as a result of termolecular transition states. Kinetic data support that [136]:



Tertiary amines are very effective in catalyzing reactions of anhydrides with epoxies:

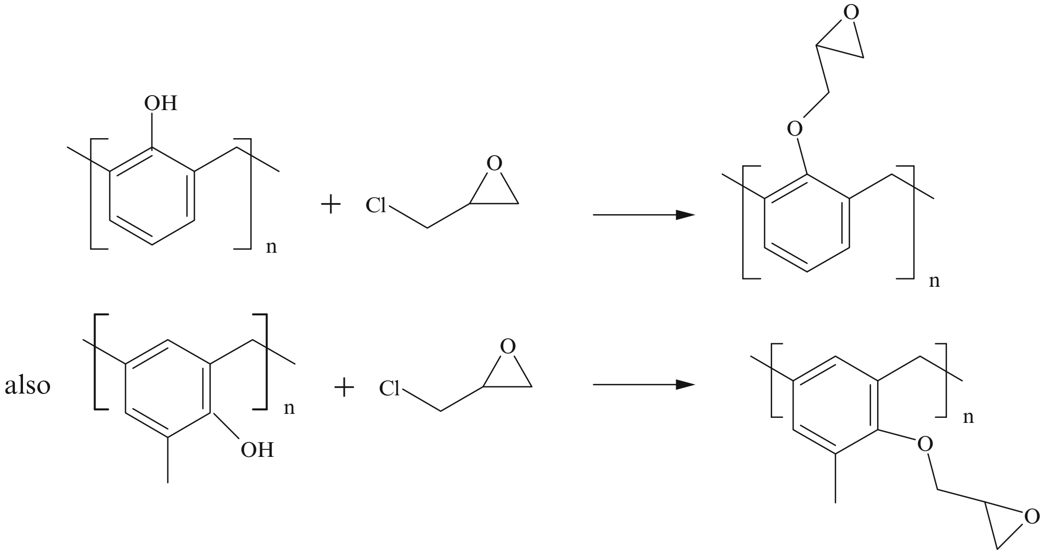


Reactions in the presence of alcohols take a somewhat different path [142, 143]:

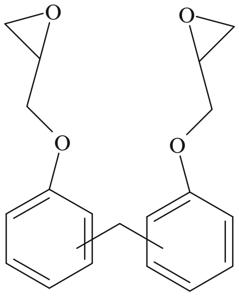


where, R′OH represents both epoxide molecules with hydroxyl function and other alcohols in the system.

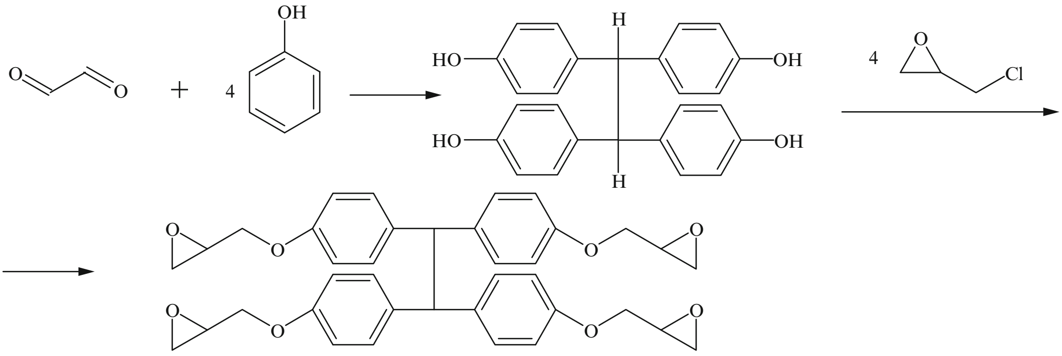
Another similar group of epoxy resins, called *epoxy novolacs*, forms from reactions of epichlorohydrin with low molecular weight phenolic novolacs (phenolic novolac resins are discussed in the next section):



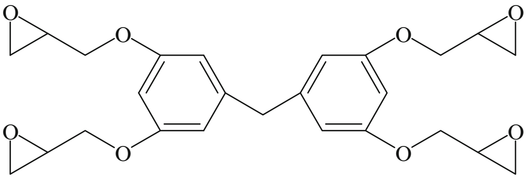
where, *n* is typically 2.2–3.8 for liquid epoxy novolacs and 3–7 for solid resins. Epoxy resins are also prepared commercially from Bisphenol F that is a blend of *ortho* and *para* diphenol methanes:



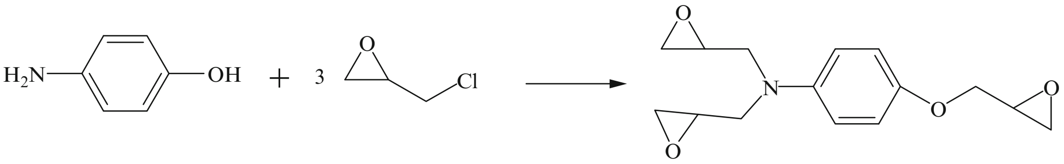
Another material is based on a condensation product of glyoxal with phenol:



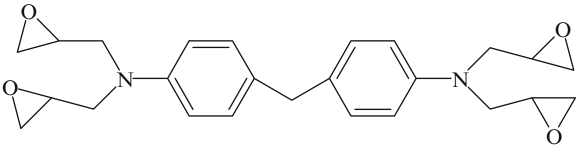
Epoxy resins formed by condensations of epichlorohydrin with resorcinol-based phenolic resins are also formed commercially:



Several nitrogen-containing aromatic epoxy resins were also commercialized. These are condensation products of aromatic amines with epichlorohydrin. Following are some examples [140]:



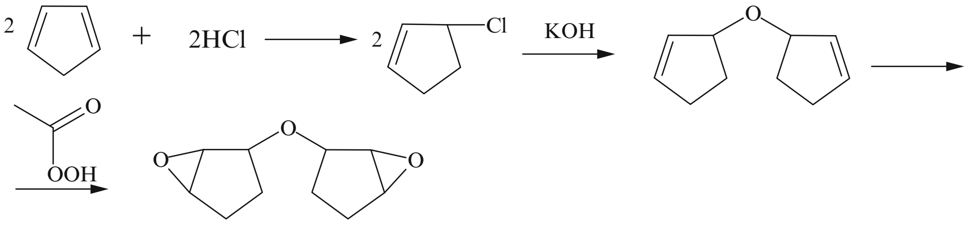
as well as:



The cross-linking reactions of tetrafunctional epoxy resins with aromatic primary diamines were investigated by spectoscopy [141]. UV-Visible and fluorescence spectroscopies of the materials, after gelation, show significant amounts of amines in the finished products. The infrared spectra also show that ether formation becomes significant only late in the cure. In addition, during the cure, especially in air, some oxidations and degradations occur [141]. This results in color formation.

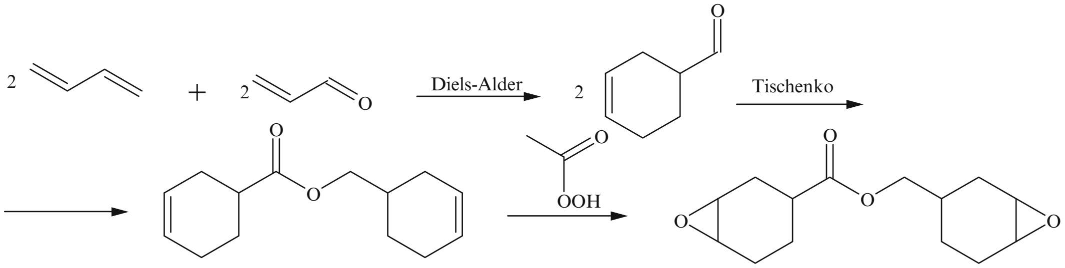
7.11.3 Cycloaliphatic Epoxides

Many cycloaliphatic epoxies are products of oxidation of cyclic olefins with peracids, like peracetic. These materials were commercialized over the years for use as active diluents, though later some were withdrawn. One commercial group of resins is obtained from cyclopentadiene:

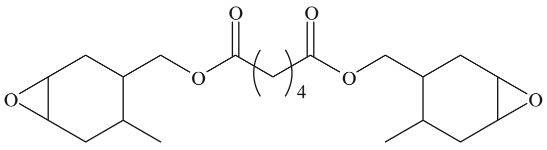


bis(2,3-epoxycyclopentyl) ether

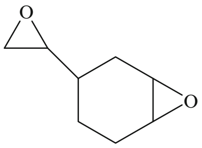
Another group of cycloaliphatic epoxy resins are prepared via Diels–Alder additions, followed by a Tischenko reaction, and completed by epoxidation. A preparation, for instance, may start with butadiene and acrolein:



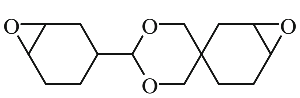
Examples of some other cycloaliphatic epoxy resins are:



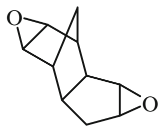
bis(3,4-epoxy-6-mehyl-cyclohexyl)adipate



vinyl cyclohexyl dioxide



2-(3,4-epoxycyclohexyl)-5,5-
spiro(3,4-epoxy)cyclohexane-*m*-dioxane



dicyclopentadiene dioxide

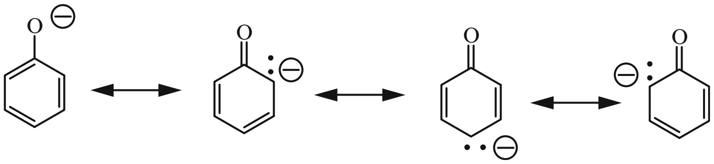
Acid anhydrides are more effective curing agents for cycloaliphatic epoxy resins than are the amines. In addition, the amines might also react with ester groups that are present in some of these materials and form undesirable by-products.

7.12 Phenol-Formaldehyde Resins

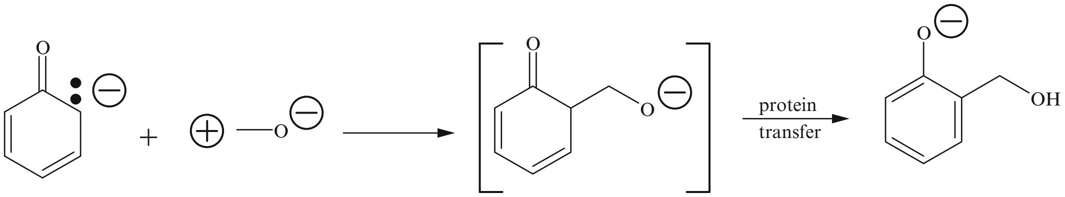
The phenolic resins are condensation products of phenol and formaldehyde [144–146, 148]. These materials were among the earliest commercial synthetic plastics. Two different methods [144–146] are used to prepare them. In the first one, the condensations are base catalyzed, while in the second one, they are acid-catalyzed. The products formed with basic catalysts are called *resols* and with acidic ones *novolacs*. Phenolic resins are used widely in coatings and laminates. The pure resins are too friable for use as structural materials by themselves. They become useful plastics, however, when filled with various fillers.

7.12.1 Resols

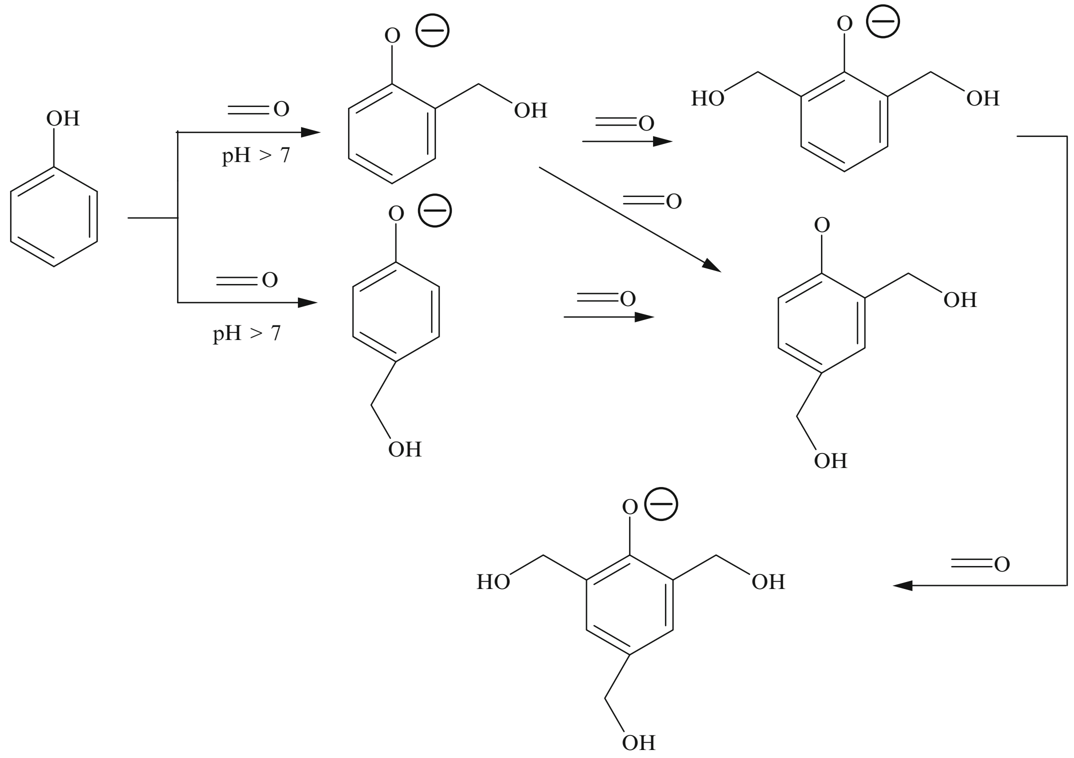
These thermosetting resins form in reactions of phenols with formaldehyde in water in the presence of catalytic amounts of bases. Under these conditions, phenol exists as a resonance-stabilized anion:



The addition of the phenol anion to formaldehyde is a typical nucleophilic reaction:



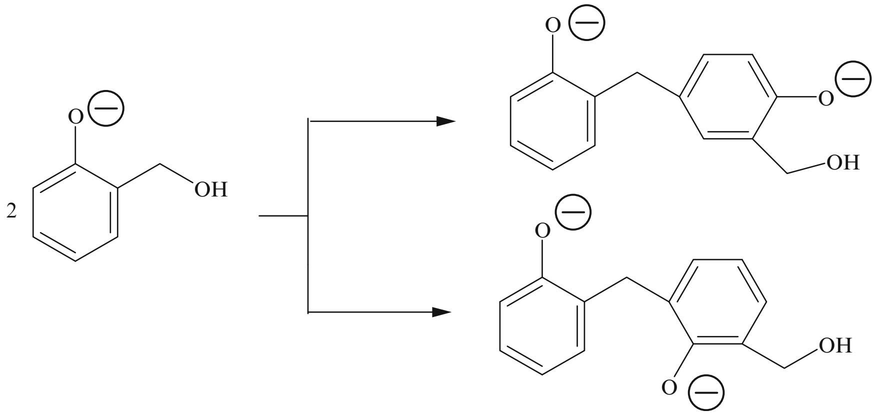
Both *ortho* and *para* methylolphenols form in the above reaction. Phenol is very reactive and monosubstituted phenols are hard to isolate from the reaction mixture, because di- and trisubstitution occurs rapidly. No substitutions were ever shown to take place in the *meta* position. The overall reaction is as follows:



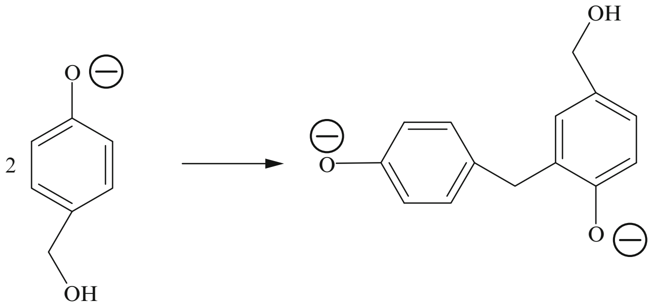
When an aqueous reaction of phenol and formaldehyde, catalyzed by sodium hydroxide, is carried out at 30°C for 5 h, the products are [147]:

2,4,6-trimethylolphenol	37%
2,4-dimethylolphenol	24%
2,6-dimethylolphenol	7%
p-methylolphenol	17%
o-methylolphenol	12%

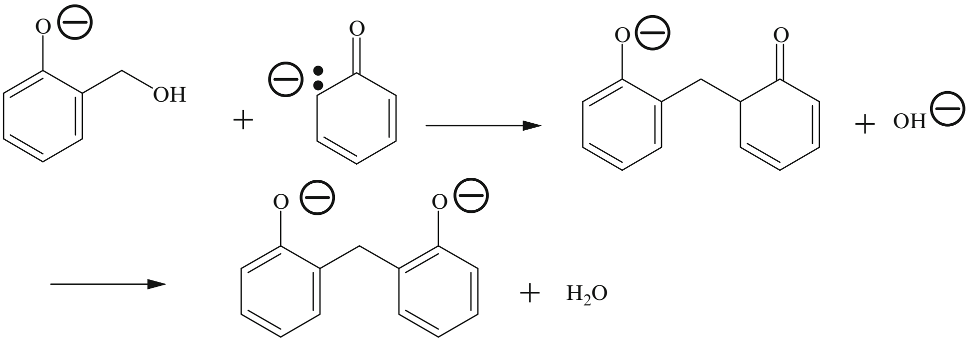
The remaining 3% is unreacted phenol. As the reaction continues, methylolphenols condense with each other to form methylene bridges:



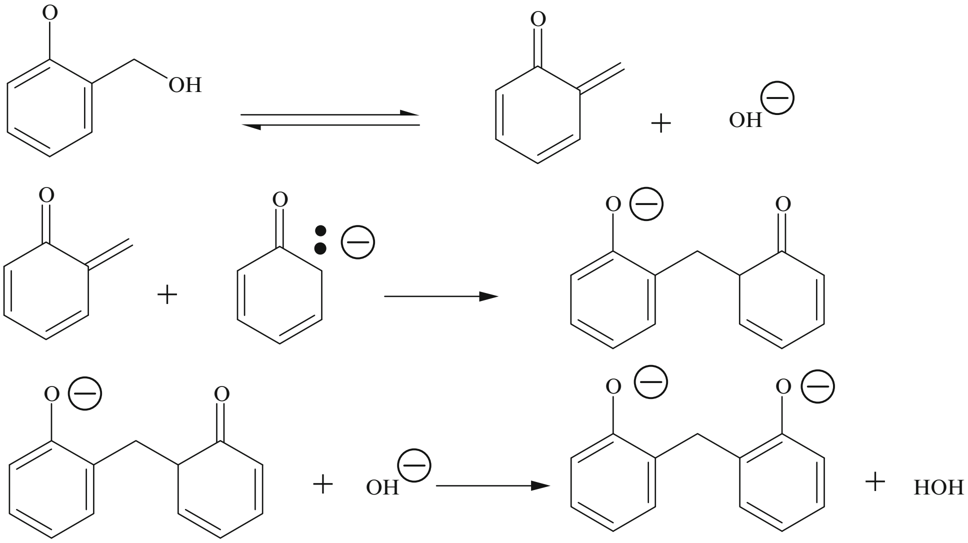
The *para* substituted methylolphenols, of course, react in the same manner:



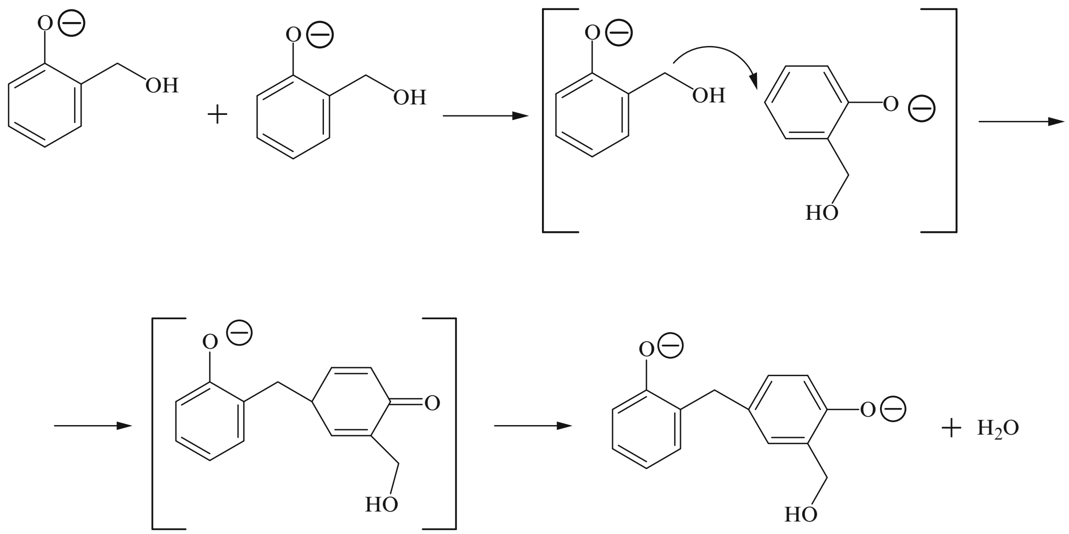
Formation of methylene bridges take place by one of two mechanisms. One is a direct S_N2 displacement:



The other one is addition of methylolated phenols to molecules of quinone methides that form at typical reaction conditions, particularly when the temperatures are elevated [144–146]:

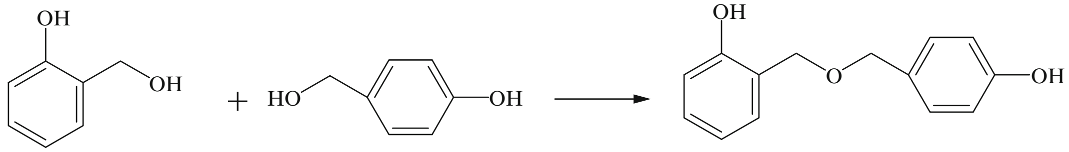


Two methylol-substituted phenols react with each other by the same mechanism:

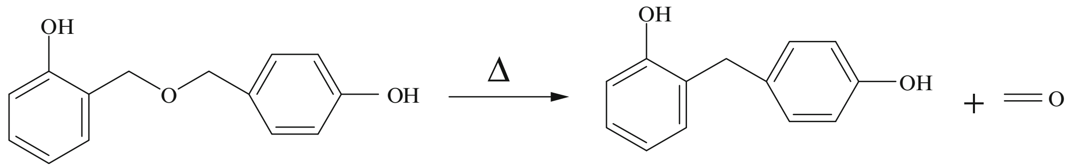


The same can be shown for *para* substituted methylolphenols. As the reaction continues, it leads to formation of trinuclear and tetra nuclear phenolic resins.

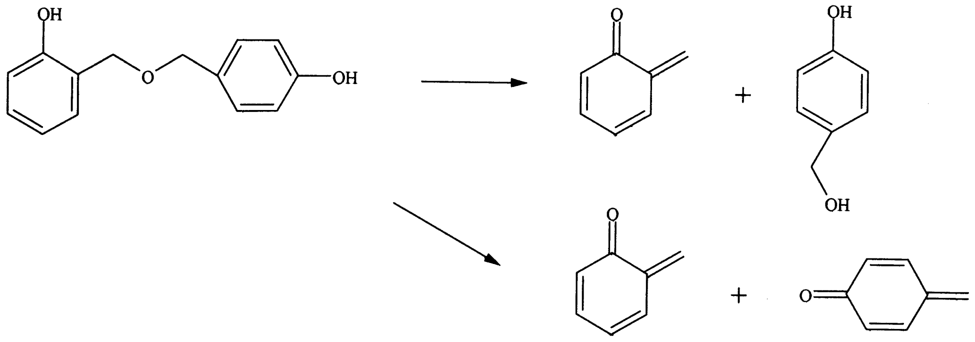
A typical liquid resole is quite low in molecular weight. It may contain no more than two or three benzene rings. Carried a little further, the condensation yields a solid resole. The pH is usually adjusted to neutral before the resoles are heated further for cross-linking. Under neutral or slightly acidic conditions, the methylol groups tend to form dibenzyl ethers:



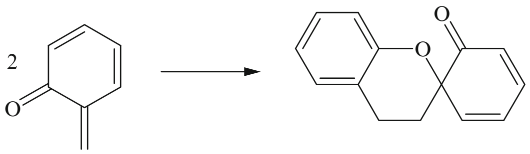
These dibenzyl ethers are unstable at higher temperatures, such as 150°C, and decompose to yield methylene bridges and formaldehyde [147]:



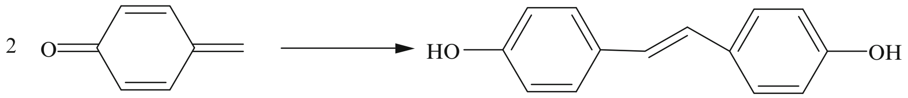
The structure of a typical resole contains both dimethylene ether and methylene bridges as well as methylol groups. Fusible and soluble resols are called A-stage resins. Further reactions cause these resins to pass through a rubbery stage where they can still be swollen by solvents. This is called B-stage. The finally cross-linked material is called C-stage resin. The cross-linking process involves complex and competing reactions. Each may be influenced by reaction conditions. When cross-linking of resoles take place at neutral or slightly acidic conditions, both methylene and ether linkages form. Upon heating, the ethers in turn split out formaldehyde, as shown above. The dibenzyl ethers [144–146, 148] also break down at elevated temperatures and form quinone methides:



The quinone methides can undergo a variety of reactions including cycloadditions with other methides to form chroman groups:

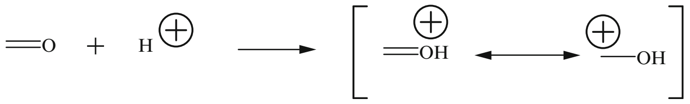


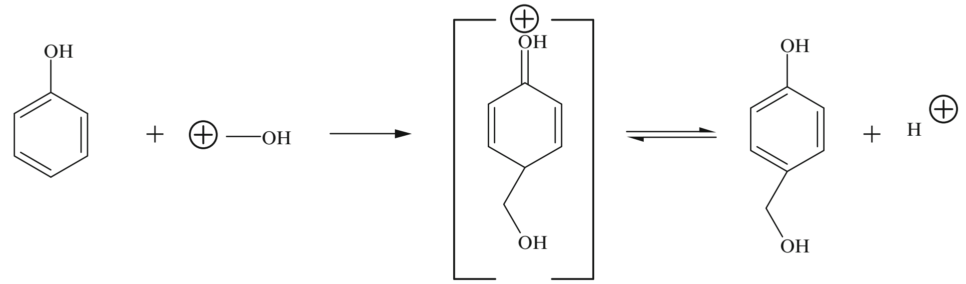
The *para* quinone methides can couple:

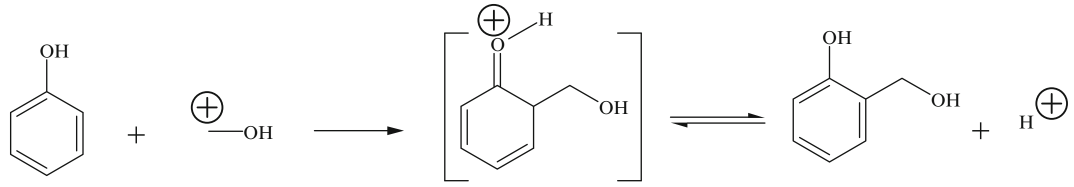


7.12.2 Novolacs

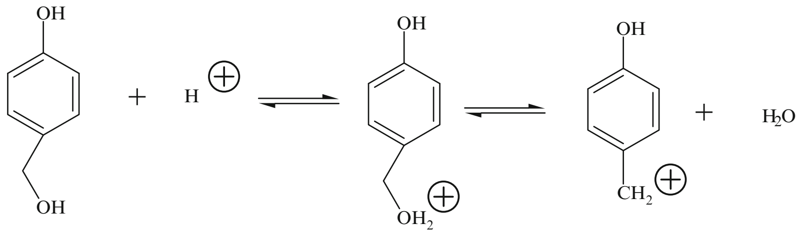
The phenolic resins that form in acid-catalyzed condensations of phenols with formaldehyde are different from resols. At pH below seven protonation of the carbonyl group of formaldehyde takes place first and is followed by electrophilic aromatic substitution at the *ortho* and *para* positions of the phenol. The initial steps of the reactions also take place in water. Here, however, a molar excess of phenol (1.25:1) must be used, because reactions on equimolar basis under acidic conditions form cross-linked resins. At a ratio of eight moles of formaldehyde to ten moles of phenol, novolacs of approximate molecular weight of 850 form [148]. When the ratio of formaldehyde to phenol is 9:10, a molecular weight of approximately 1,000 is reached. This appears to be near the limit, beyond which cross-linking results. The reaction is as follows:

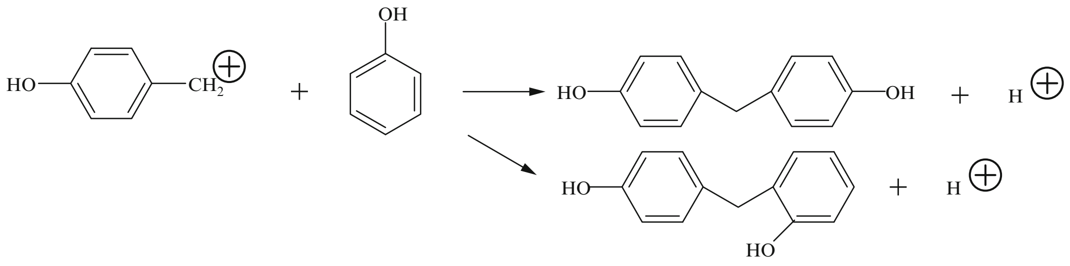






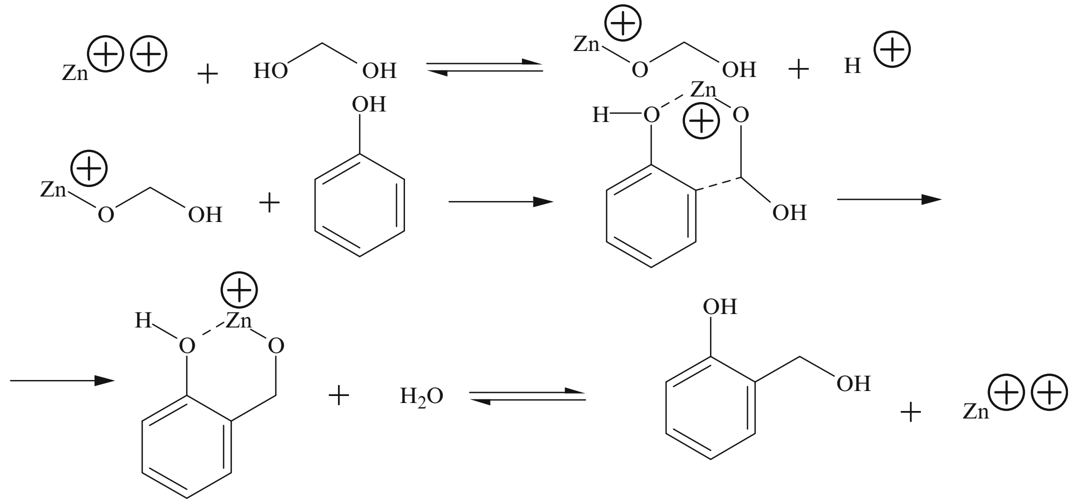
Because the reaction is taking place at pH below 7, the above shown *p*- and *o*-methylolphenols are transitory and are present in small concentrations only. Hydrogen ions convert them to benzylic carbocations that react rapidly with free phenol. This can be illustrated as follows:

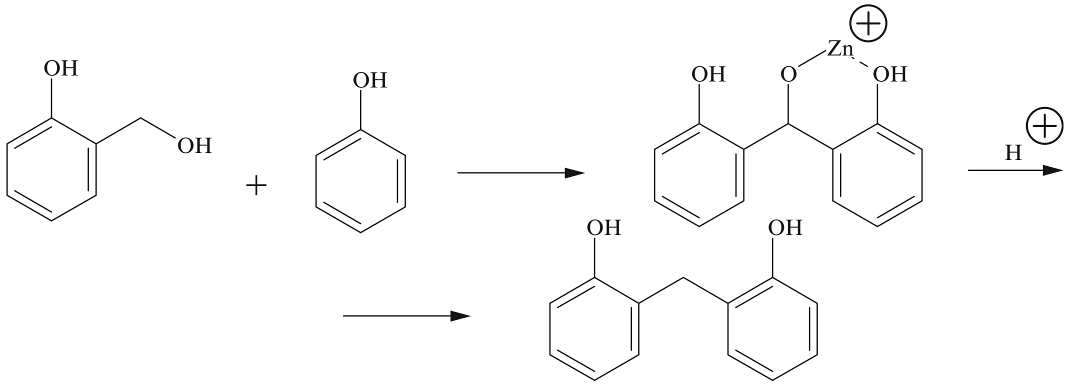




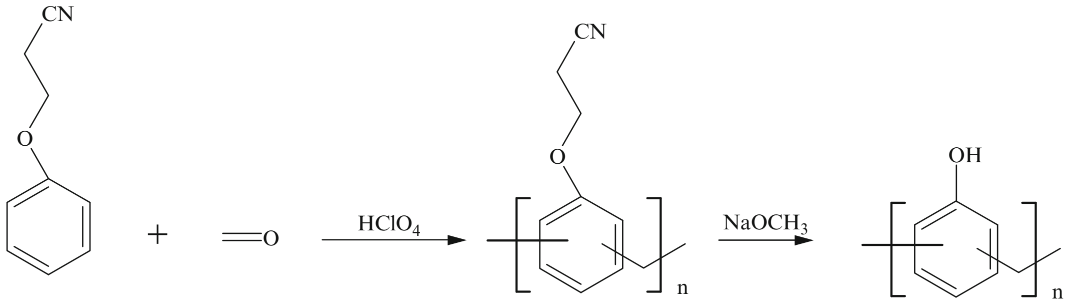
The *ortho* substituted methylolphenols react in the same manner.

Further metholylation of dihydroxy diphenyl methanes takes place until all the formaldehyde is used up. Methylol groups react with each other quickly and form methylene bridges. The *para* position is more reactive than *ortho* [144–146] at pH below 3. The opposite is true, however, at pH 5–6, where the *ortho* position is more reactive. Typical novolacs formed in these reactions are not very high in molecular weight and contain no more than six to ten benzene rings. If divalent metal salts, like zinc acetate in acetic acid, are used to catalyze the reaction, then the *ortho* positions become considerably more reactive [150]. As a result, *ortho*-methylene bridges predominate in the products:

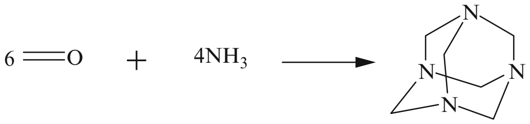




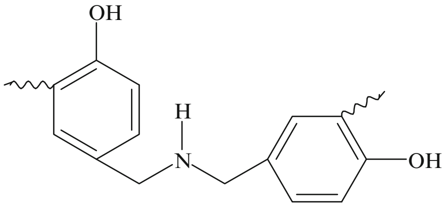
It is possible to form high molecular weight novolacs by carrying out the reactions of alkyl phenyl ethers with formaldehyde in acetic acid in the presence of perchloric acid [149]:



Novolacs are cross-linked by additions of more formaldehyde to the soluble, thermoplastic materials. The additional formaldehyde can be in the form of paraform, an oligomer of formaldehyde that decomposes to formaldehyde upon heating. It can also come from hexamethylenetetramine, a condensation product of formaldehyde with ammonia:



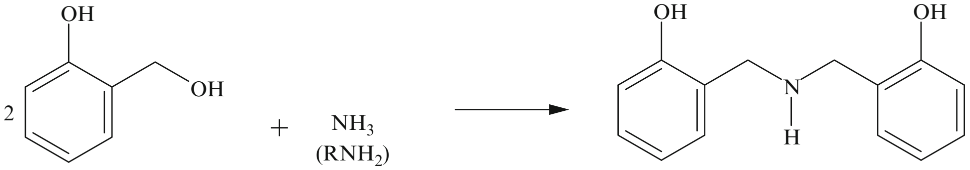
Hexamethylenetetramine decomposes to formaldehyde and ammonia upon heating. Some of the ammonia is picked up by the novolacs with the result that there are some benzylamine bridges in the product:



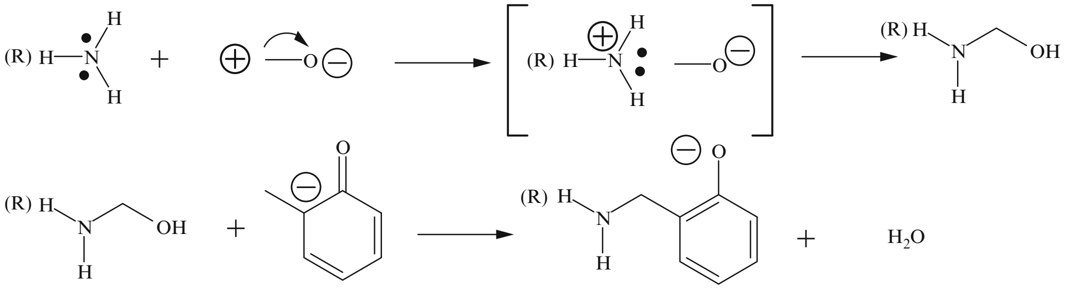
The mechanism of this reaction is discussed in the next section.

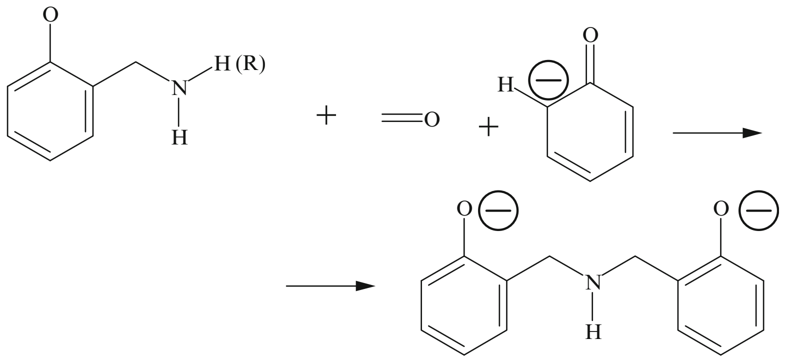
7.12.3 *Ammonia-Catalyzed Phenolic Resins*

These resins differ from the other resols, because there are some benzylamine bridges present in their structure. The reactions result in early losses of water and allow higher molecular weight buildups before the resins gel. Nitrogen-containing resols are darker in color than regular resols. The di benzylamine bridges form as follows [145]:



The overall mechanism can be shown as a special case of a Mannich reaction:





In amine or ammonia-catalyzed reactions [145], the additions and the condensations occur almost simultaneously with each other. Methylol groups are still present in the finished resins to the extent of 15–30 groups per 100 phenol residues. The structures are branched and the degree of branching depends upon the amine used.

7.12.4 Typical Commercial Preparations

The resols are usually prepared in typical reaction kettles, using 1.5–2.0 moles of formaldehyde per mole of the phenol. The reactions are rapid and the condensations to resoles might be accomplished in 1 h. Formaldehyde is often added in the form of formalin. The quantity of the added caustic or ammonia might comprise one percent of the phenol in the reaction mixture. These reactions are carried out at water reflux for a specified time. The pH is then lowered to neutral and the water is distilled off, usually at reduced pressure. The progress of the condensation is followed by measuring the melting point, the gel time (time required for the material to become thermoset at a specified temperature), solubility, or free phenol content.

Better quality novolacs and resoles are prepared in stainless steel resin kettles. For novolacs, a typical recipe might call for mole of phenol to 0.8 moles of formaldehyde (usually added as formalin, a 37% solution in water). Acid catalysts, like oxalic, hydrochloric, or others, are added in amounts of 1–2% by weight of the phenol. Oxalic acid is favored over hydrochloric, sulfuric, or phosphoric due to corrosion problems. In addition, vapors of hydrochloric acid tend to react with vapors of formaldehyde and form a carcinogenic compound, 1,1′-dichlorodimethyl ether. The reactions are conducted at the reflux temperature of water for 2–4 h. Maleic acid is sometimes used to form high melting novolacs. In a typical preparations of novolacs, molten phenol, usually kept at 65°C, is introduced into the reaction kettle and heated to 95°C. The catalyst is then added. This is followed by addition of the formaldehyde solution to the kettle with stirring, at a rate that allows a gentle reflux. After addition, heating and stirring are continued until almost all the formaldehyde is used up. At that point, the resins separate from the aqueous phase. Water is distilled off and the temperature is raised in the process to about 160°C. The unreacted phenol is removed by vacuum distillation. The end of the reaction may be determined by the melting point of the product or by its melt viscosity.

Cresols are also often used in preparations of phenolic resins. These may be individual isomers or mixtures of all three. Cresilic acids, mixtures of all three isomers, rich in *m*-cresol and low in *o*-cresol are preferred.

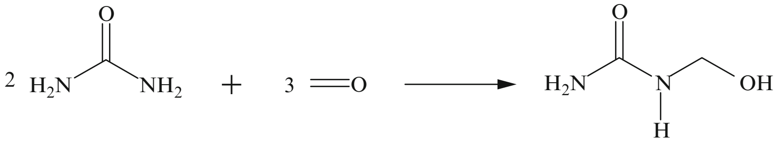
Xylenols (all six isomers) are now also in common use to form alkali-resistant grades of phenolic resins. High 3,5-xylenol mixtures are preferred. Also, resorcinol, which forms very reactive phenolic resins, is used in preparations of cold-setting adhesives. Higher homologues of phenol, like Bisphenol A, are used to prepare special phenol-formaldehyde condensates.

7.13 Amino Polymers

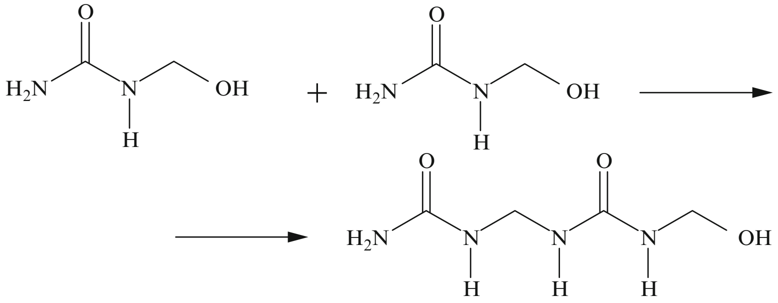
Currently, the bulk of the commercial polymers that would fit into this category are urea-formaldehyde and melamine-formaldehyde resins [151]. Over the years, however, many other materials that might fit into this group were prepared but not adopted for use for various reasons.

7.13.1 Urea-Formaldehyde Resins

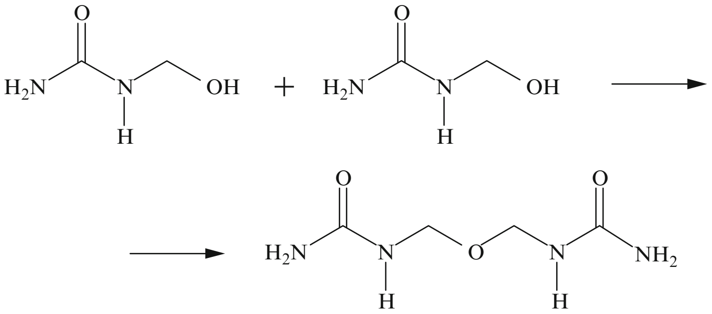
These thermosetting resins find applications in coatings, adhesives, laminating, and molding compositions. The materials are formed in water at a pH above 7 at the start of the reaction, because the methylol derivatives that form condense rapidly at acidic conditions. The initial step, where urea undergoes a nucleophilic addition of formaldehyde, can be shown as follows:



In the past, it was believed by some that further condensations that take place at pH below 7 include formations of cyclic intermediates. This, however, was never demonstrated [151]. NMR spectra of urea-formaldehyde resins show [152] that condensations under acidic conditions proceed via formations of methylene linkages:



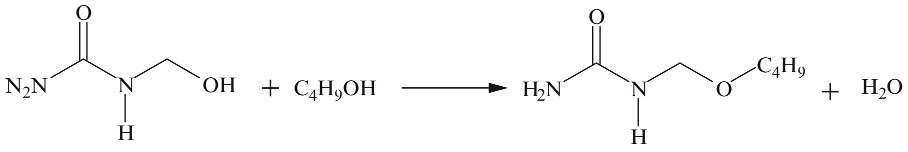
Under alkaline conditions, on the other hand, dimethylene ether groups form instead [152]:



In addition, the more highly condensed water-soluble resins contain hemiformal groups.

Further reactions may not result in formation of polymeric materials [153]. This is especially true when the ratios of formaldehyde to urea are low. Some are of the opinion that linear oligomeric condensates form instead. These urea-formaldehyde condensates separate as colloidal dispersions that are stabilized by association with excess formaldehyde [153]. The cross-linking reaction consists of agglomeration of colloidal particles with an accompanying release of formaldehyde. This opinion is supported by several observations: (1) when one plots the logarithm of solution viscosity against time during the polymerization, the plot exhibits a sharp break. Also, the plot differs from similar ones for phenol-formaldehyde condensation reactions that show continuous increases in viscosity. (2) Scanning electron micrographs of the fully cured resins show surface characteristics that resemble more the surfaces of coagulated and coalesced colloidal particles than those of high molecular weight polymers. (3) X-ray diffraction patterns and laser Raman spectra of the cross-linked resins show that there are crystalline areas in the material and absence of water. Similar patterns are obtained from hydrogen-bonded proteins with close chain packing. On the other hand, FT-IR studies [154] show that methylene and ether cross-links are present in the cured resin. There are also indications of the presence of cyclic ether units. The above information also suggests that the final structure of the urea-formaldehyde resin may be a function of the feed ratio and the pH at which it was formed.

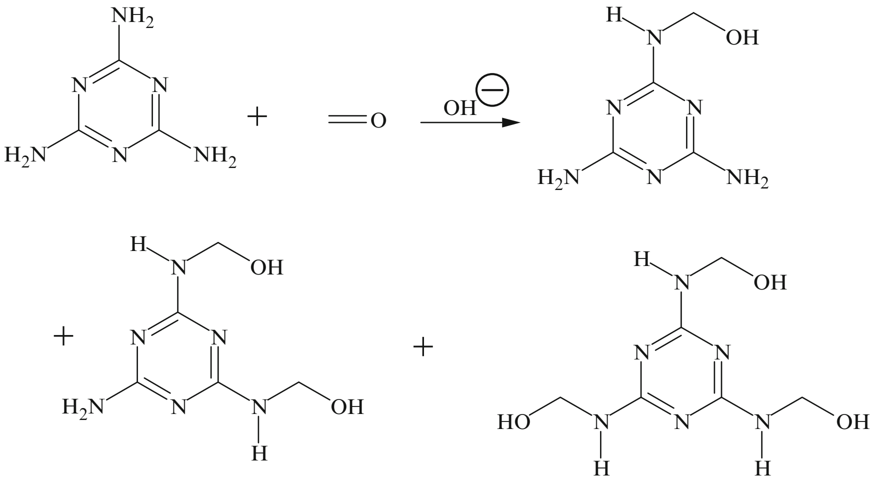
Urea-formaldehyde resins for surface coatings are commonly modified for solubility in organic solvents by reacting them with alcohols to form ether groups. Usually, *n*-butyl alcohol is used. The reaction is carried out under basic conditions, before acidification:



After etherification, the reaction mixture is acidified and the resin is further reacted to acquire the desired degree of condensation. A typical butylated urea-formaldehyde resin contains 0.5–1.0 moles of butyl ether groups per mole of urea.

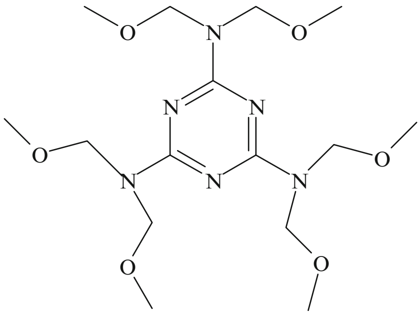
7.13.2 Melamine-Formaldehyde Resins

These resins are quite similar to urea-formaldehyde condensates and, probably, for that reason, find similar applications. Melamine reacts with formaldehyde under slightly alkaline conditions to form mixtures of various methylolmelamines [155]:



Further heating causes condensation into resins. The rate of such resinifications is pH-dependent.

Melamine-formaldehyde resins are also etherified for solvent solubility. Methanol is often used and hexamethyl ether of hexamethylolmelamine as well as higher homologues are available commercially. The hexamethyl ether can be shown as follows:



The ethers cleave upon acidification and network structures form. For methylolated melamines that are not etherified, acidification is not necessary and heating alone is often adequate for network formation. Melamine-formaldehyde resins have the reputation of being harder and more moisture-resistant than the urea-formaldehyde ones.

7.14 Silicone Polymers

These semiinorganic materials are important industrially [156–160]. They exhibit good thermal stability, good electrical insulating characteristics, water repellency, and can act as release coatings for some materials. In addition, these properties are maintained over a wide range of temperatures. As a result, these polymers have many diverse uses.

7.14.1 Polysiloxanes

The silicon atom is below carbon in the periodic table with a similar electronic arrangement, which in silicon is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$. The larger atomic radius, however, makes the silicon–silicon single bond much less energetic. Because of this, silanes (Si_nH_{2n+2}) are much less stable than alkanes. The opposite, however, is true of silicon–oxygen bonds that are more energetic (about 22 kCal/mole) than the carbon oxygen bonds. Polysiloxanes, therefore, have recurring Si–O linkages in the backbones.

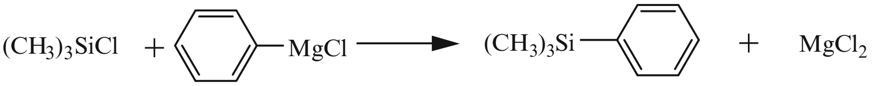
The starting materials can be prepared through hydrolyses of alkyl or arylsilicone halides [156–160]. Organosilicone halides, in turn, are made commercially by heating alkyl or aryl halides with silicon at 250–289°C. Copper catalyzes this reaction:

$$RCl + Si \xrightarrow[Cu]{250-280\ ^{o}C} SiCl_4 + RSiCl_3 + R_2SiCl_2 + R_3SiCl$$

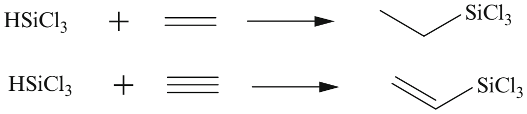
The same materials can also be formed by the Grignard reaction:

$$RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$$

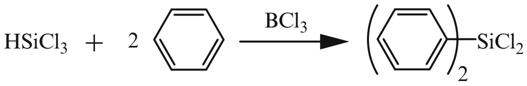
$$RMgCl + R_2SiCl_2 \longrightarrow R_3SiCl + MgCl_2$$



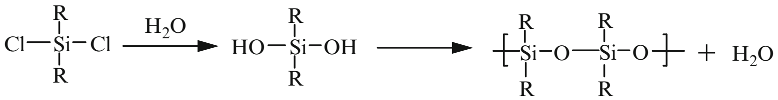
Alkyl silanes can also be prepared by additions of trichlorosilanes to ethylene or acetylene:



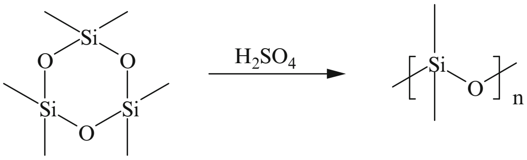
Trichlorosilane reacts with aromatic compounds in the presence of boron trichloride:



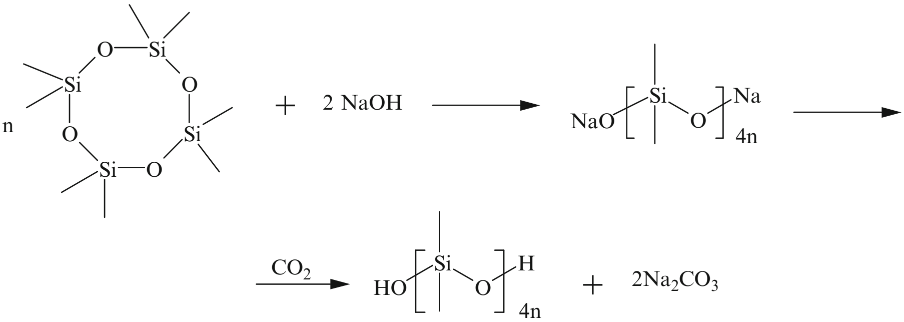
The siloxane linkages can result from hydrolysis of the halides. The products of hydrolyses, silanols, are unstable and condense:



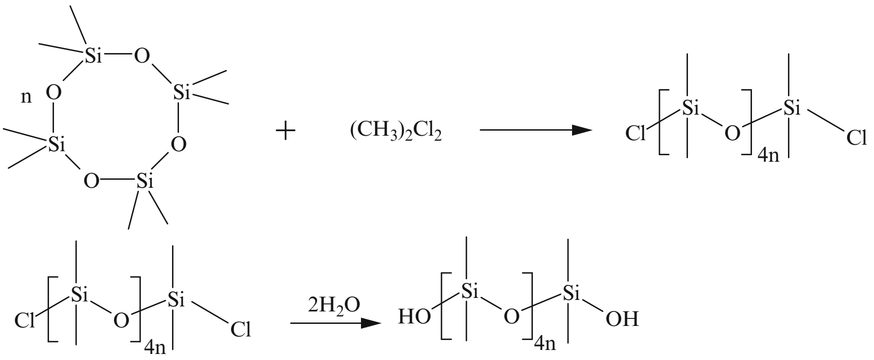
The above shown reaction is one possible route to siloxane polymers. As a general method, however, this approach is not very satisfactory, because ring formations accompany the reactions. Some rings that form from hydrolyses of trichlorosilanes are structurally complex [161]. They may even possess three-dimensional structures [162, 163]. High molecular weight polymers, however, form readily by ring opening polymerizations. Such polymerizations can be applied to the simple rings that form from dihalides or complex ones from trihalides. Ring opening polymerizations, carried out on purified (by distillation) cyclic intermediates, are catalyzed by either acids or bases [164], leading to linear siloxane polymers:



Acid-catalyzed polymerizations yield lower molecular weight polymers that are mostly oils. The molecular weights of these oils can be controlled by additions of hexamethyldisiloxane during the polymerization reactions. When catalyzed by bases, high molecular weight elastic polymers form.



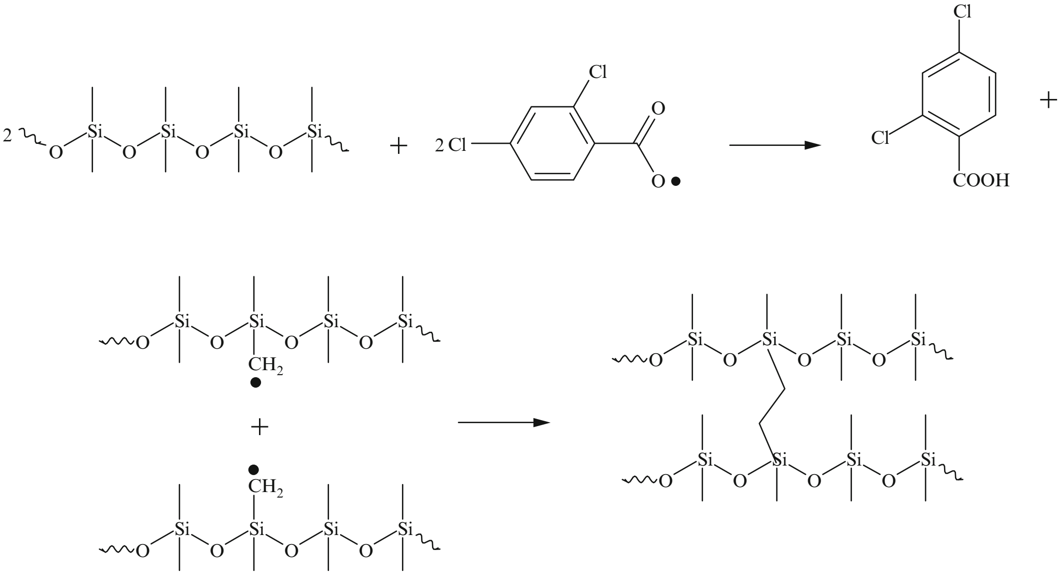
Another method of forming polydialkyldisiloxanes is by reacting difunctional oligomers with cyclic organisilicons:



Molecular weights of polydimethyl siloxanes can reach 700,000 or higher. Within the range of molecular weights between 4,000 and 25,000, the materials are fluids of various viscosities. Most common commercial liquid polydimethyl siloxanes are prepared from dimethyl dichloro siloxane. Many elastomers are also based on dimethylsiloxane. Special polymers are prepared with other substituents.

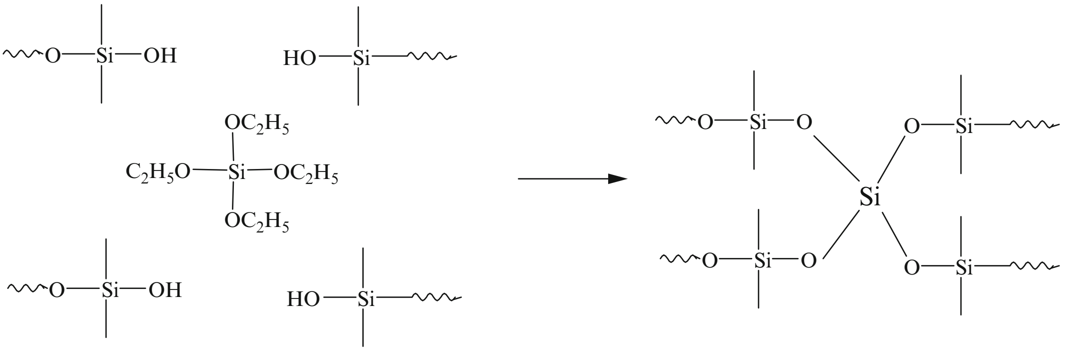
7.14.2 Silicone Elastomers

The elastomers from high molecular weight silicone polymers must be cross-linked to obtain rubber-like properties. One way this is accomplished is through hydrogen abstraction by free-radicals that are generated by decomposition of added peroxides. 2,4-Dichlorobenzoyl peroxide is often used for this purpose. It is decomposed between 110 and 150°C. The reaction can be shown as follows:

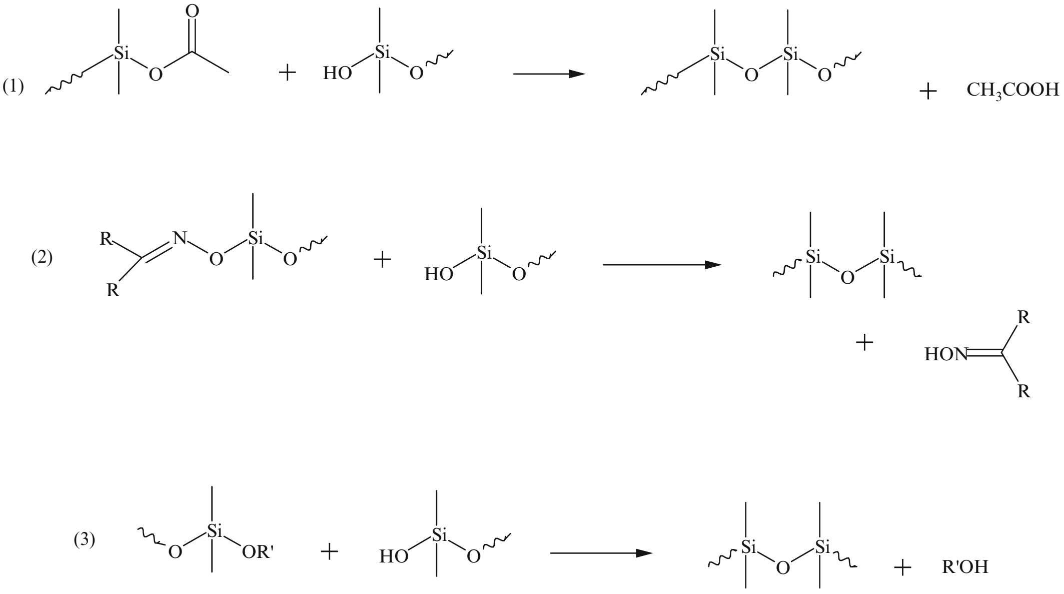


The same can be accomplished by replacing a small quantity of the methyl groups with vinyl ones. This can be done by including a small amount of vinyl methyldichlorosilane into the monomer mix (about 0.1%). The product with a small quantity of pendant vinyl groups cross-links readily by free-radical mechanism. When portions of the methyl groups on the polysiloxane backbones are replaced with phenyl structures, the elastomers exhibit particularly good low temperature properties [159].

Room temperature cross-linkable polysiloxane elastomers (commonly called *RTV*-s) are prepared by two techniques. In the first one, chloro siloxanes with functionality larger than two are added to hydroxyl-terminated prepolymers. The products are subsequently cross-linked by a second addition of polyfunctional compounds like tetraalkoxysilane in the presence of tin catalysts, like stannous octoate. Cross-linking occurs at room temperature. This reaction may vary from 10 min to 24 h:



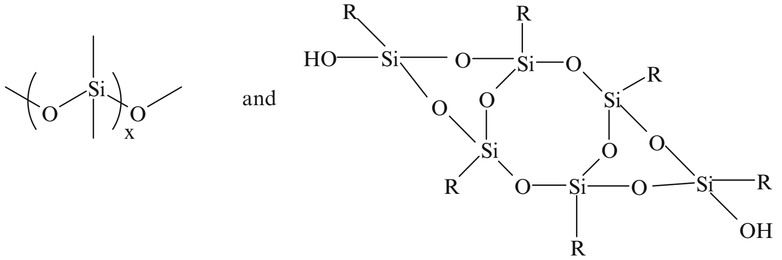
In the second one, polysiloxanes terminated by hydroxyl groups are either: (1) acetylated, (2) converted to ketoximes, or (3) etherified. The cross-linking is activated by reaction with atmospheric moisture:



The acetate-capped RTV-s exhibit good adhesion to substrates, but the released acetic acid can be corrosive.

7.14.3 Polysiloxane Coating Resins

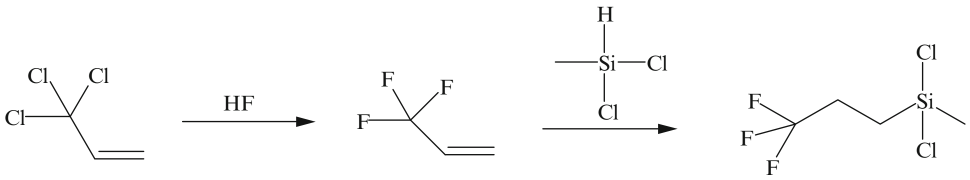
These materials are usually prepared in two stages. In the first one, low molecular weight intermediates are formed. In the second one, the intermediates are reacted with other resins possessing functional groups, like alkyds, polyesters, or acrylic resins. The most common low molecular weight intermediates are:



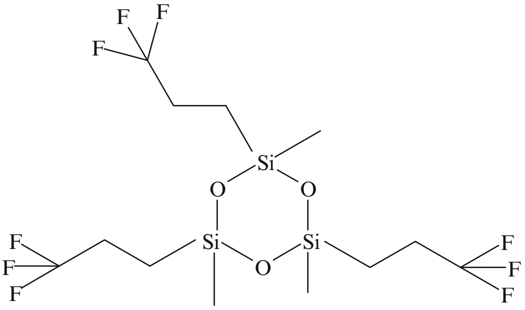
where $x = 3–6$.

7.14.4 Fluorosilicone Elastomers

The elastomers are based on polysiloxanes that contain trifluoropropyl methyl siloxane units. The materials are used as sealants, elastomers, and fluids for aerospace applications. The monomers are prepared according to the following scheme:



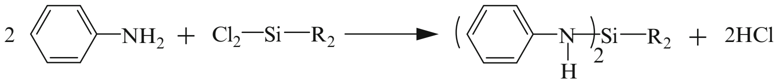
The above dichloro silane is converted to a cyclic trimer:



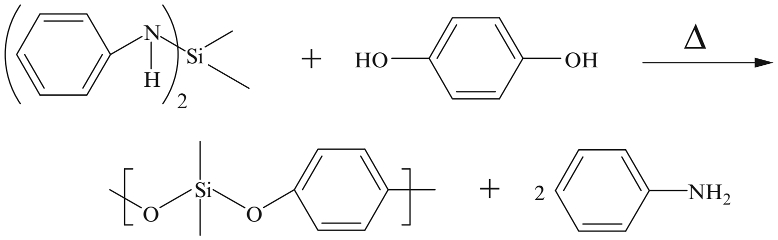
Ring opening polymerizations with basic catalysts convert the trimers to polymers at elevated temperatures. Some vinyl silane is usually copolymerized with the material for subsequent cross-linking. These elastomers are reported to be capable of maintaining their original strengths at temperatures as high as 205°C for long periods of time.

7.14.5 Polyarylsiloxanes (Also See Sect. 7.17.4)

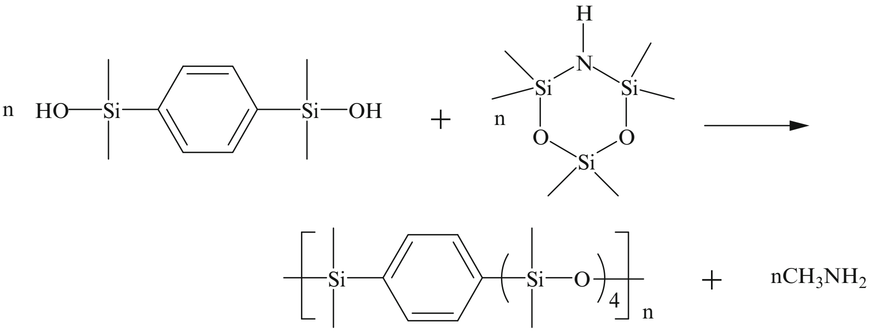
Many different polyarylsiloxanes were reported in the literature. Only a few of them are in general industrial use at present, though many exhibit interesting physical properties and might be used in the future. Preparation of one such material [164] starts with a reaction of aniline with dichlorosilane in the presence of an HCl scavenger:



The product, dianilinosilane, is reacted with diphenols, like hydroquinone:



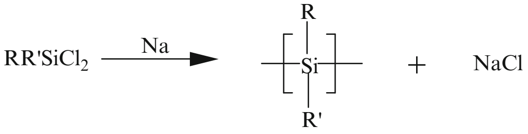
Polymers prepared by the above procedure have molecular weights up to 80,000 [164]. It is also possible to start with diphenoxysiloxane and catalyze the reaction with sodium or lithium metals. Reactions of cyclic silazanes with arylene disalanols yield polymers with molecular weights as high as 900,000 [164]:



7.15 Polysilanes

Polymers with silicon–silicon single bonds in the backbone have been known for some time. It was only within the last 10–15 years, however, that high molecular weight materials were developed [165]. Behind the current interest in these materials is a realization that they have various potential applications. These are in ceramic fibers [166], in microlithography [165, 167], in photoconduction [168], and as nonlinear optical materials [169].

The polymers are prepared from disubstitued dichlorosilanes by reacting them with alkali metal dispersions in a reductive coupling process. The polymerizations appear to have the characteristics of chain-growth rather than step-growth reactions [170]:



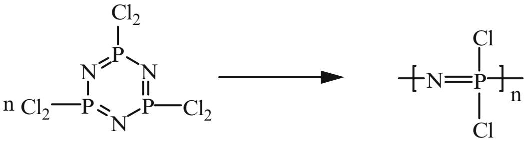
$$RR'SiCl_2 \xrightarrow{Na} \left[\overset{R}{\underset{R'}{Si}} \right] + NaCl$$

The above illustrated reaction with sodium dispersions requires greater than 80°C temperatures to proceed satisfactorily. When mixtures of different dialkylsubstituted dichlorosilanes are reacted in this manner, copolymers form [171].

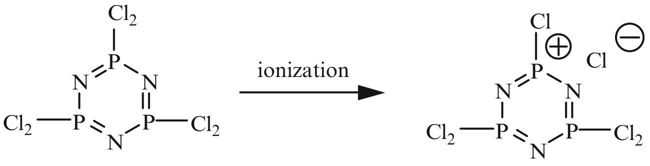
Recently, an ambient temperature sonochemical reductive coupling process was developed [172]. The reaction is carried out in the presence of an ultrasound and results in relatively high (M_n = 50,000–100,000) molecular weight materials with narrow molecular weight distributions. In addition, it was reported [172] that polymers can also be formed by anionic ring opening polymerization of cyclotetrasilanes to yield polymers with molecular weights of 10,000–100,000.

7.16 Phosphonitrile Polymers

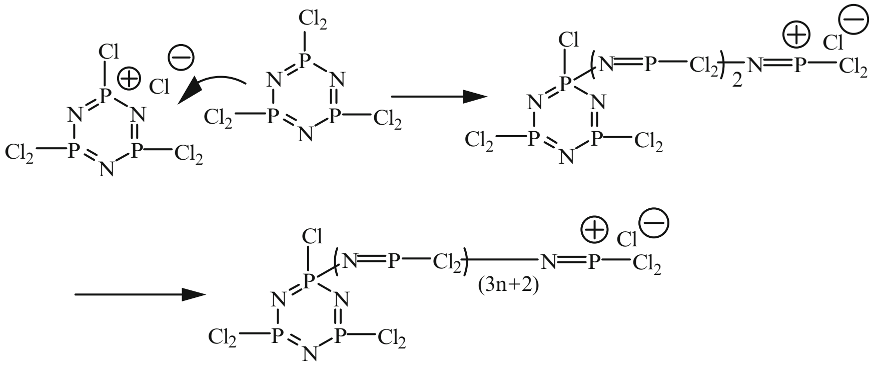
These polymers, also called *polyphosphazenes*, are useful materials when they are substituted with organic compounds [173]. They are prepared from hexachloro-cyclotriphosphazenes by ring opening polymerizations:



It is believed that the mechanism of polymerization involves an attack by electron-rich nitrogen of one cyclic monomer upon another one. At first, a cation forms through ionization of a phosphorus chloride bond [173]:

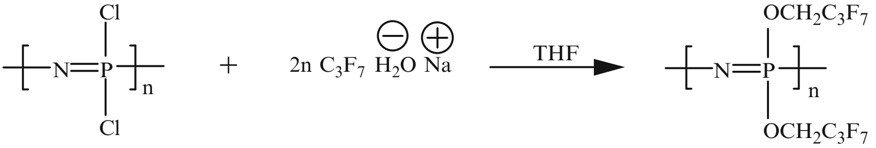


This is followed by an attack on another monomer molecule:



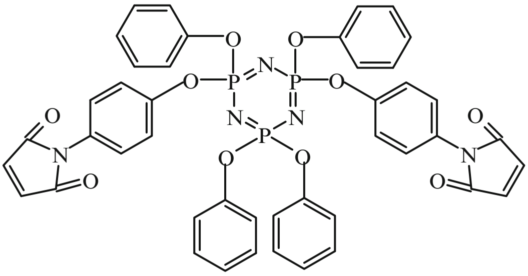
Alkyl, aryl, alkoxy, and aminocyclotriphosphazenes fail to polymerize. This is believed to be due to an absence of easily ionizable halogen to phosphorus bonds. At the same time, materials that presumably facilitate ionization of the phosphorus to halogen bonds, such as water, carboxylic acids, and metals, accelerate the polymerization [173].

The all-inorganic polymer decomposes readily at elevated temperatures and is very sensitive to hydrolytic attack. Quantitative replacements of the halogen groups, however, are possible with alkoxy, aryloxy, alkyl, aryl, or amino groups to yield much more stable materials. The replacements are achieved by refluxing the inorganic polymer in an ether solvent for several hours with sodium alkoxide or aryloxide, a metal alkyl, or aryl, or with a primary or a secondary amine. Of particular interest are substitutions with fluoroalkoxy groups, like the following:

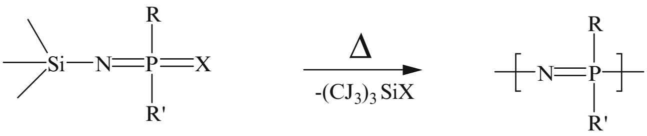


Mixed fluoroalkoxy compounds can be used to obtain a variety of properties. The materials find application as elastomers, because they exhibit good chemical resistance and good thermal stability. In addition, many retain the useful elastomeric properties at low temperature. As a result, among other applications, they are attractive for use as sealants and as fuel lines in arctic environment.

Phosphonitrile polymers are self-extinguishing or fire retardant. This led to the development of flame- and heat-resistant polyimide composites that are prepared from maleimide-substituted phosphazenes [231, 232]. The maleimide group is used for cross-linking. The substituted phosphazene can be illustrated as follows:



A deferent approach to the synthesis of polyphosphazenes was reported [179]. It is based on condensation of suitable Si–N–P precursors:



where, R,R′ = alkyl, aryl; X = OCH_2CF_3, O–Ph.

In this preparation, the desired substituents are introduced before the polymerization. The resultant polymers [179] are soluble in various solvents. Their molecular weight distributions vary from 1.4 to 3.5 and M_w from 50,000–150,000.

7.17 High-Performance Polymers

The polymers that are found in common commercial uses, such as fibers, films, or structural resins, fail to withstand elevated temperatures above 250°C for long periods of time and decompose. There is a need, however, in various technologies for materials that can tolerate temperatures over 300°C for reasonably long periods. Many such materials might be too high priced for common commercial use. They find application, however, in specialized areas that include space, aeronautic, or military technologies, where a higher price is justified by greatly enhanced performance.

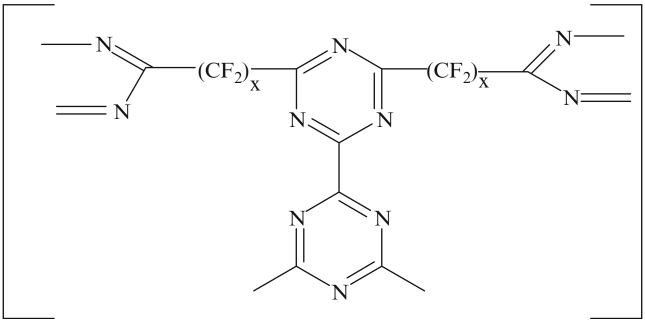
In developing tough, heat-resistant polymers the chemists pursued several goals [191]. These were:

1. To improve heat stability of the available polymers by introducing structural modifications.
2. To develop new macromolecules based on chemical structures capable of withstanding high temperatures.
3. Because many inorganic molecules are more thermally stable than the organic ones, to develop inorganic and inorganic–organic polymeric materials.

Improvement of thermal stability of existing polymers has to be based on the following considerations: (1) The primary bond energy between atoms in a polymeric chain is the greatest source of thermal stability. The strength of these bonds, therefore, imposes an upper limit on the vibrational energy that a molecule may withstand without bond ruptures. In cases of cyclic repeating units, as in ladder polymers, a rupture of one bond in a ring may not lead to loss of molecular weight. In such polymers, two bonds would have to break within the same ring for the chain to rupture, and the probability of that is low. This means that ladder polymers should exhibit greater heat stability than single-stranded chains [183]. (2) Secondary bond forces or the cohesive energies contribute additional stability to the molecule. (3) Resonance energy of aromatic and heterocyclic structures contributes an additional amount of thermal stability and bond strength. (4) Polymers with high melting or softening temperatures are generally more heat-resistant.

7.17.1 *Fluorine Containing Aromatic Polymers*

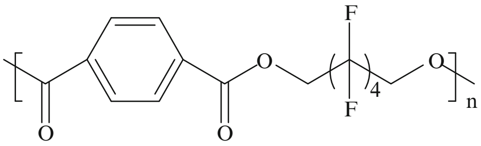
The high strength of the carbon-fluorine bonds and the shielding effect of the highly electronegative fluorine atoms improve heat stability. One such material was synthesized by heating perfluoroalkyl amidines above their melting points. Ammonia evolves and triazine ring containing polymers form [174]:



The thermal stability of these polymers in vacuum is about equivalent to polytetrafluoroethylene [174].

Among other fluorine containing materials reported in the literature are a group of polyesters [175]:

1.



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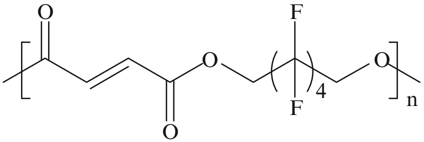

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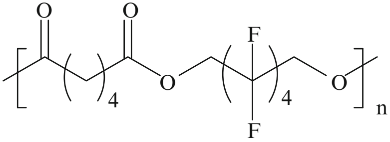
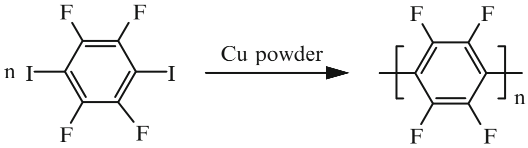
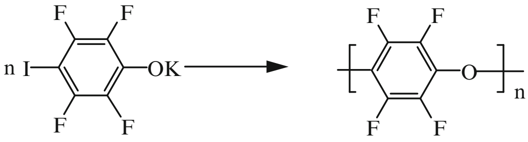


Their heat stability and other physical properties, however, do not appear to be superior to conventional materials. The Ullmann reaction can be used to prepare polyperfluorophenylene [176]. The products, however, are low in molecular weight:

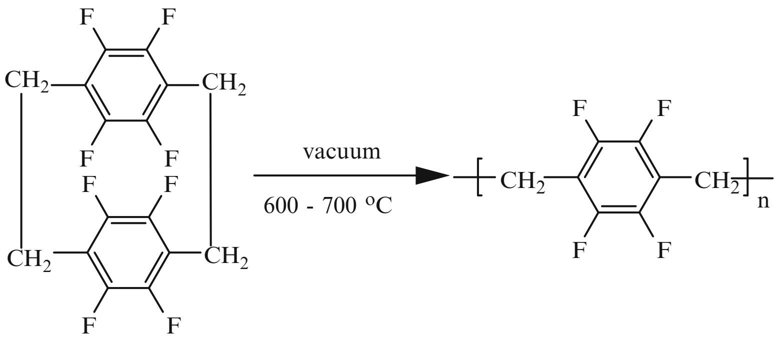


Higher molecular weight materials, like poly(perfluorophenylene ether), form from potassium pentafluorophenoxide [177], where M_n is about 12,500:



Liu et al. reported improved process for synthesizing fluorinated polymers in supercritical carbon dioxide [177]. The improvement consisted of modifying the reaction system and designing and using sampling tubes.

Low molecular weight fluorine containing polymers form from perfluoroaromatic compounds through a loss of aromaticity when they react with bis(fluoroxy)-difluoromethane [180]. More interesting is formation of poly(α,α,α′,α′-tetrafluoro-*p*-xylylene) by a polymerization technique that closely resembles the preparation of poly(*p*-xylylene) by vacuum pyrolysis of a dimer [181]:

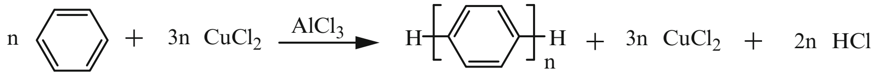


The resultant polymers maintain useful mechanical properties for up to 3,000 h in air at 250°C.

Fluorinated epoxy resins are another group of materials that might potentially possess improved thermal stability. This, however, has not been demonstrated. It was shown [190] though that these materials can be key intermediates in organic coating and plastics that require special properties, like hydrophobicity, oleophobicity, light stability, and low friction.

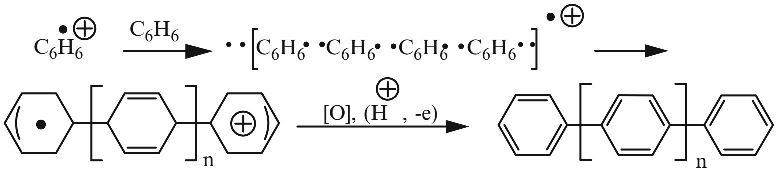
7.17.2 *Polyphenylene*

This polymer is completely aromatic in character [182]. Polymerization of benzene to polyphenylene was, therefore, investigated quite thoroughly [184, 185]. Benzene [186] and other aromatic structures [184, 185] polymerize by what is believed to be a radical-cationic mechanism. In this type of polymerization, benzene polymerizes under mild conditions in the presence of certain Lewis acids combined with oxidizing agents [186–188]:



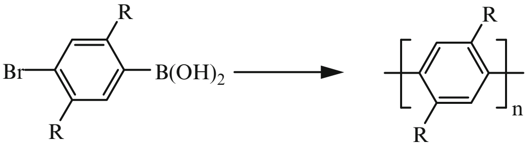
The yield of polymers reaches a maximum value (close to quantitative) at an aluminum chloride to cupric chloride molar ratio of 2:1 [180]. Solvents, concentrations, and temperatures affect the molecular weights of the products [189]. Other Lewis acids that are effective in benzene polymerizations are $MoCl_5$, $FeCl_3$, and $MoOCl_4$. The products, however, possess greater degrees of structural irregularity [183].

Theoretical considerations indicate [183] that during the polymerization the benzene rings become associated in a stacked end to end arrangement. As a result, the radical-cation becomes delocalized over the entire chain:



The σ bond formation shown above can also be accompanied by simultaneous depropagation and loss of benzene molecules. Chain buildup stops when the radical-cation on the terminal phenyl group becomes too small to promote further association.

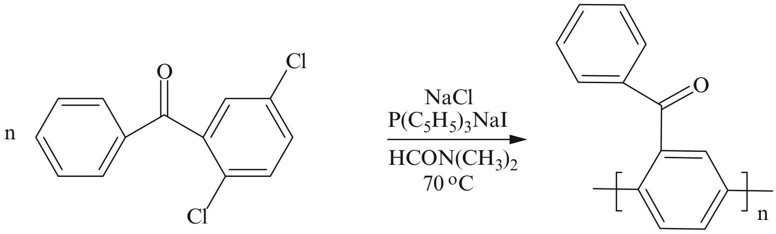
The polymer is very stable up to 500–600°C and oxidizes very slowly. It is, however, quite insoluble with a very high melting point that makes is difficult to process and even to determine its molecular weight. Introduction of irregularity into the polymeric structure by copolymerizing terphenyl, biphenyl, or triphenylbenzene with benzene results in formation of soluble products. Their molecular weights, however, are low up to 3,000 [192]. They melt between 300 and 400°C and contain phenyl branches and some fused rings. The copolymers can be cross-linked with xylylene glycol or with benzene-1,3,5-trisulfonyl chloride. Soluble alkyl substituted poly(*p*-phenylene)s were prepared [193] by a coupling process, using palladium catalysts:



Syntheses also include formations of copolymers with other aromatics compounds that lack substituents. The polymers with hexyl or longer side chains are soluble in toluene [193].

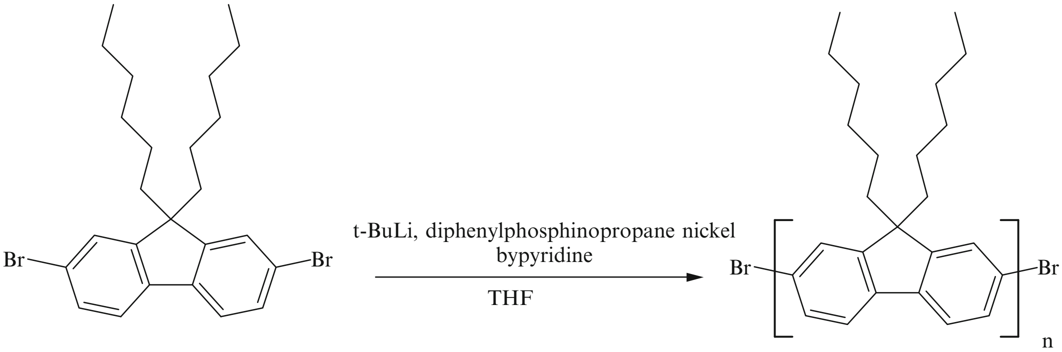
Goodson et al. [246] reported formation of soluble derivatives of poly(*p*-phenylene) of high molecular weight via Suzuki coupling reactions catalyzed by palladium (0) precursors in the presence of either triphenylphosphine or tri(*o*-tolyl)phosphine. Use of triphenylphosphine, however, apparently resulted in incorporation of the phosphine [246].

Formation of poly(benzoyl-1,4-phenylene) with the aid of a nickel-catalyzed reaction was reported [247]:



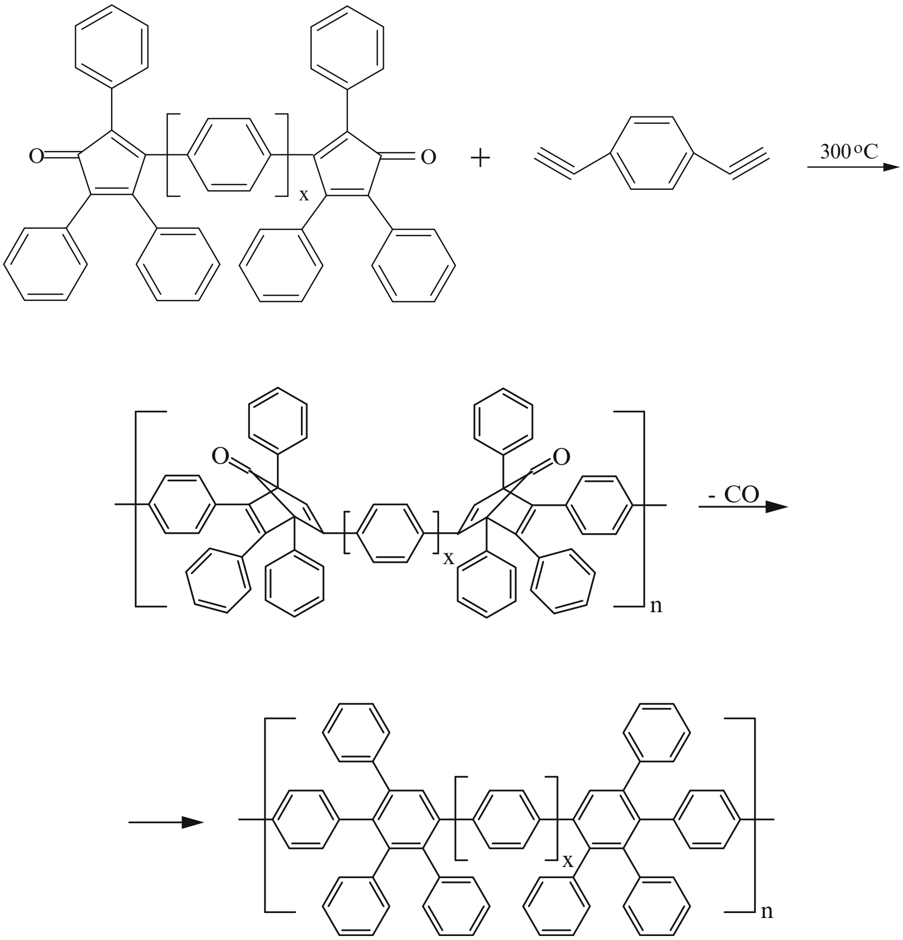
When sodium iodide is replaced with 2,2′-bipyridine, the reaction proceeds faster. The polymers prepared with bipyridine exhibit a glass transition of 217°C and loose only 3% of their weight at 500°C either in air or in nitrogen [247].

Carter et al. [247] used organolithium-activated nickel catalysts to synthesize polyarylates



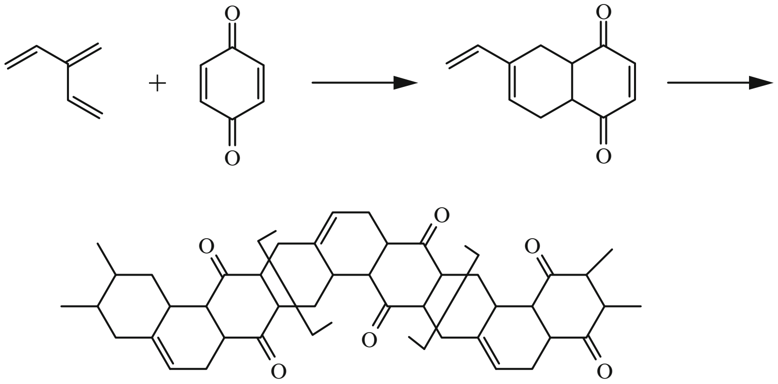
7.17.3 Diels–Alder Polymers

The Diels–Alder reaction has been used to form many polymeric materials. One such material, for instance, forms from a reaction of diethynylbenzene with cyclopentadienone [194–196]. The products, phenylated polyphenylenes, reach molecular weights of M_n up to 40,000:



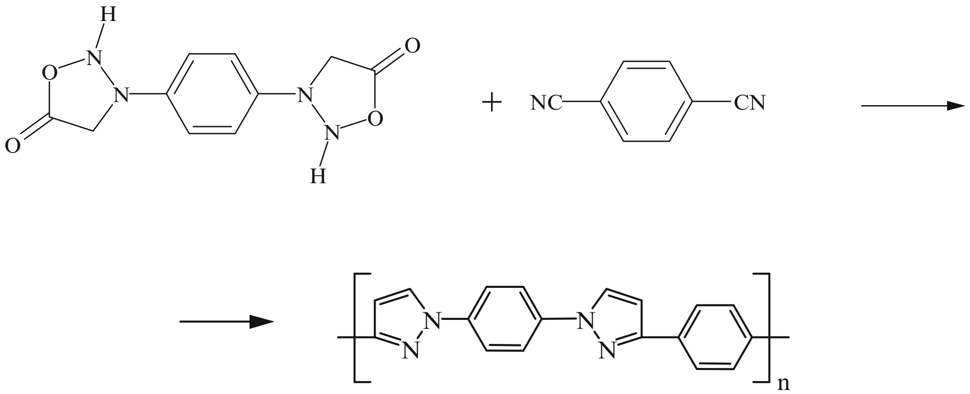
where $x = 1,2$. These polymers are amorphous and form clear films that are stable in air up to 550°C.

Another example is condensation of 2-vinyl-1,3-butadiene with *p*-benzo-quinone. The product is a ladder structure, or a double-stranded polymer [197]:

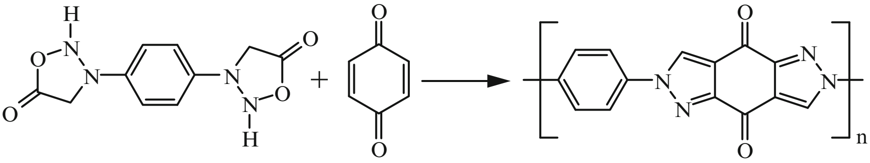


This double-stranded polymer, shown above, is soluble only in hexafluoroisopropyl alcohol [198] and is infusible. When, however, some of the rings are made flexible by condensing 2-vinyl-1,3-butadiene with a large ring bis fumarate, the solubility improves [198].

Some stable polymers also form in 1,3-dipole addition reactions [190]. Bis-sydnones, for instance, condense with diacetylene to form pyrazole rings in the polymer backbone. The reactions presumably proceed through Diels–Alder intermediates [199]:

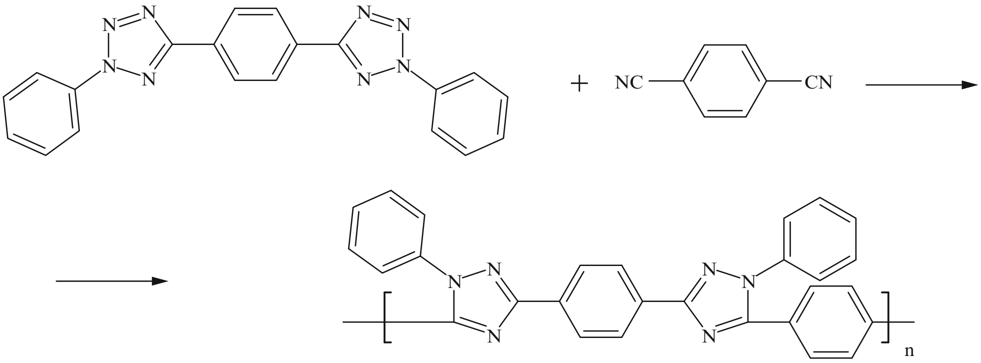


Similarly, bis-sydnones condense with quinone [199]:

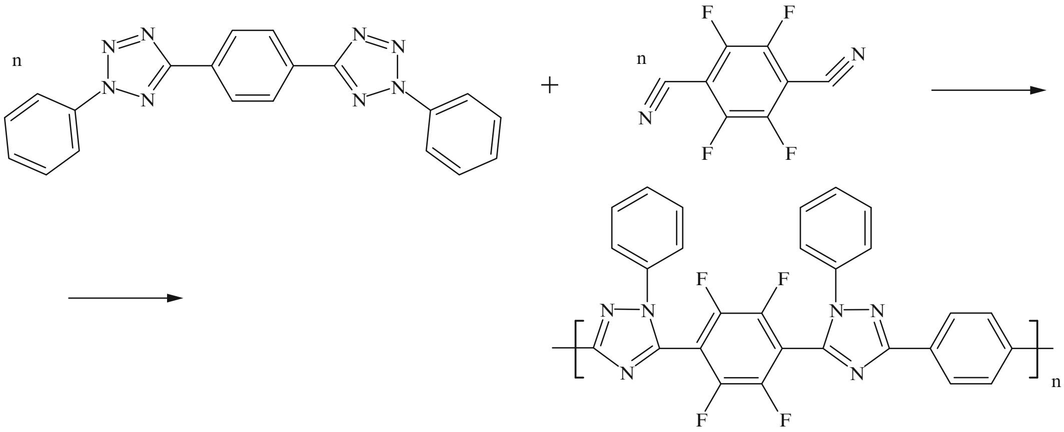


The resultant polymers are not high in molecular weights and only slightly soluble in solvents like dimethylformamide. Their powders decompose near 420°C in air and near 500°C in a nitrogen atmosphere.

1,3-Dipolar additions of bisnitrileimines (generated from tetrazoles with dienes or with di nitriles) result in formations of polypyrazoles and polytriazoles [200]. Some examples of these reactions are:

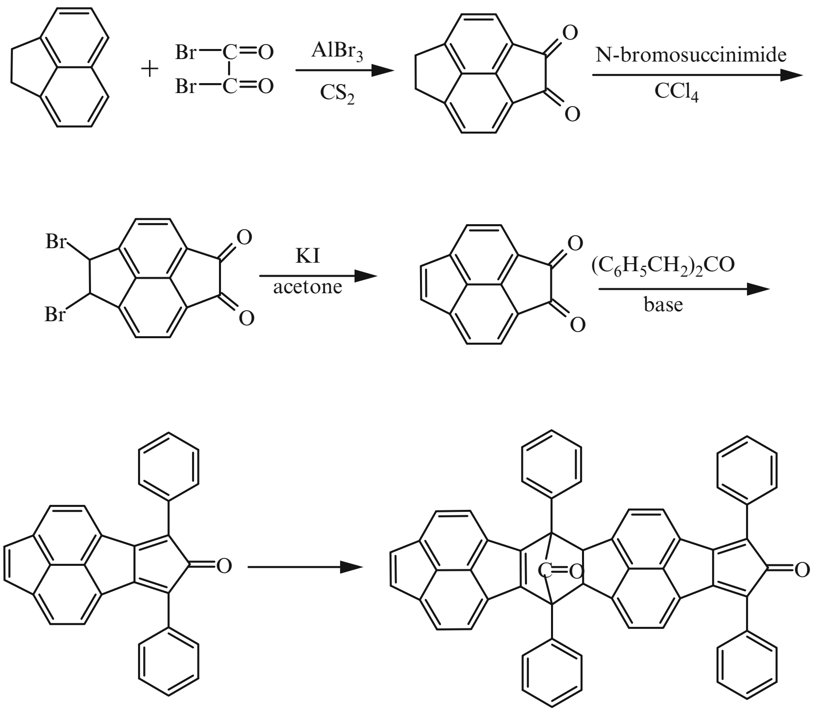


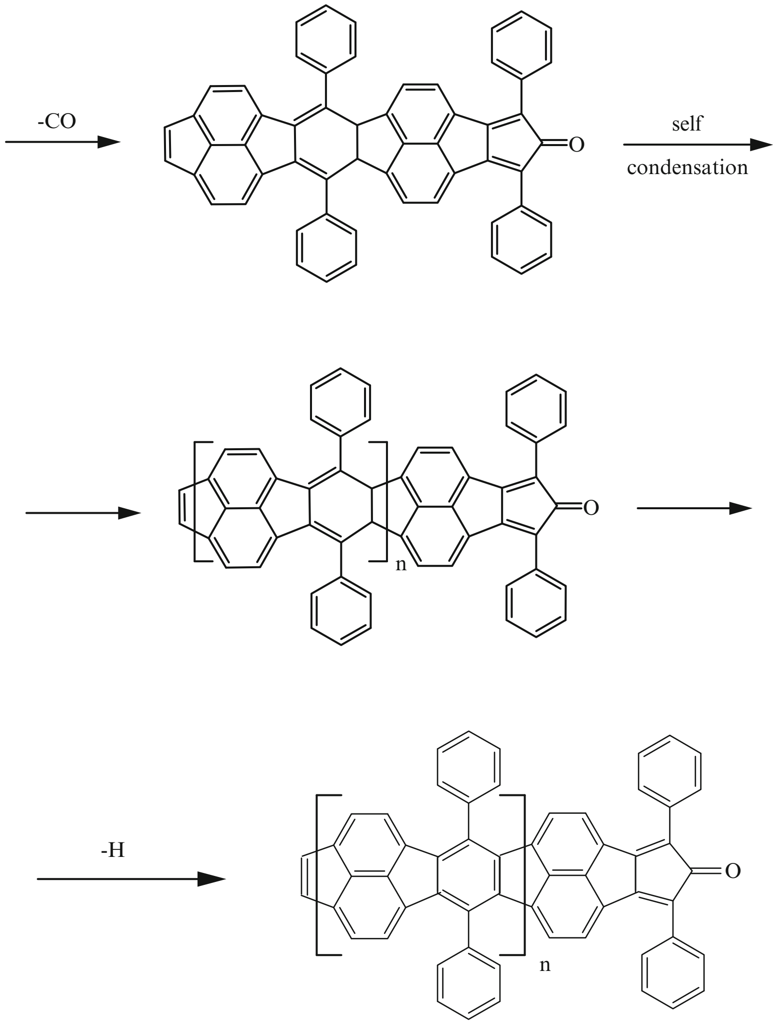
and



By this condensation, high molecular weight polymers can form [200]. They decompose near 500°C in air or in nitrogen atmosphere.

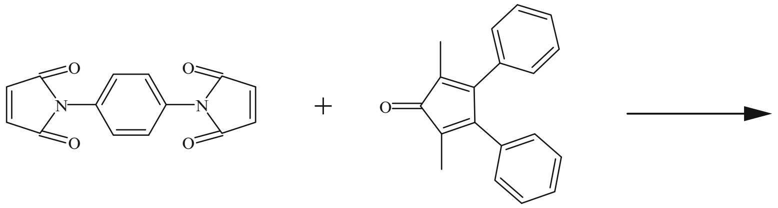
Cyclopentadienone derivatives condense by the Diels–Alder reaction in homopolycycloaddition. The reactions involve a series of steps consisting of initial cycloaddition, followed by loss of carbon monoxide through an expulsion of a bridge carbonyl group [201]:

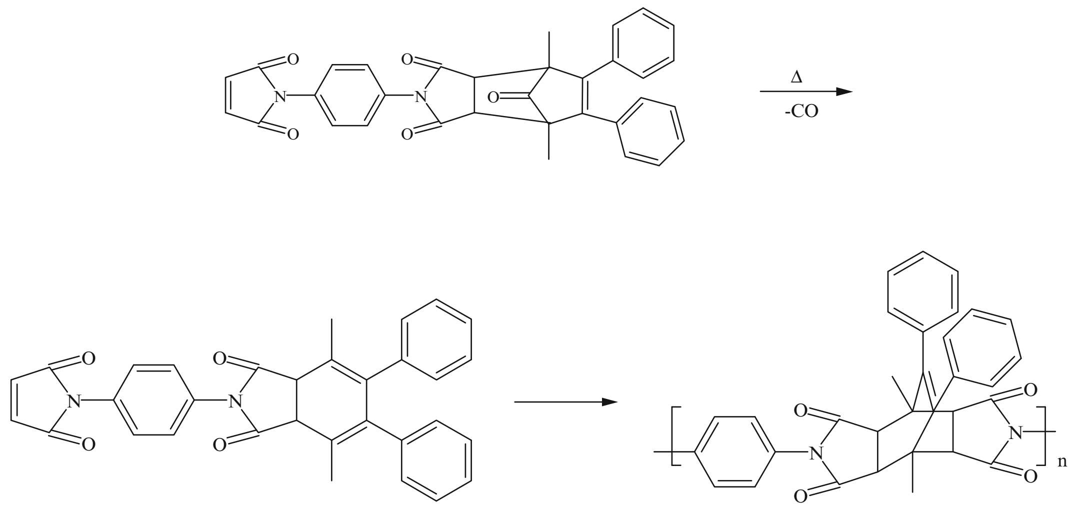




The products are ladder polymers of varying molecular weights. They loose approximately 30% [201] of their weight at 700°C in a nitrogen atmosphere.

Another example is condensation of bis dienophiles with dienes [202]:





Only low molecular weight polymers form, however, together with some insoluble, possibly crosslinked material. Bis maleimides also condense with bisfulvene [202]. The products of these condensations depolymerize reversibly. Also, reactions of maleic anhydride with dienes, like bicycloheptene, bicyclohexene, dicyclopentenyl ether, and dicyclohexenyl ether, yield soluble, low molecular weight polymers [204]:

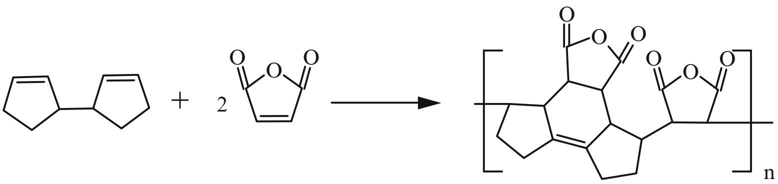
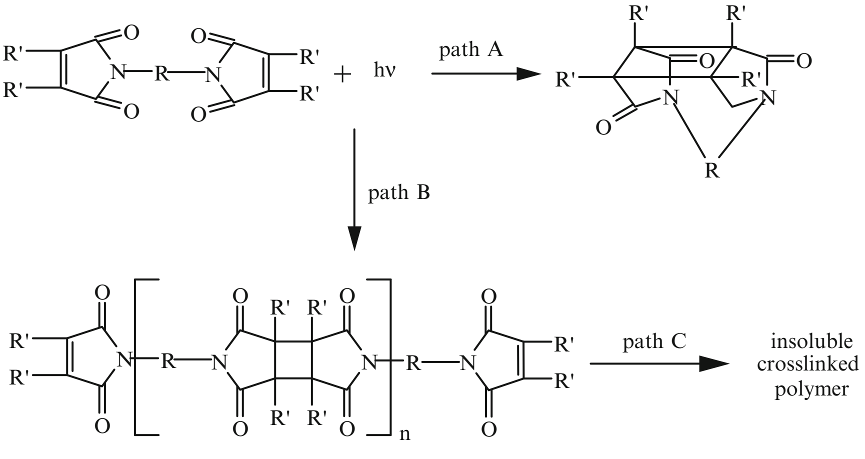


Photo-cycloaddition reactions also form low molecular weight polymers with heterocyclic rings in the backbone. The reactions are photoinitiated with benzophenone to obtain repeated $2\pi + 2\pi$ photo-cycloadditions of bismaleimides [205]:



where, $R = (CH_2)_x$.

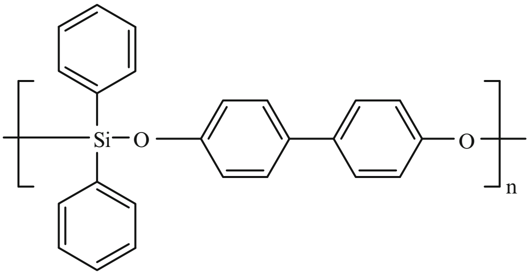
These polymeric materials form transparent, flexible films [205].

Diels–Alder reaction can also be used to modify the chemical structures of some aromatic polyamides. This improves their heat stability, raises their T_g value, and makes them rigid at higher temperatures [203].

7.17.4 Silicon-Containing Aromatic Polymers

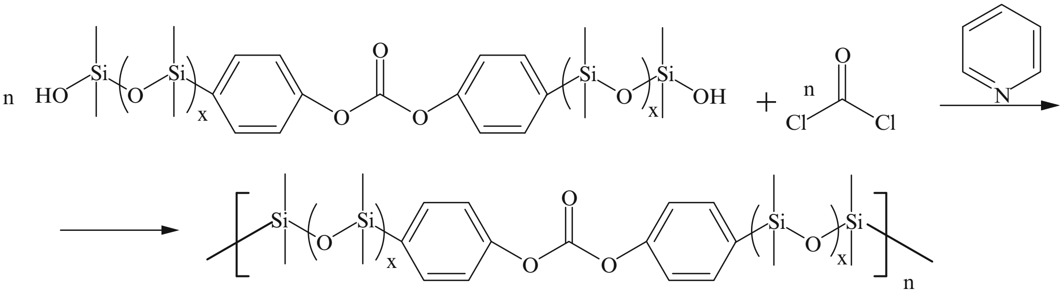
These materials have the potential of being stable at high temperatures. One typical preparatory procedure consists of condensing bisphenols with suitable silicon derivatives [227]:

Many of these polymers are soluble and exhibit good heat stability. An example is one such material prepared by this procedure and shown below:



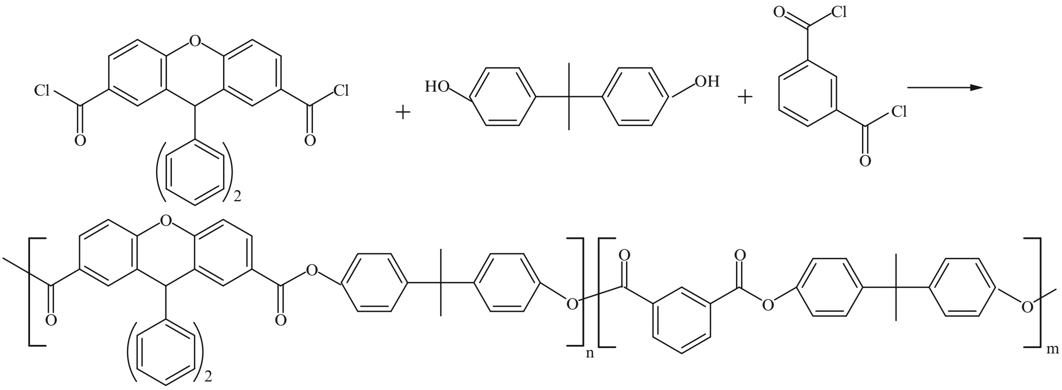
It looses only 10% of its weight at 600°C [191].

The starting materials can also be silanols, as for instance in a synthesis of polycarbonates [227]. Preformed bis-silanols are used in this particular example:



where, $x = 0$ or 1.

One publication describes syntheses of copolyesters and copolyamides that contain phenoxalin rings [228]:



The copolymers show little degradation at temperatures up to 400°C. In addition, the copolymers with high phenoxailin content are soluble in several solvents [228].

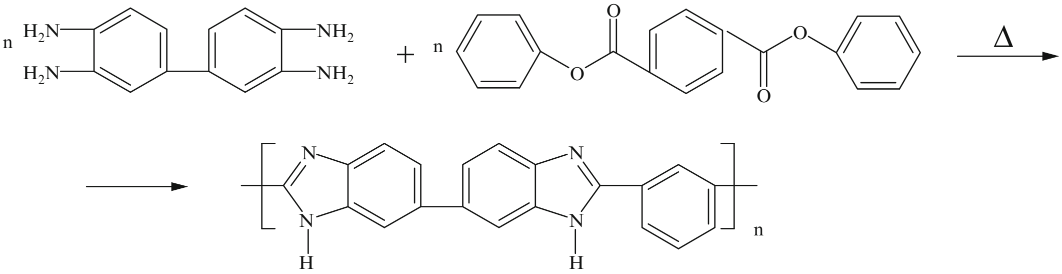
There are also reports in the literature of attempts to modify polysiloxane backbones to increase heat stability. These modifications consist of making changes in the electronic character of the Si–O bonds to prevent rearrangements at high temperatures to low molecular weight cyclic products. It is known that by making the bonds more ionic than covalent increases heat stability [191]. A metal that is more electropositive, therefore, is used to form metal-oxygen linkages and form polymers that are more ionic in character. Such metals are aluminum, titanium, tin, and boron. The results, however, so far are disappointing.

7.17.5 Direct Condensation Polymers

Many polymers with enhanced heat stability can be prepared simply by direct condensation. These aromatic polymers often contain heterocyclic unit. The materials are high melting, somewhat infusible, and usually low in solubility. Many aromatic polyimides belong here. Polyimides, as a separate class of polymers, were discussed in an earlier section, because many are common commercial materials. On the other hand, the materials described in this section might be considered special and, perhaps, at this points, still too high priced for common usage.

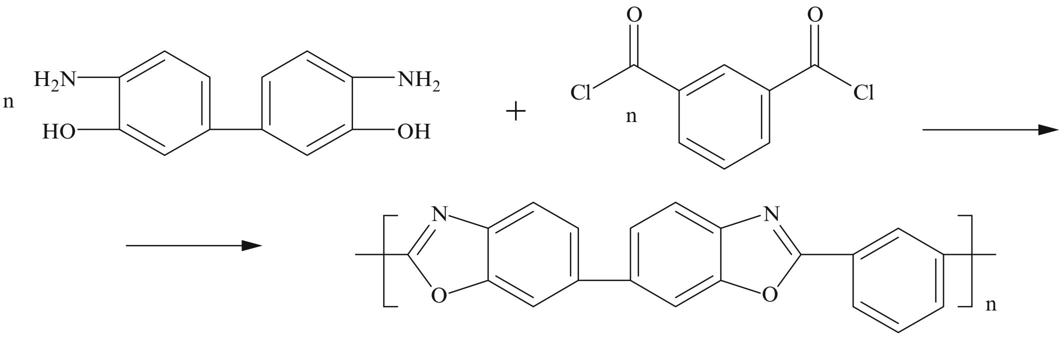
7.17.5.1 Polyimidazoles, Polybenzthiazoles, and Related Polymers

Many *polybenzimidazoles* are prepared by direct condensation. They are colored polymers that mostly melt above 400°C. One such material is formed from 3,3′-diaminobenzidine and diphenyl isophthalate by heating the two together at 350–400°C in an inert atmosphere [206]:

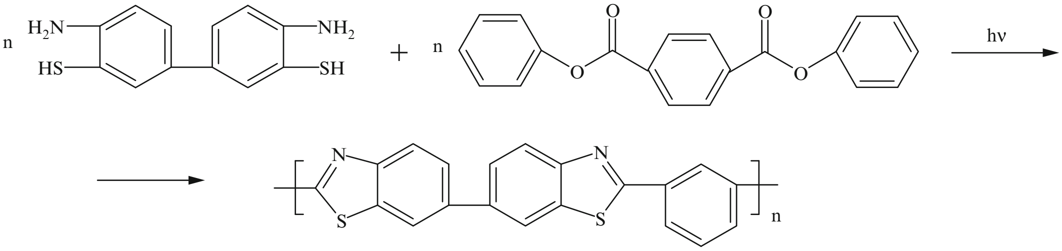


Films and fibers from this material exhibit good mechanical properties up to a temperature of 300°C. Above that temperature, however, they degrades rapidly in air [206].

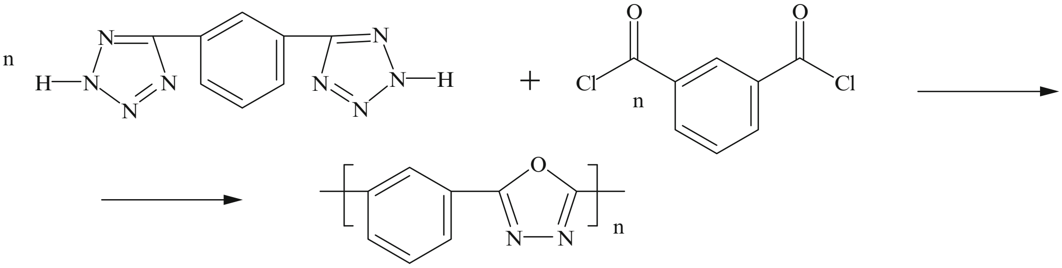
Similar polymers are *polybenzoxazoles* [207, 208]:



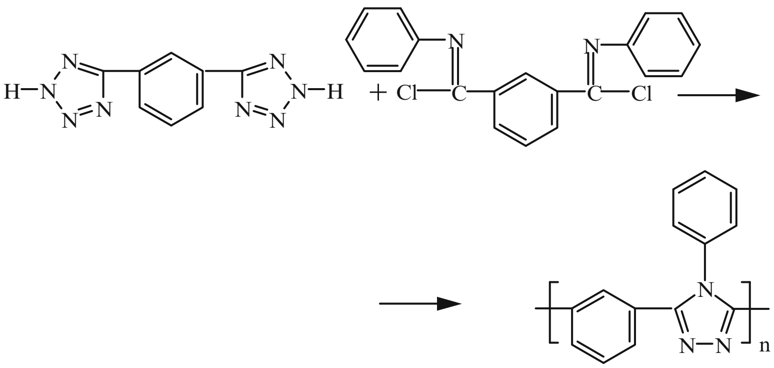
The same is true of *polybenzthiazoles* [209]:



Polyoxidiazoles also belong to this general class of materials [210]:

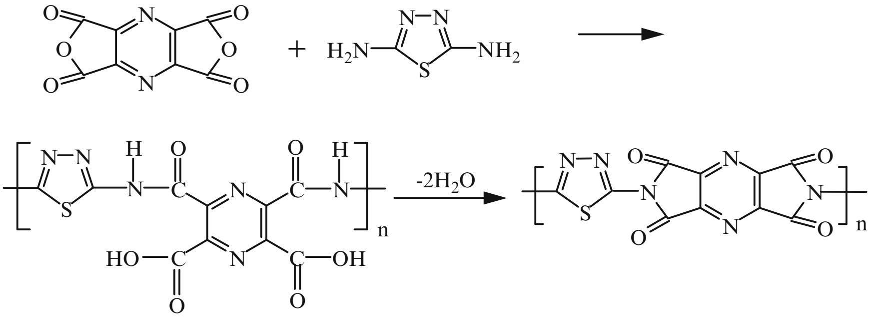


and *polybenztriazoles* [211]:



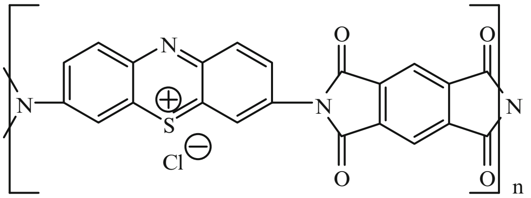
All of the above materials maintain useful properties up to 300°C in air and can be formed into fibers.

Some polymeric materials are completely free from hydrogens. An example is *polysulfodiazole* [212], a polyimide prepared from pyrazine-1,2,4,5-tetracarboxylic acid anhydride and diaminothiazine [213]. This material exhibits particularly good heat stability [213]:



Films from this polysulfodiazole maintain their strength and stability at 592°C. Preparations of several other, similar polyimides was reported [219]. A polyimide, however, prepared from diaminothiazole with pyromellitic dianhydride chars at 320°C in air. The chemistry and preparations of the principal types of polyheteroarylenes were review by Krongauz [214].

A series of thermally stable, organic solvent-soluble polyimides were synthesized by reacting 3,7-diaminophenothiazinium chloride (thionine) with four different dianhydrides [243]. These polyimides can be illustrated as follows:

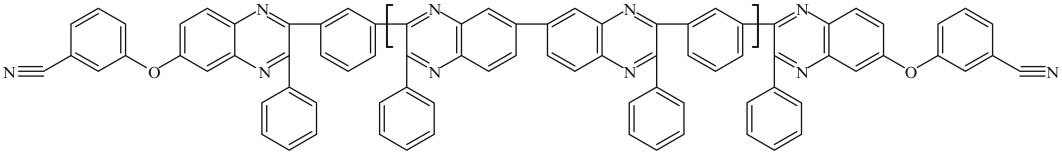


Many polymers that are described in this section can be prepared in either one or in two steps. In the one-step process, polyphosphoric acid is often employed as a solvent. It is a proton donor, promotes condensation, and acts as a cyclodehydrating agent, frequently yielding polymers of high molecular weights. Shaping the resulting polymers, however, can be a problem due to infusibility and insolubility. When prepared in two steps, the polymer can be shaped into films or fibers first, before much cyclization takes place, while the material is still fusible and solvent-soluble. This is followed by further heating to complete the process. Cyclization in this process occurs in solid polymers that become increasingly rigid as the reaction progresses. The products, however, prepared by this procedure are not as fully cyclized as are those formed in the one-step process in phosphoric acid solution.

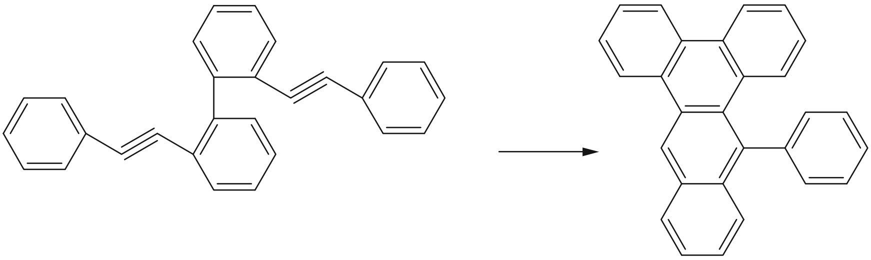
7.17.6 Oligomers with Terminal Functional Groups

The above-described two-step processes yield polymers that evolve volatiles upon further heating because the condensations continue. To overcome this drawback, prepolymers were developed that undergo addition-type reactions at fairly moderate time-temperature schedules [215, 216].

Such prepolymers are *terminated by functional groups*. Following is an example of one such material, an oligomer, polyquinoxaline terminated by acetylene groups:



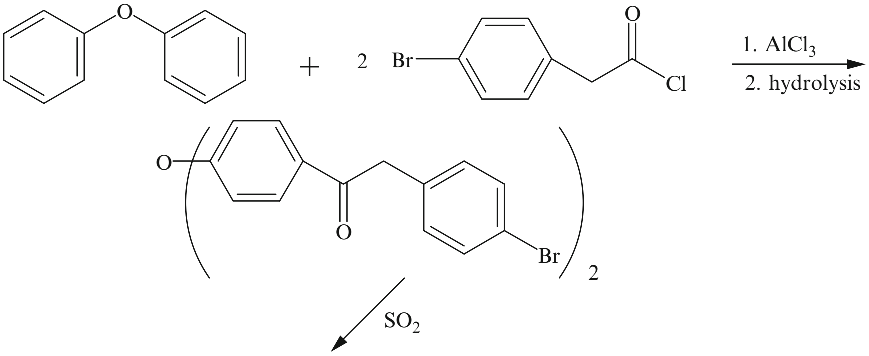
No volatiles can be detected by mass spectrometry [215, 216] or by thermo gravimetric analyses during the cross-linking reaction. The thermo oxidative stability of the resultant polymers is at least equivalent to polyphenylquioxalines not terminated by acetylene. The cross-linking reaction was shown on a model compound to be an intramolecular cyclization [215–217]:

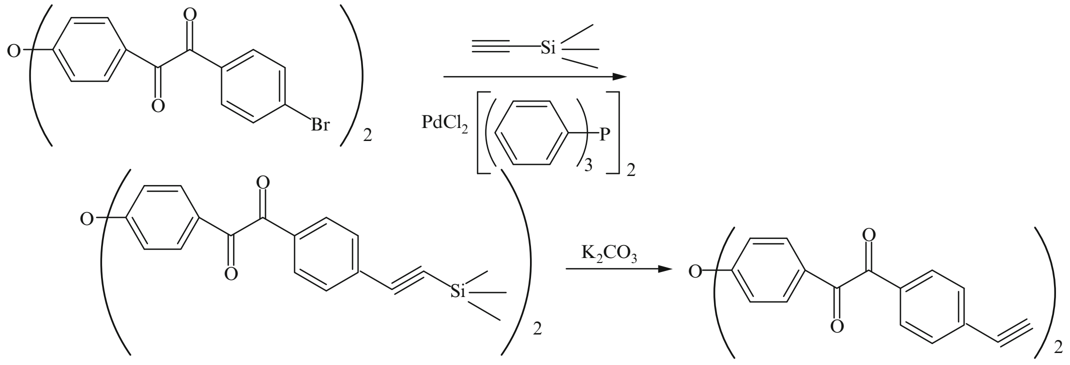


It is not necessary for the acetylenic groups to be on the terminal ends of the prepolymers. They can also be located as pendant structures [216].

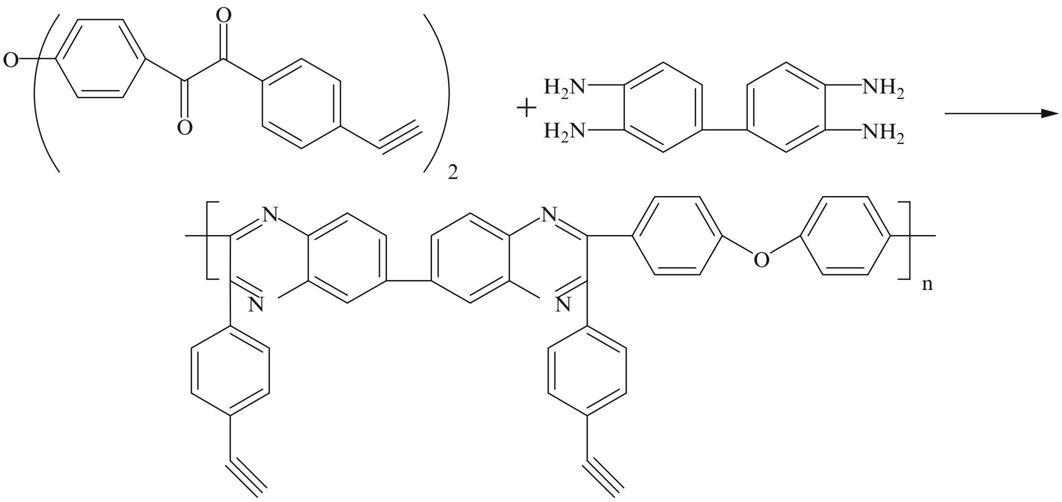
Aromatic polyamides with terminal acetylenic groups [218] were formed from 2,2′-diiododiphenyl-4,4′-dicarbonyl chloride reacted with aromatic diamines. The phenylethynyl groups were introduced by reacting the iodine moieties with copper phenyl acetylide. Thermal treatment converted the prepolymers to 9-phenyl dibenzanthracene-based rigid-rod polymers that fail to melt below 500°C.

High molecular weight polyquinoxaline polymers were prepared from 3,3′,4,4′-tetraamino-biphenyl that was reacted with aromatic bis(α-diketones) and/or ethynyl-substituted aromatic bis (α-diketones) [219]. The polymers contain 0, 5, 10, 30, and 100% pendant groups. Also, ethynyl-substituted diketones were synthesized by the following procedure:





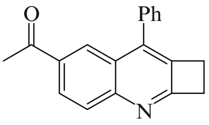
The synthesis is completed by condensation with a tetramine:



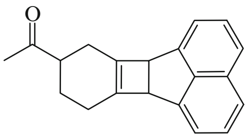
Above shown reactions yield polymers with high T_g values. The materials, however, exhibited lowered thermo oxidative stability. The same was found to be true when the ethynyl moieties were replaced by phenylethynyl groups [219].

Other functional groups that were investigated [229] are phenylethynyl, phenylbutadiynyl, phenylbutenyl, biphenylene, styryl, maleimide, nadimide (5-norbornene-2,3-dicarboximide), cyanate, and *N*-cyanourea [230]. The advantage of terminally capped prepolymers is that they melt at lower temperatures and can be dissolved in different solvent. Heating of these materials converts them to thermally stable polymeric networks.

A recent paper reports preparation of quinoline oligomers that were end-capped with 4-acetylbenzocyclobutene, 6-acetyl-8-phenyl-1,2-dihydro-[3, 4]cyclobuta-[1,2-*b*]quinone (CBQ), and 8-acetyl-6*b*,10*b*-dihydrobenzo-[*j*]cyclobuta-[1,2-α]-acenaphthalene(BCBAN) [230]. The structures of the two cross-linking groups are:



CBQ

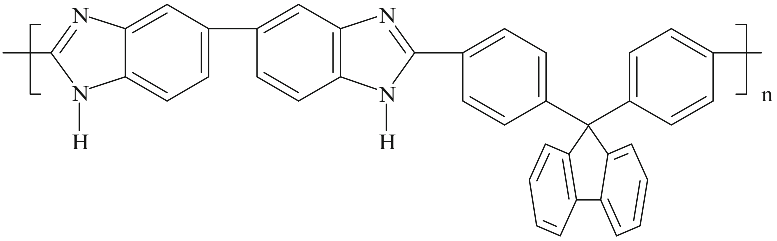


BCBAN

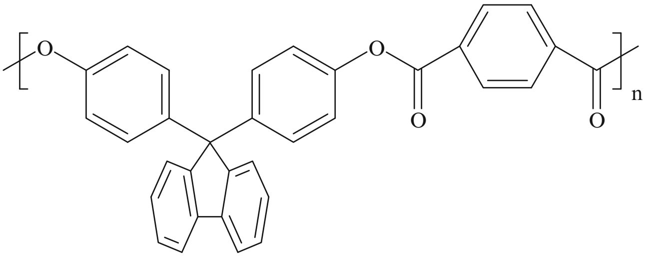
It was reported [230] that the oligomer capped with BCBAN yields a cured film that exhibits good flexural moduli and superior heat stability in air at 400°C.

7.17.7 Cardo Polymers

These are a special group [201, 208, 220] of polymeric materials. The name cardo comes from Latin, meaning loop [201, 208]. The polymers contain cyclic structures that may be perpendicular to the aromatic backbones. An example would be a cardo polybenzimidazole:



Another example is a cardo polyester [201, 208]:

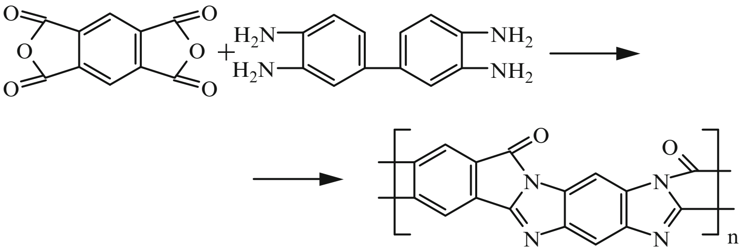


Many cardo polymers exhibit improved solubility in different solvents with little sacrifice in properties. A survey was made of the physical properties of different cardo copolyimides with varying microstructures [220]. As might be expected, copolyimides with increasing aliphatic fragment content were shown to exhibit the highest impact and flexural strength.

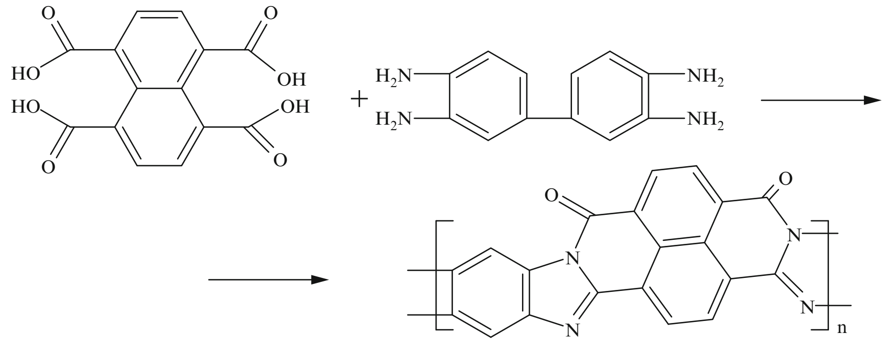
7.17.8 Double-Stranded Polymers

Preparations of many double-stranded polymers were reported. For instance, polypyrrolones were formed from 2,3,5,6-tetraaminobenzene and various dianhydrides or tetracarboxylic acid compounds [213]. Following are two examples:

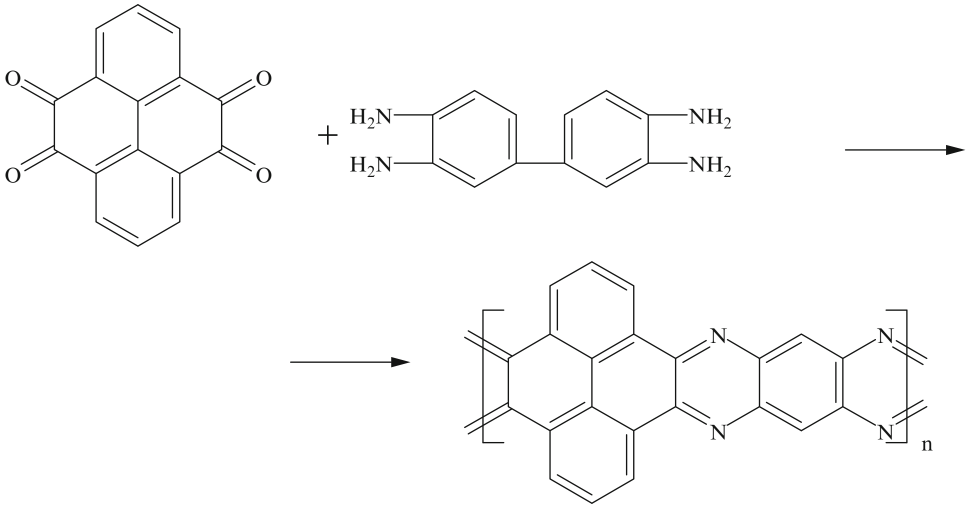
1.



2.



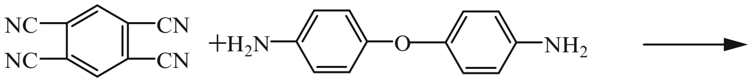
Different ladder polyquinoxalines were prepared as well. One example is shown below [233]:

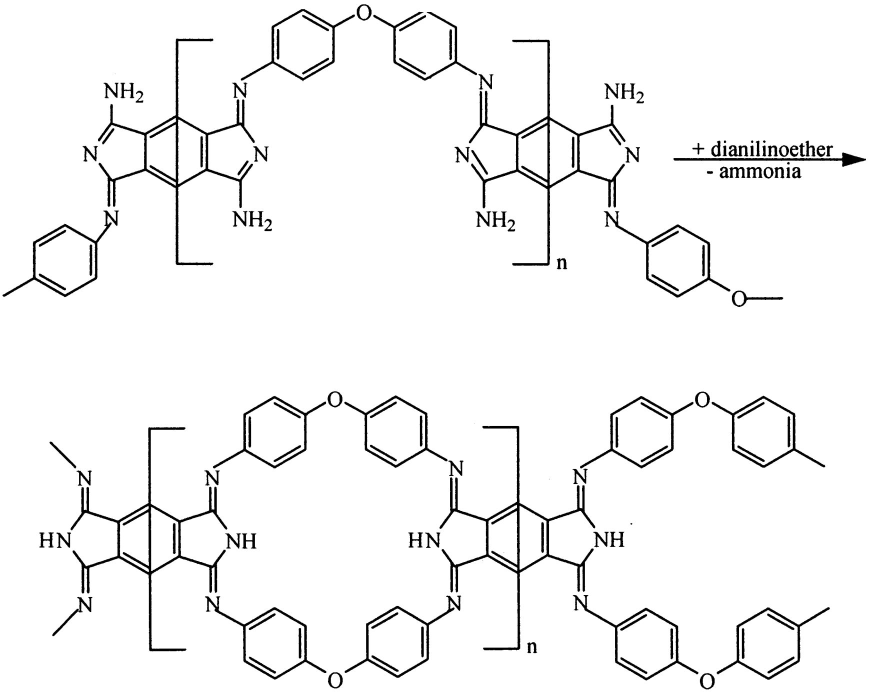


Some ladder polyquinoxalines were found to be stable in air at 460°C and in nitrogen up to 683°C.

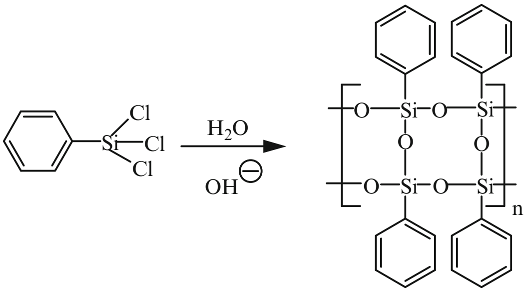
Not all attempts at formations of ladder polymers yielded completely cyclized fused ring structures. For instance, an attempt to form a polymer from tetraaminonaphthalene with naphthalene tetracarboxylic acid dianhydride failed to yield complete cyclizations [222].

An interesting polymer containing macrocyclic rings was formed from pyromellitic tetranitrile by condensation with dianilino ether [223]:



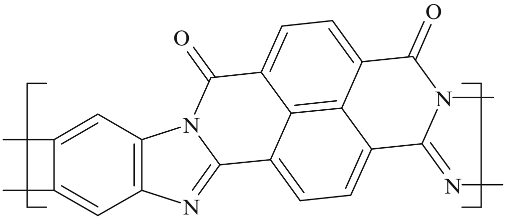


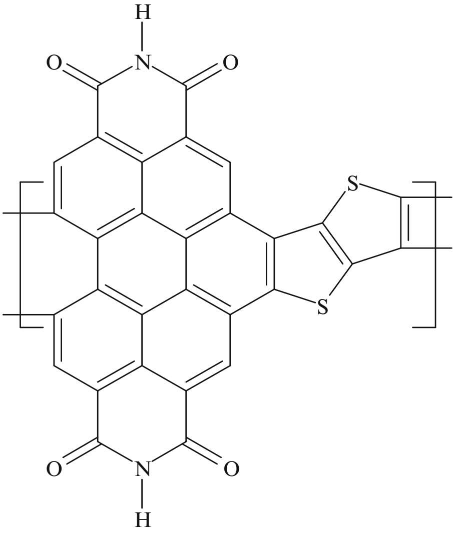
The description of all the double-stranded polymers that were synthesized and reported in the literature is beyond the scope of this book. This section is concluded by mentioning two more materials. One prepared by an alkali catalyzed polymerization of phenyltrichlorosilane [224]:



The above polymer is *cis*-syndiotactic [225] with a *cis*-anti-*cis* arrangement of the phenyl groups. It is stable at temperatures up to 525°C.

The other ones are a soluble ladder conjugated polymer, composed of perylene diimides and thieno [3,2 b]thiophene was prepared recently by a synthesis via photo cyclization by irradiation with sunlight [224]. These soluble polymers, prepared for photonic applications, can be illustrated as follows:

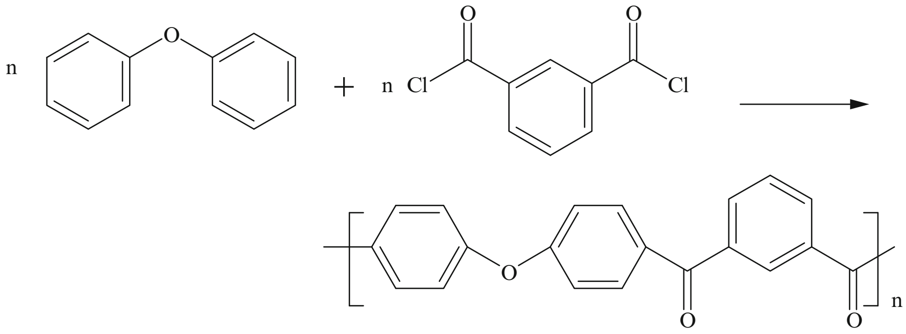




7.17.9 Poly(arylene ether)s and Poly(arylene ether ketone)s

High-performance polymeric material are poly(arylene ether)s and poly(arylene ether ketone)s. They can be used as structural resins because in composite fabrications they offer an attractive combination of chemical, mechanical, and physical properties.

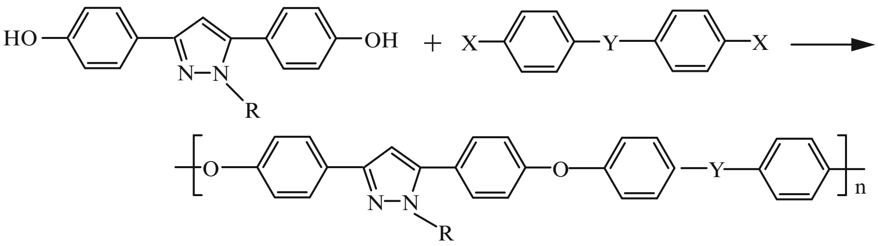
Commercial poly(ether ketone)s that are also poly(arylene ether)s are formed from diacid chloride by the Friedel–Craft reaction [234].



Similar polyketones form from dicarboxylic acids rather than dicarboxylic acid chlorides, when P_2O_5—methanesulfonic acid is used as a catalyst [235]. All these materials form a group of tough, high melting resins.

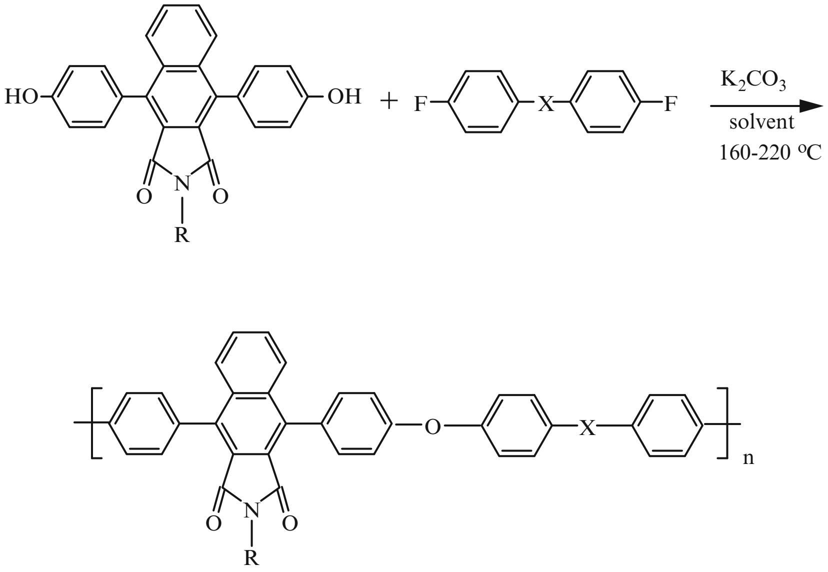
Some current preparations of poly(arylene ether)s are carried out by nucleophilic displacements of activated aromatic dihalides or dinitro groups by alkali metal bisphenates. The reactions take place in polar aprotic solvents. The glass transition temperatures, tensile strengths, and tensile moduli of these materials tend to increase when heterocyclic units are incorporated into the backbones. Poly(arylene ether)s containing imide [236], phenylquinoxaline [237–239], imidazoles [240], pyrazoles [241], 1,3,4-oxadiazoles [240], benzoxazoles [240], and benzimidazoles [240] groups were prepared.

The preparation of such polymeric materials can be illustrated as follows [241]:



where R = H, Ph; X = Cl, F; Y = carbonyl, sulfone, or a diketone aryl group. The above shown medium and high molecular weight polymers exhibit good solubility in solvents like dimethyl acetamide and good thermal stability. The same is true of the other poly(arylene ether)s mentioned above. As a result, these high-performance thermoplastics have the potential of being useful in low cost composite fabrications.

One paper [242] describes preparation of poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s that exhibit particularly good heat stability. The synthesis can be illustrated as follows:



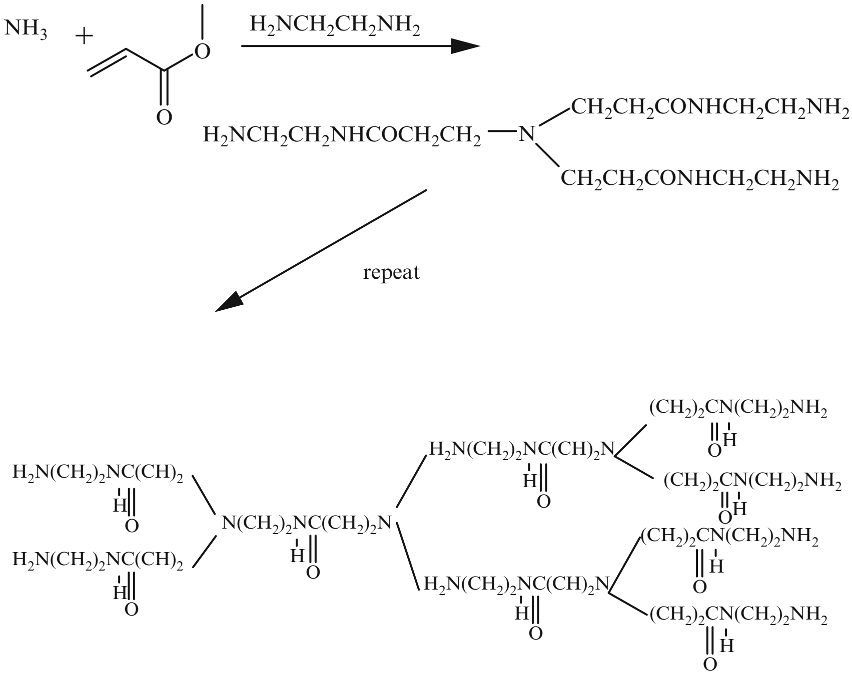
where: R = CH_3; $CH_3(CH_2)_{11}$; Phenyl; X = SO_2; CO; Isophthaloyl; Based on thermogravimetric analyses, the phenyl substituted polymers lose only 10% of their weight in air and in nitrogen at 550°C. In addition, the polymers have high glass transition temperatures and remain soluble in common solvents, like chloroform and methylene chloride. These are high molecular weights polymers that can be cast from solution to give tough, flexible films [242].

7.18 Dendrimers and Polyrotaxanes

One of the fascinating things about polymer chemistry is the ability of the chemists to develop new and interesting molecular structures. This can result in formation of materials with unique properties. Among such materials are dendrimers and polyrotaxanes.

7.18.1 Dendrimers and Hyperbranched Polymers

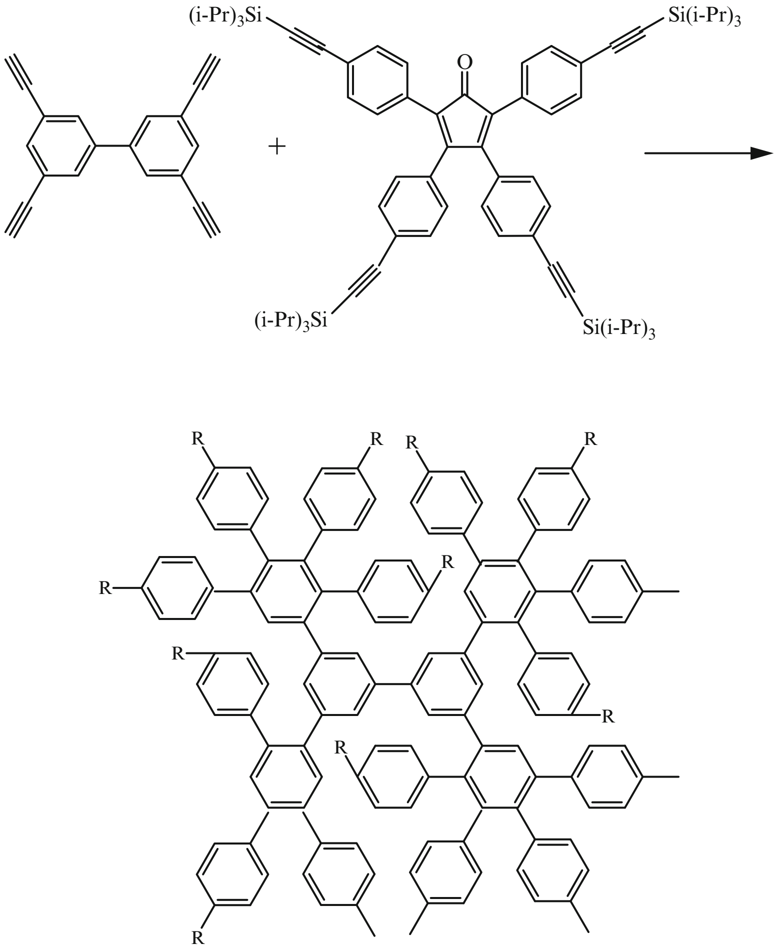
Highly branched polymeric materials with large number of end groups can offer unique physical properties. Dendrimers (described in Chap. 1) differ from linear polymers in viscosity and thermal behavior. A variety of applications have been forecast for these highly branched globular macromolecules. One early approach to dedrimer synthesis relied upon the Michael reaction using repeated sequential additions of an amine to α,β-unsaturated ester [248]:



In the first step, ammonia is added to an excess of methyl acrylate. The product is reacted with an excess of ethylenediamine to form a star molecule with three arms. The product of the second step is then reacted with an excess of methyl acrylate. This is followed by a reaction with an excess of ethylenediamine to form a molecule with six arms. The sequences are repeated to yield a star polymer. Such star polymers are sometimes referred to as *starburst polymers*.

A recent publication described preparation of dendrimers from functional aliphatic polyesters that are based on 2,2-bis(hydroxymethyl)propionic acid [249]. *N*,*N*′-dicyclohexylcarbodiimide was used as the coupling agent in a double-stage convergent approach that reduced the number of synthetic and liquid chromatographic steps required in the preparations and purifications. The hydroxyl functional dendrimers were then subjected to a variety of surface modifications by reactions with different acid chlorides [249].

Another publication describes formation of polyphenylene dendrimers that formed nanoparticles with 102 benzene rings [250]. In this preparation, an A—B type monomer, 2,3,4,5-tetrakis(4-triisopropylsilylethynylphenyl)-cyclopenta-2,3-dienone, is condensed in a [4 + 2]cycloaddition with 3,3′,5,5′-tetraethynyl-biphenyl:

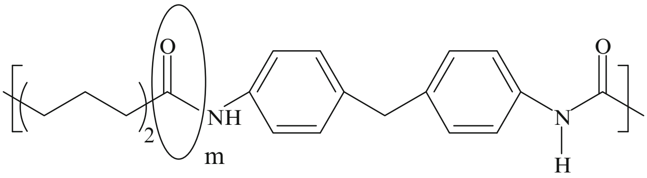


The above condensation reactions were carried out at 180–200°C in aromatic solvents [250].

Preparation of dendrimers usually involves numerous synthetic steps. Some attempted to simplify the process by merely forming hyperbranched polymer. The products have less perfect structures than dendrimers, but offer the advantage of being synthesized in only one step. A recent publication describes preparation of hyperbranched poly(ε-caprolactone)s [251]. Living ring opening polymerizations were carried out with the aid aluminum benzyl oxide as the initiator. The resultant polymers were then functionalized with benzylidine-protected 2,2′bis(hydroxymethyl)propionic acid. After a subsequent deprotection, α-carboxylic-ω-dihydroxyl functional AB_2 macromonomers formed. These AB_2 polyesters were then condensed into hyperbranched polymers through a room-temperature esterification synthesis using dicyclohexylcarbodiimide and 4-(dimethylamino) pyridinium 4-toluenesulfonate [251].

7.18.2 Polyrotaxanes

Preparation of polymeric materials that consist of linear structures threaded through large rings (see Chap. 1) has intrigued many. The result is that various publications have appeared in the literature describing such preparations [252, 253]. In many instances, crown ethers are used to have polyesters, polyamides, polyurethanes, or polystyrene threaded through them [254]. One approach to the synthesis is to carry out the polymerization reaction in the presence of the macrocycles and to form the threading in one step [254]. Another approach is to stir a solution or a melt of an aliphatic crown ether and a linear polymer like a polyurethane [255]. The hydrogen bonding between the NH groups of the polymer and the ether oxygen atoms of the cyclic species is described as the driving force for the threading. The products of such preparations are described as pseudorotaxanes:



The degree of threading was found to increase with increasing molar feed ratio of crown ethers to the polymeric NH groups [255].

Polymeric rotaxanes were reviewed recently by Harada et al.

7.19 Thermodynamics of Step-Growth Polymerization

The number average degree of polymerization $\bar{P}_n$ for a condensation reaction of a diacid with a glycol and elimination of water is a function of the extent of the reaction. We can, therefore, write:

$$\bar{P}_n = 1/(1-p)$$

In such a reaction, the equilibrium being constant, the rate constant is independent of the molecular size. It is, therefore, possible to write.

$$K = pn_{\mathrm{H}}/(1-p)^2.$$

where, n_{H} is the concentration of water formed in the reaction, and p is the extent of the reaction. By the same token, the average degree of polymerization can be written as

$$\bar{P}_n = (2K/n_{\mathrm{H}})/[(1+4K/n_{\mathrm{H}})^{1/2}-1]$$

if K/n_{H} is equal to 1 then,

$$\bar{P}_n = (K/n_{\mathrm{H}})^{1/2}$$

Therefore,

$$\delta \ln \bar{P}_n/\delta(1/T) = \frac{1}{2}[\delta \ln K/\delta(1/T) - \delta \ln n_{\mathrm{H}}/\delta(1/T)]$$

The free energy change in step growth condensation, $\Delta F = \Delta H - T\Delta S = RT \ln K$. By plotting ln K against reciprocals of absolute temperatures, one obtains roughly a linear relationship. Sawada wrote, therefore,

$$\delta \ln \bar{P}_n/\delta(1/T) = \alpha\Delta H$$

where, α is a constant and ΔH is the enthalpy change of the reaction.

Review Questions

Section 7.1

1. Describe the types of monomers that can undergo step-growth polymerizations.
2. Illustrate step-growth polymerization on formation of poly(butylene adipate), showing dimers, tetramers, etc.
3. Does the size of the molecule influence the reactivity of the functional group? Explain.
4. How would you express the rate of disappearance of one of the functional groups?
5. Assuming that the concentrations of the two reacting functional groups are stochiometrically equal, write the rate equation.
6. Write the equation for the degree of polymerization in step-growth polymerization.
7. What is stoichiometric imbalance and how is it designated?
8. Write the expression for the molecular weight average of the product and also for the molecular weight distribution.
9. By including the average functionality factor, write the equation for the degree of conversion.
10. Discuss ring formations that can accompany step-growth polymerizations.
11. Explain how step-growth polymers are formed in the melt and by interfacial polycondensation. Why isn't the preparatory technique applicable to preparation of aliphatic polyesters yet works well in preparation of aliphatic polyamides?
12. In trying to form a polyester from γ-hydroxybutyric acid what percent conversion is required to obtain a molecular weight of 25,000.

Section 7.2

1. Write chemical equations for eight common synthetic methods for preparing polyesters. Can you discuss advantages and disadvantages of each synthesis?
2. Describe, giving chemical equations, catalysts, and reaction conditions for commercial preparations of poly(ethylene terephthalate)
3. Explain, including chemical structures, how polyester elastomers are formed.
4. What are the linear unsaturated polyesters? Explain. Show by chemical reactions how they are prepared. How are they cross-linked? Explain with the help of chemical reactions.
5. Describe network polyesters. Explain how they are prepared by two different techniques.
6. What are short, medium, and long oil alkyds?
7. There are two different techniques for forming polycarbonates. Describe each.
8. What is the synthetic route to polycarbonates with the aid of crown ethers? Explain with the help of chemical equations.
9. What are the commercial uses for polycaprolactone?

Section 7.3

1. Discuss nylon nomenclature.
2. Discuss the chemistry of preparation of nylons 1, 3, 4, and 5 showing all the equations.
3. Discuss the common synthetic routes to caprolactam.
4. Describe conditions for the preparation of nylon 6.

5. Describe with chemical equations the preparations of nylon 7 and 9. What are the shortcomings of the process used in Russia? Explain.
6. Describe with chemical equations the synthetic route to nylons 8 and 12.
7. How is nylon 11 produced from methyl ricinoleate. Show all the steps.
8. Describe with chemical equations the commercial synthesis of Trogamid T?
9. What are fatty polyamides and how are they formed?
10. What is nylon 6T and how is it produced?
11. Discuss the chemistry of preparation of fully aromatic polyamides, showing chemical structures.
12. Explain with an example how the Heck reaction can be extended to form aromatic polyamides.

Section 7.4

1. Discuss the chemistry of aromatic polyamide-imides and aromatic polyester-imides. Give examples.

Section 7.5

1. What are the most common commercial procedures for preparations of aromatic polyimides? Describe with illustrations.
2. What dianhydrides are most commonly used commercially in preparations of polyimides?
3. Illustrate with chemical reactions how polyimides can be formed from aromatic diisocyanates and aromatic dianhydrides. Do the same for ketimines and *N*,*N*′-bis(trimethylsilyl) compounds.
4. How can polyimides be formed from reactions of diimides with dihalides? Show the chemical reactions.
5. Show reactions for formation of polyimides from reactions of sulfur halides with unsaturated diimides and from diepoxides with diimides.
6. Illustrate and explain the photochemical reactions of bis maleimides with benzene to form polyimides.
7. Illustrate how polyimides can form by Diels–Alder reactions.

Section 7.6

1. Discuss and illustrate with chemical equations the formation of poly(phenylene oxide) by oxidative coupling reaction of 2,6-disubstituted phenols.
2. What is the commercial material called Noryl. Explain.
3. What are phenoxy resins. Describe how they are prepared and explain how they are used.

Section 7.7

1. Discuss polyacetals and describe the polyacetals available commercially today.

Section 7.8

1. Describe how poly(*p*-xylylene) was originally prepared.
2. Discuss transport polymerization and explain how it is currently practiced commercially.
3. Describe the other routes to polyxylylenes. What are the properties of polyxylylenes?

Section 7.9

1. What are the important industrial sulfur-containing polymers?
2. Show the synthetic routes by which aromatic sulfones can be prepared.
3. Describe the preparation of poly(phenylene sulfide), properties, and uses.
4. How are poly(alkylene sulfide) prepared and used commercially?

Section 7.10

1. Illustrate with chemical equations the routes to forming polyisocyanates.
2. What are the mechanisms of reactions of isocyanates with hydrogen donors? How are these reactions catalyzed? Discuss the mechanism.
3. Discuss polyurethane fibers. How are they made? What are their properties?
4. Discuss polyurethane elastomers, including properties and preparation.
5. Discuss polyurethane foams. How are they prepared?

Section 7.11

1. Discuss the chemistry of epoxy resins based on diglycidyl ethers of Bisphenol A, their preparations, and cross-linking reactions with amines, dianhydrides, and dicyanodiamide.
2. What are epoxy novolacs and what are some new epoxy resins containing nitrogen?
3. Discuss the chemistry of cycloaliphatic epoxides.

Section 7.12

1. Discuss the chemistry of resoles, showing by chemical reactions how they form. What are quinone methides, and what is meant by stages A, B, and C resins?
2. Describe the chemistry of novolacs, how they are formed and cross-linked?
3. Explain what the products are in an ammonia or amine-catalyzed condensation of phenol with formaldehyde.
4. Describe typical commercial preparations of resols and novolacs.

Section 7.13

1. Discuss the chemistry of urea-formaldehyde resins, their preparation, and uses.
2. Do the same as question one for melamine-formaldehyde resins.

Section 7.14

1. How do silicon compounds differ from carbon compounds?
2. How can the starting materials be prepared for the silicone resins?
3. How are high molecular weight silicone resins formed by ring opening polymerization? What are the products from acid catalysis and basic catalysis?
4. Describe silicone elastomers. What are RTV-s, explain and show the way they are cross-linked.
5. Discuss fluorosilicone elastomers.
6. Discuss polyarylsiloxanes.

Section 7.15

1. Why is there an interest in polysilanes? Show by chemical reactions how are they formed.

Section 7.16

1. What are polyphosphazines, how are they formed and used?

Section 7.17

1. What chemical options are available to improve heat stability and toughness of polymeric materials?
2. Discuss fluorine containing aromatic polymers.
3. Discuss the chemistry of preparation of polyphenylene.
4. Discuss Diels–Alder polymers giving at least four examples and showing all the structures of the starting materials and the products.
5. Discuss silicon-containing aromatic polymers.
6. What are direct condensation polymers? How are polybenzimidazoles, polybezoxazoles, polybenzthiazoles, polyoxidiazoles, polybenzotriazoles, and polysulfodiazoles prepared? Illustrate with chemical equations.
7. Discuss the chemistry of oligomers that are terminated by functional groups to form thermoset, high heat-resistant materials.
8. What are cardo polymers, what are their advantages, and how are they prepared?
9. Discuss double-stranded polymers and how they are prepared.
10. Discuss the chemistry of poly(arylene ether)s and poly(arylene ketone)s.

Section 7.18

1. Describe dendrimers and polyrotaxanes

Further Reading

M.E. Rodgers and T.E. Long, eds. *Synthetic Methods of Step-Growth Polymers*, Wiley, New York, 2003

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Chapter 8
Naturally Occurring Polymers

8.1 Naturally Occurring Polymers

There are many naturally occurring polymeric materials. Many are quite complex. It is possible, however, to apply an arbitrary classification and to divide them into six main categories. These are:

1. Polysaccharides. This category includes starch, cellulose, chitin, pectin, alginic acid, natural gums, and others.
2. Proteins or naturally occurring polyamides found in animal and vegetable sources.
3. Polyisoprenes or natural rubbers and similar materials that are isolated from saps of plants.
4. Polynucleotides include all the deoxyribonucleic acid (DNAs) and all the ribonucleic acids (RNAs) found in all living organisms.
5. Lignin or polymeric materials of coniferyl alcohol and related substances.
6. Naturally occurring miscellaneous polymers, like, for instance, shellac, a resin secreted by the Lac insect. This is a complex cross-linked polyester of 9,10,16-trihydroxy-exadecanoic acid (aleuritic acid). The structure also includes some unsaturated long-chain aliphatic acids together with other compounds [1].

8.2 Polysaccharides

Fischer [2] carried out some of the original investigations of the monomeric species of many polysaccharides during the last century. He was able to demonstrate the configurational relationships within some monosaccharides.

The monomers in these naturally occurring polymers are five- or six-carbon sugars. There is considerable variety among the polysaccharides and the polymers generally tend to be polydisperse, depending upon the source.

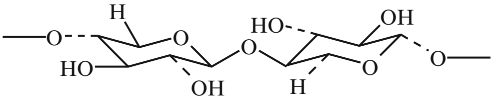
8.2.1 Hemicelluloses

Hydrolyses of hemicelluloses yield mixtures of glucose, glucuronic acid, xylose, arabinose, galactose, galacturonic acid, mannose, and rhamnose. Some common polymers of pentoses, also known as pentosans, are xylan, galactan, araban, and others. Pentosans are found in large amounts (20–40%)

A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_8,

in cereal straws and in brans. Large-scale industrial preparations of furfural, for instance, are based on these materials.

Xylan, one of the better-known hemicelluloses, is a component of plant cell membranes. This pentosan occurs in association with cellulose. The structure of xylan was shown to be 1,4-polyxylose [3]:



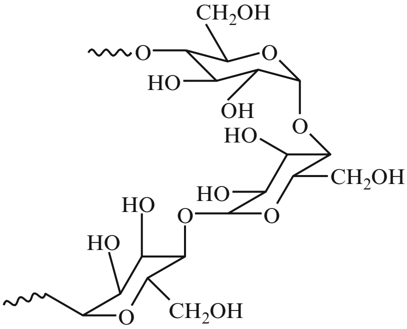
Another hemicellulose, ***Galactan***, is a minor component of some coniferous and deciduous woods. Larch wood was shown to contain about 8% of this polymer [4].

Araban, or polyarabinose is found in plant saps. All ***pectins*** also belong to the family of hemicelluloses. These are gelatinizing substances that are found in many plants, particularly in fruit juices. Crude pectins contain pentosans, galactosans, and similar materials. Purified pectins yield on hydrolysis galacturonic acid and methanol. These high molecular weight polymers are believed to consists to a good extent of poly (galacturonic acid), partially esterified with methyl alcohol. In addition, the polymers contain galactose and arabinose molecules. The polymer is probably linear [5–10] with a 1,4-glucosidal linkage between monomers. The relative amount of various components depends upon the source of the pectin. Citrus pectin, for instance, is rich in galacturonic acid but poor in galactose and arabinose.

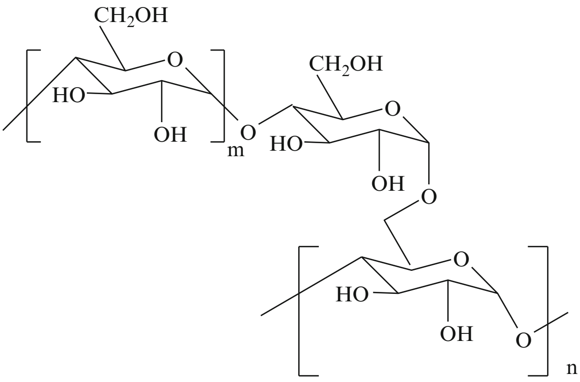
Plant gums and mucilages are high molecular weight polysaccharides composed of hexoses and pentoses. They also contain some uronic acid units. Among the gums there is gum arabic, gum tragacanth, and many others.

8.2.2 Starch

This is the most widely distributed substance in the vegetable kingdom and is the chief reserve carbohydrate of plants. Starch consists of single repeat units of D-glucose linked together through 1 and 4 carbons by α-linkages (*cis*) [10]. There are two types of starch molecules, ***amylose*** and ***amylopectin***. The first one is mainly a linear polymer. Its molecular weight can range from 30,000 to 1,000,000, though it is mostly 200,000–300,000. Amylose is often pictured in a spiral form due to the conformation of the α-glucoside bonds:



Amylopectin, on the other hand, is branched through carbon 6:



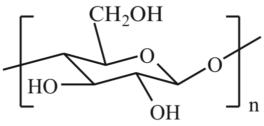
The ratios of amylopectin to amylose in many natural starches are about 3:1. The main commercial source of starch in this country is corn. Lesser amounts of industrial starch are obtained from potatoes, wheat, and tapioca (not necessarily in that order). The extraction of starch from plant material is done by grinding the plant tissues in water. The slurry is then filtered to obtain a suspension of starch granules. These granules are then collected with the aid of a centrifuge and dried.

When a water suspension of starch granules is heated to 60–80°C, the granules swell and rupture. This results in formation a viscous colloidal dispersion containing some dissolved starch molecules. Cooling this dispersion results in formation of a gel, due to aggregation of the amylose molecules. It is essentially a crystallization phenomenon, known as ***retrogration.*** By comparison, amylopectin molecules cannot associate so readily due to branching and will not gel under these conditions.

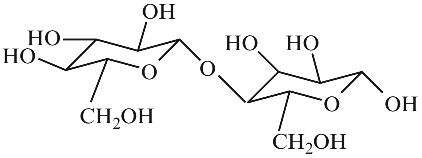
Starches are modified chemically in various ways. Some acetate and phosphate esters are produced commercially, as well as hydroxyalkyl and tertiary aminoalkyl ethers. Both unmodified and modified starches are used principally in papermaking, paper coating, paper adhesives, textile sizes, and as food thickeners. There are many reports in the literature on graft copolymers of starch. The work is often done in search of biodegradable materials for packaging and agricultural mulches. Most chemical modifications of starch parallel those of cellulose.

8.2.3 Cellulose

This polysaccharide is found widely in nature. It is a major constituent of plant tissues (50–70%, depending upon the wood), fibers, and leaf stalks. Chemically cellulose is 1,4-β-poly-anhydroglucose [12] (*trans*):



where *n* represents several thousand units. Hydrolysis of cellulose yields 95–96% D-glucose. This establishes its structure. Acetolysis of cellulose, however, yields cellobiose, a disaccharide, 4-O-β-D-glucopyranosyl-D-glucopyranose:



The structure of cellulose is, therefore, officially based on cellobiose units. Careful molecular weight measurements by many [12] established that the DP of cellulose ranges from 2,000 to 6,700, depending upon the source. The polymer is highly crystalline and is characterized by a very high degree of intermolecular and intramolecular hydrogen bonding. This prevents it from being thermoplastic as it decomposes upon heating without melting.

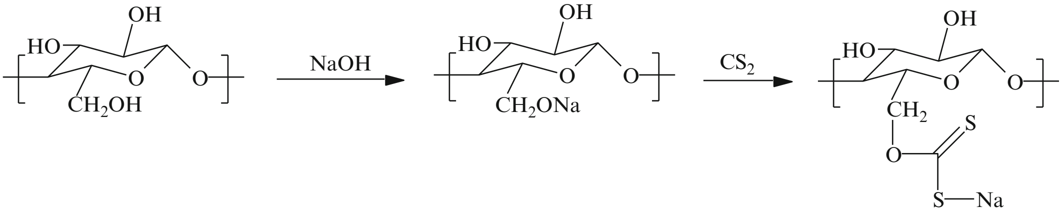
8.2.3.1 Regenerated Cellulose

Cellulose is used in many forms. Often it is modified chemically to render it soluble in organic solvents. In other modifications, it is treated in a manner that allows forming it into desired shapes, like films or fibers, followed by restoration of its chemically insoluble form. The material is then called regenerated cellulose.

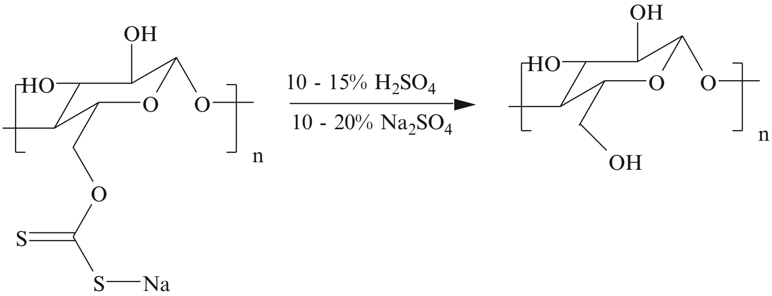
Several processes evolved for preparation of regenerated cellulose. One, developed as far back as 1884, converts it first to a nitrate ester. The nitrated material is dissolved in a mixture of ethyl alcohol and diethyl ether and extruded into fibers. The fibers are then denitrated by treatment with ammonium hydrogen sulfide at about 40°C. The product is called *Chardonnet silk*. It appears that this process is no longer practiced anywhere.

In another process cellulose is dissolved in ammoniacal cupric hydroxide ($Cu(NH_3)_4(OH)_2$). The solution is then spun as a fiber into a dilute sulfuric acid solution to regenerate the cellulose. The product is called ***Cuprammonium rayon.*** The material may still be manufactured on a limited scale.

The third, probably major commercial process used today, forms a material that is known as *Viscose rayon*. The regenerated cellulose is prepared and sold as a fiber as well as a film, known as *cellophane*. The viscose, or more properly referred to as the *xanthate* process, consists of forming cellulose xanthate by reacting alkali cellulose with carbon disulfide:



In a typical procedure, cellulose is steeped in an approximately 20% aqueous sodium hydroxide solution at room temperature for anywhere from 20 min to a whole hour. It is believed that this treatment results in formation of sodium alcoholate at every hydroxymethyl group. The resultant material is pressed out to remove excess liquid, shredded, and aged for 2–3 days. The aging is known to cause some molecular weight reduction. After aging, the alkali cellulose is treated with carbon disulfide for 2–4 h to form cellulose xanthate. The amount of xanthate groups in the product average out to one per every two glucose units. The material is dissolved in a dilute sodium hydroxide solution and again aged for 2–5 days. During the aging period, some xanthate groups decompose. The solution is then spun into dilute sulfuric acid to regenerate the cellulose and form fibers:



The rayon fibers are washed, bleached, and submitted to other various treatments, like dyeing, etc., depending upon intended use.

When cellulose xanthate is extruded through narrow slits into acid baths, cellophane films form. These films are usually plasticized by washing in baths containing some glycerin.

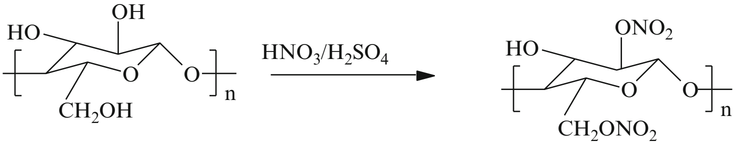
8.2.3.2 Derivatives of Cellulose

Many *derivatives of cellulose* have been synthesized over the years [12–14]. These include esters of both organic and inorganic acids, ethers, and various graft copolymers. Only some of them, however, achieved commercial importance.

One of the earliest commercial esters of cellulose was ***cellulose nitrate***. It was originally prepared as an explosive (***guncotton***) in the middle of the nineteenth century, and later as a medical aid (*collodion*, for covering wounds). Later films from cellulose nitrate were used in photography, called ***celluloid***. Nitrocellulose was also probably the first successful commercial plastic, used to form many articles. Today it is generally displaced by other materials. Cellulose nitrate, however, is still being used in some surface finishes, though here too it is gradually being displaced.

Cellulose is nitrated by mixtures of nitric and sulfuric acids. The type of acid mixture used depends on the intended products. For the preparation of plastic grade materials, 25% of nitric acid is combined with 55% of sulfuric acid and 20% water. The dried cellulose is soaked for 20–60 min at 30–40°C. There is little change in appearance as the structure of the cellulose is maintained. The bulk of the acid is then removed, usually by spinning in a centrifuge and the remaining acid washed out with copious amounts of water. The product is often bleached with sodium hypochlorite and washed.

The degree of nitration is controlled by reaction conditions and particularly by the amount of water in the nitrating bath. Products with 1.9–2.0 nitrate groups per each glucose unit are used in plastics and lacquers. Some materials, however, with a nitrate content as high as 2.0–2.4 groups per each glucose have been used in some lacquers. The higher nitrate content of 2.4–2.8 groups per each glucose is in materials intended for use as explosives. The esterification reaction can be illustrated as follows:



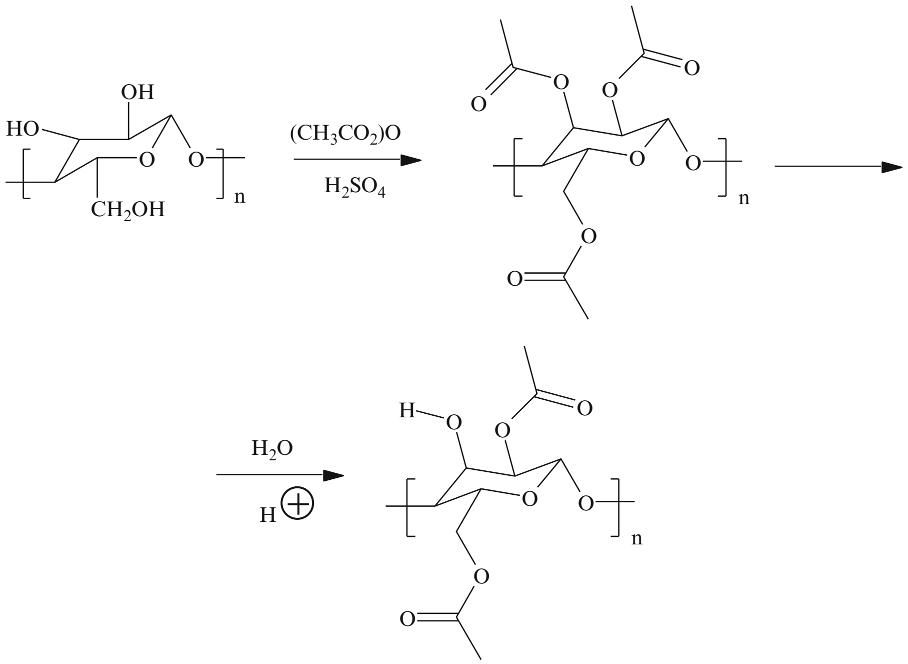
The molecular weight of cellulose nitrates used in plastics and lacquers is usually reduced. This is done by heating the slurry of the polymer in water at about 130–160°C for up to 30 min under pressure.

Cellulose acetate was also prepared originally in the nineteenth century. Commercial development, however, started early in twentieth century. In the 1920s acetate rayon and acetate fibers were developed and cellulose acetate became an important molding material. At about the same time cellulose lacquers were also developed. Today, however, many of these materials have been replaced by other polymers.

The acetylation reaction of cellulose is often prepared by forming a solution in a mixture of acetic anhydride and sulfuric acid. This results in formation of a triacetate. When a lower degree of esterification is desired, the triacetate is partially hydrolyzed. A two-step procedure is needed because it is not possible to control the degree of esterification in the reaction with acetic anhydride and sulfuric acid. In a typical process, dry cellulose is pretreated with 300 parts acetic anhydride, 1 part sulfuric acid, and 400 parts methylene chloride. The reaction mixture is agitated while the temperature is maintained at 25–35°C for 5–8 h. By the end of that period, all the cellulose is dissolved and the cellulose triacetate has formed in the solution.

Partial hydrolysis is accomplished by adding to the methylene chloride solution aqueous acetic acid (50%). The solution is then allowed to stand to reach the desired degree of hydrolysis. This usually takes about 72 h at room temperature. Sulfuric acid, still present from acetylation, is then neutralized by addition of sodium acetate and most of the methylene chloride is distilled off. The partially hydrolyzed cellulose acetate is then precipitated by addition of water and washed thoroughly. The washing also includes a 2-h wash with very dilute sulfuric acid to remove hydrogen sulfate esters that cause polymer instability.

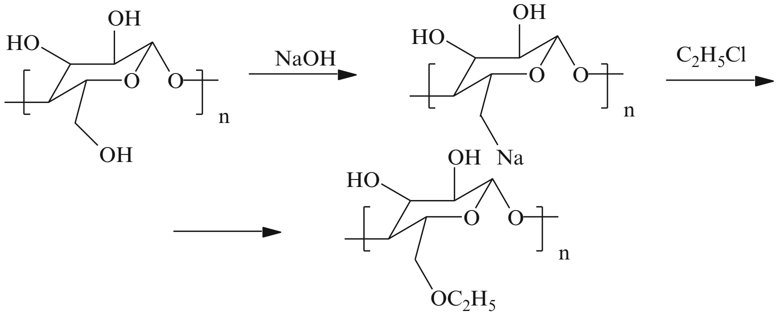
The process can be illustrated as follows:

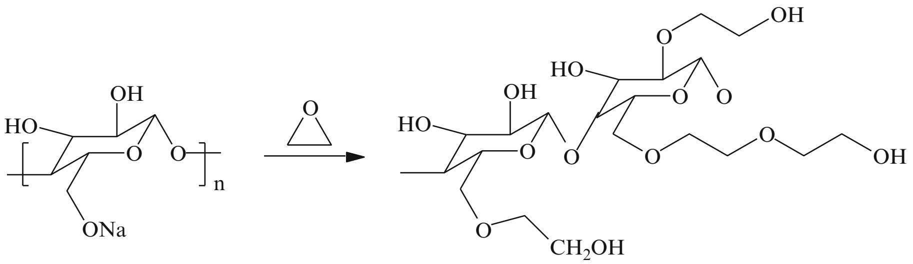


Cellulose triacetate is also prepared by a heterogeneous process in the presence of benzene, a non-solvent. The triacetate that forms in both processes is hard to mold, but it can be used in films and fibers. The diacetate is more suited for plasticization and molding.

Many other esters of cellulose were prepared at various times, including some mixed esters. Various cellulose acetate-butyrates are manufactured today and are perhaps the best known of the mixed esters. They are synthesized in the same manner as cellulose acetate. Mixed anhydrides are used in esterification reactions catalyzed by sulfuric acid. The products are then slightly hydrolyzed. The butyric groups enhance flexibility and moisture resistance. The materials have the reputation of being tough plastics and are used in such applications as tool handles. Lower molecular weight grades are also used in surface finishes.

Several ***cellulose ethers*** are also prepared commercially. The original patents for preparation of cellulose ethers date from 1912. In spite of that, cellulose ethers never attained the industrial importance of cellulose esters. The ethers are prepared by reacting alkali cellulose with an alkyl halide or with an epoxide:

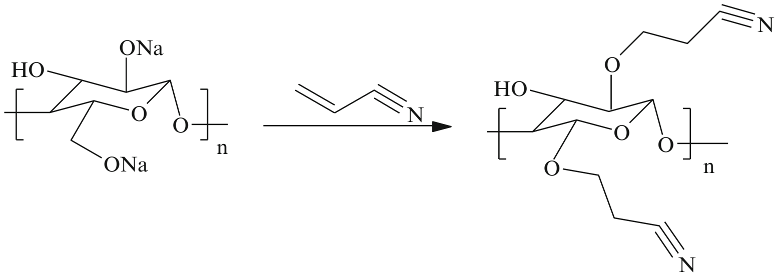




Typical commercial ethers are methyl, ethyl, hydroxyethyl, hydroxypropyl, carboxy-methyl, aminoethyl, and benzyl.

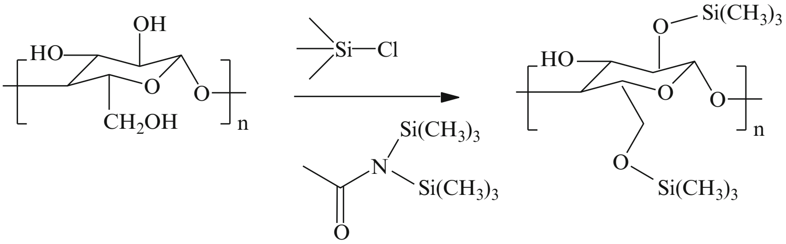
Ethyl cellulose is used industrially as a plastic similarly to cellulose acetate. The water-soluble ethers, like methyl, carboxymethyl, and hydroxyethyl, are used as thickeners in foods and in paper manufacturing.

Cellulose can be reacted with acrylonitrile to form a cyanoethylether. The Michael condensation takes place with alkali cellulose:

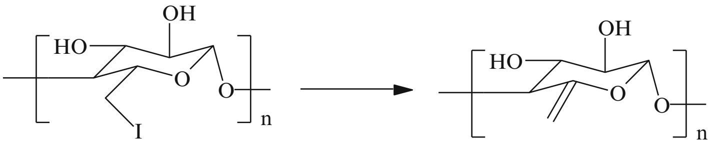


Cyanoethylated cellulose does not appear to be used commercially in any quantity.

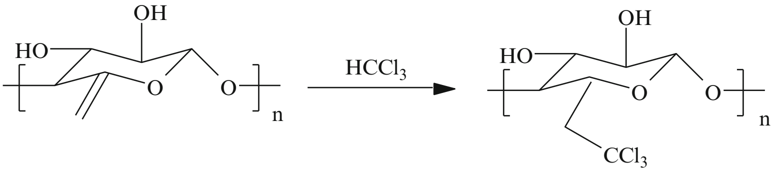
Very stable silyl ethers form when cellulose is treated with trimethyl chloro-silane or with bis (trimethylsilyl)-acetamide [15]:

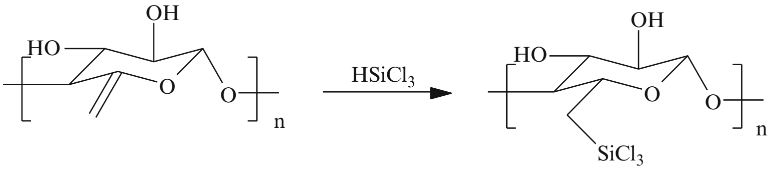


Some interesting approaches to cellulose modification are possible via formations of double bonds in the glucopyranosine unit at the 5,6 positions [16]. This is accomplished by dehydro-halogenating a previously formed 6-iodocellulose:



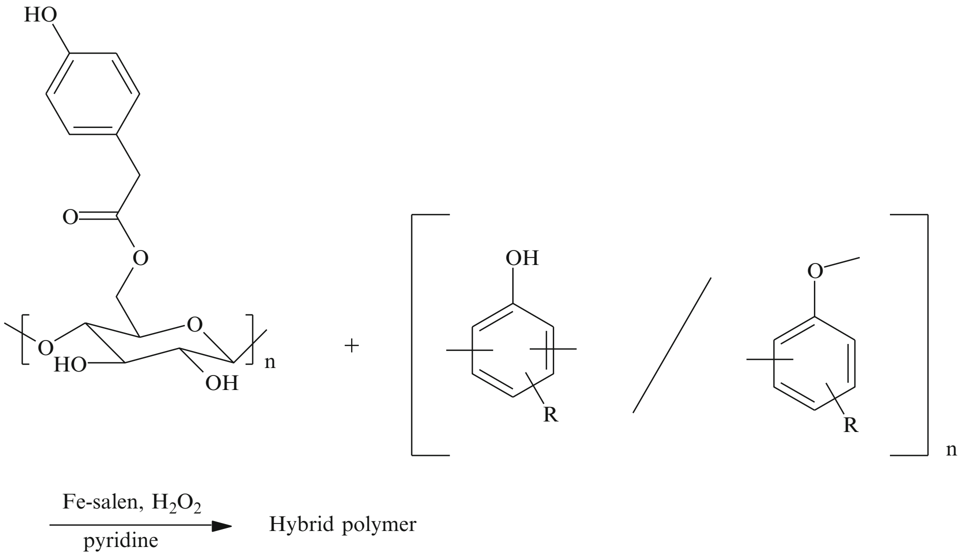
The resultant unsaturated compound can be converted into a number of derivatives. Examples of some of them are:





Other compounds that can be added across the double bonds are carbon tetrachloride, phosphorus trichloride, and methyl alcohol. Many graft copolymers of cellulose were reported. Some are described in Chap. 9.

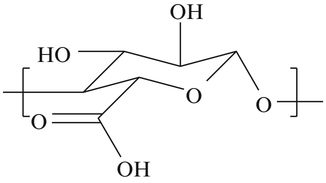
In wood, cellulose is present with lignin, a natural phenolic polymer, described in Sect. 8.3. Kobayshi and coworkers [16] grafted phenolic resins onto cellulose to form an artificial wood polymer.



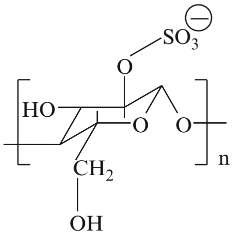
The reaction was catalyzed by a complex of iron with *N*,*N*′-ethylene bis(sallicylidene amine) as well as a horseradish peroxidase enzyme to carry out oxidative coupling of phenols using hydrogen peroxide as an oxidizing agent. The product is a new type of plastic.

8.2.4 Miscellaneous Polysaccharides

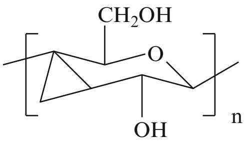
Other polysaccharides found in nature include ***alginic acid*** that is isolated from certain brown seaweeds [17]. The monomers of this polymer, similar to cellulose, are linked *trans* or β to each other, through the 1,4 positions:



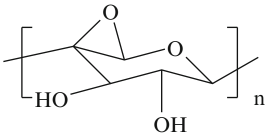
A sulfate group bearing polysaccharide is isolated from another seaweed that is red in color. This polymer is called ***carrageenan.*** It consists of two fractions [17]. The first one has the galactose units linked though 1 and 3 or 1 and 4 carbons. A sulfate group is found at carbon 2 on some units:



The second fraction has the some galactose units linked 1 and 4 and others have ether group linking carbons 3 and 6:

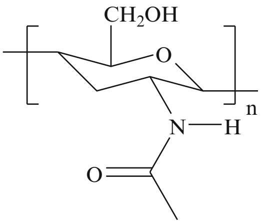


and



A similar polysaccharide is also obtained from seaweeds that is called ***agar***. It is similar in structure, but has less sulfate groups per chain.

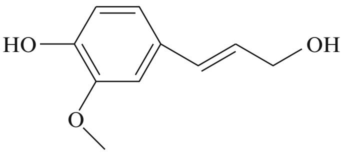
Crab and shrimp shell wastes are an abundant source of ***chitin***, a nitrogen atom-containing polysaccharide:



The polymer can be deacetylated to yield an amine group bearing polysaccharide.

8.3 Lignin

These polymers are also constituents of wood (about 25–30%) [18, 19]. It is uncertain what the molecular weights of the polymers are as the materials are quite complex in structure. The extraction processes of lignin result in considerable loss of molecular weights. The structures of lignin vary, depending upon the source. Generally, they are considered to be polymers of coniferyl alcohol:



An idealized picture of lignin that formed from coniferyl alcohol was published by Freudenberg [20]. It appears reasonable, however, that some lignins might, perhaps, also form in different trees, from other compounds not coniferyl alcohol, but related to it and also found in woods. Also it appears plausible that several of such compounds, including coniferyl alcohol, actually participate together in lignin formation, depending upon the species of wood. Figure 8.1 shows the chemical structures of some of these compounds.

Many attempts were made to convert lignin to a useful material for coatings and adhesives. Only very limited success, however, has been achieved. A reaction product with formaldehyde can be used as a wood adhesive. In addition, lignin obtained from wood pulping by the sulfate process (as a sulfonate) has been utilized to a limited extent as an asphalt extender and as an oil-well drilling mud additive.

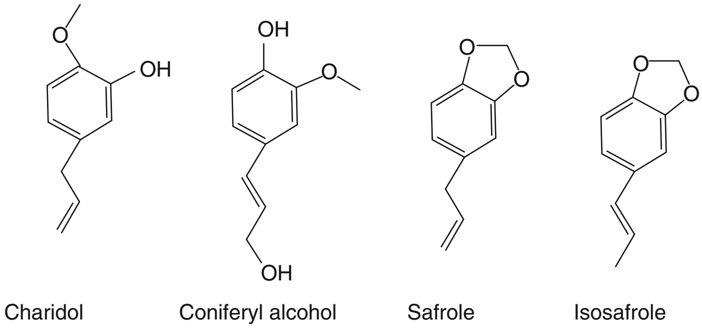


Fig. 8.1 Compounds that occur in various woods and might, perhaps, participate in formation of lignin

8.4 Polyisoprene

Natural rubber is polyisoprene [21]. It is produced commercially from the sap of trees called ***Hevea brasilensis*** and sometimes referred to as ***Hevea rubber***. These trees yield a latex containing approximately 35% rubber hydrocarbon and 5% nonrubber solids, like proteins, lipids, and inorganic salts. The remaining 60% of the latex is water. The hydrocarbon polymer consists of 97% *cis*-1,4 units, 1% *trans*-1,4 units, and 2% 3,4 units, in a head to tail structure. Molecular weights of naturally occurring polyisoprene range from 200,000 to 500,000. A verity of shrubs and small plants, including some weeds, like dandelion and milkweed also contain polyisoprene in their sap. The ***guayule*** shrub, which grows in Mexico and in southern United States, is a good potential source of natural rubber. Work is now going on in various places to cultivate this shrub for potential rubber production.

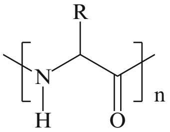
An almost all ***trans***-1,4 polymer called *gutta-percha* is found in the exudations of various trees of the genus ***Palaquium, Sapotaceae, and Habit***. The molecular weights of these polymers range from 42,000 to 100,000. *Balata* and ***chicle***, also mainly *trans*-1,4-polyisoprenes, are found in saps of some plants in West Indies, Mexico, and South America.

Chapter 9 deals with various reactions of polymers including those of natural and synthetic rubber. That includes vulcanization of rubber. While there are very many commercial applications of the ***cis*** isomer, **gutta-percha** utilization is limited to wire coatings, impregnation of textile belting, and as a component of some varnishes. Its use is limited, because it is considerably harder than natural rubber.

8.5 Proteins

These materials are building blocks of animal tissues [22, 26, 28, 31]. To a lesser extent they are also found in vegetable sources. Because the major constituents of animal bodies, including skins, hairs, and blood, are proteins, they are of much greater interest to the biochemists. Nevertheless, some proteins are important commercial materials. These include animal glues, silk, and wool. It is beyond the scope of this book, however, to render a thorough discussion of the proteins. For that reason, only some basic principles are presented here.

Proteins are naturally occurring polyamides, polymer of α-amino acids. The structure can be illustrated as follows:



Because R represents many different groups, many different combinations of α-amino acids are possible and the proteins are very complex molecules. The arrangement or sequence of amino acids in proteins is referred to as their ***primary structure***. The amide linkage is referred to in biochemistry as the ***peptide linkage*** or *the* ***peptide group***. A dipeptide then is a compound consisting of two amino acids, a tripeptide of three, etc. *Polypeptide* refers to proteins, though the term is often reserved for lower molecular weight fractions, usually less than 10,000. Many proteins are monodisperse. This distinguishes them from many other naturally occurring polymers, such as polysaccharides, that are polydisperse.

8.5.1 α-Amino Acids

Twenty-five known naturally occurring amino acids were isolated from various proteins by hydrolysis. All but one of them, glycine, possess an asymmetric carbon. Table 8.1 lists the naturally occurring amino acids and gives their structures [26, 28, 31].

Among the above shown amino acids, a certain number are known as *essential amino acids*. They are not synthesized by human bodies and must be ingested for human metabolism.

All the optically active amino acids (that means all except glycine) have an L configuration. In addition, all amino acids exist as zwitterions.

8.5.2 Structures and Chemistry of Proteins

Proteins can be separated into two major groups, ***fibrous proteins*** and ***globular proteins***, depending upon their shapes. The fibrous proteins are long molecules that function as structural materials in animal tissues. Hydrogen bonding holds these water insoluble molecules together to form extended coiled chains. To this group belong *collagen*, protein of the connecting tissues; ***myosin***, protein of the muscles; ***keratin***, protein found in hair, nails, horns, and feathers; and ***fibroin***, protein of silk fibers.

Globular proteins are held by strong intramolecular hydrogen bonds in spherical or elliptical forms. Their intermolecular forces are weak and they are soluble in water and in dilute salt solutions. To this group of proteins belong enzymes, many hormones, egg albumin, and hemoglobin.

Some proteins also contain a non-peptide portion that is attached chemically to the polyamide chain. The non-peptide moieties are called ***prosthetic groups***, and the proteins with such groups are called ***conjugated proteins***. Examples are hemoglobin and myoglobin that consist of polypeptide portions with iron–porphyrin prosthetic groups attached. This particular prosthetic group, called ***heme***, is illustrated in Fig. 8.2. There are also a number of proteins that are associated with a nucleic acid. They are known as ***nucleoproteins***.

Numerous studies of protein structures have shown that the common conformations of the protein chains (fibrous) can be either as an α-helix, β-sheets, or random coils [26]. The steric arrangement or the conformations of the proteins are referred to as the *secondary structure*, while the composition of α-amino acids in the polypeptide chains is called the ***primary structure*** [26]. Based on X-ray crystallography data, Pauling et al. [24] deduced that an *α-helix* type configuration is formed because it accommodates hydrogen bonding of each nitrogen to a carbonyl oxygen (see Fig. 8.3). It allows space for all bulky substituents in amino acids and stabilizes the structure. The α-helix is probably the most important secondary structure in proteins [26]. The two α-helix illustrations are after Pauling et al. [24]. The one on the left shows right-handed helix. It is interesting to note that an α-helix conformation may

Table 8.1 Naturally occurring amino acids [26, 28–31]

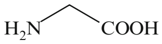
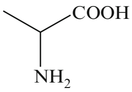
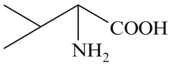
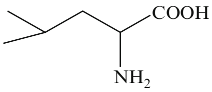
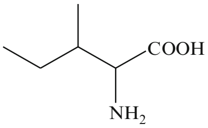
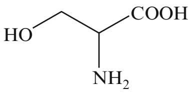
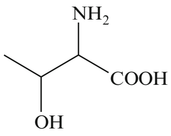
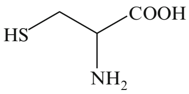
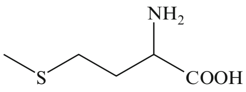
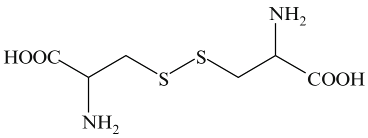
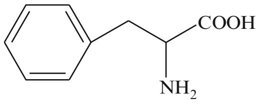
Name	Structure	Optical rotation
Glycine		(+)
Alanine		(+)
Valine		(+)
Leucine		(−)
Isoleucine		(+)
Serine		(−)
Threonine		(−)
Cysteine		(−)
Methionine		(−)
Cystine		(−)
Amino acids with aromatic groups		
Phenylalanine		(−)

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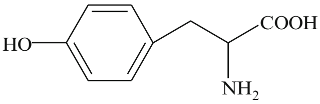
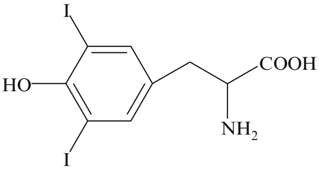
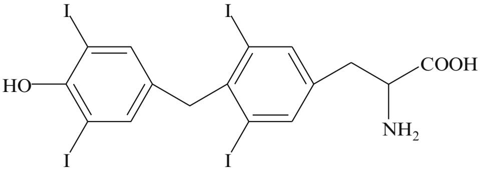
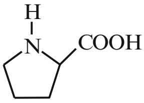
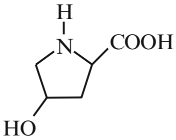
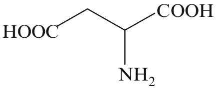
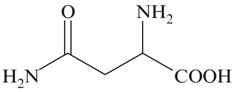
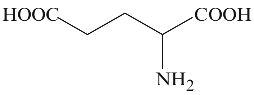
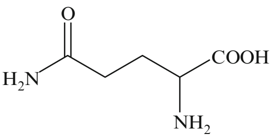
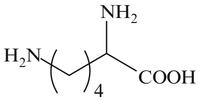
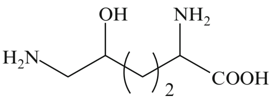
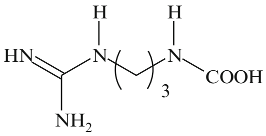
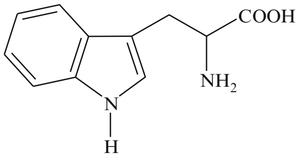
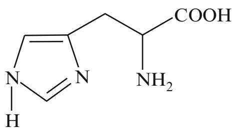
Table 8.1 (continued)

Name	Structure	Optical rotation
Tyrosine		(−)
Diiodotyrosine		(+)
Thyroxine		(+)
Amino acids with heterocyclic structures		
Proline		(−)
Hydroxyproline		(−)
Acidic amino acids		
Aspartic acid		(+)
Asparagine		(−)
Glutamic acid		(+)
Glutamine		

(continued)

Table 8.1 (continued)

Name	Structure	Optical rotation
Basic amino acids		
Lysine		(+)
Hydroxylysine		(−)
Arginine		(+)
Tryptophane		(−)
Histidine		(−)

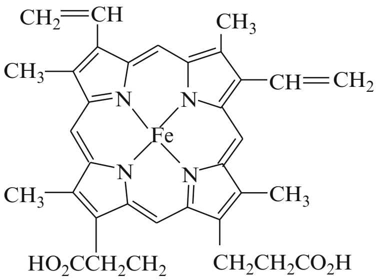


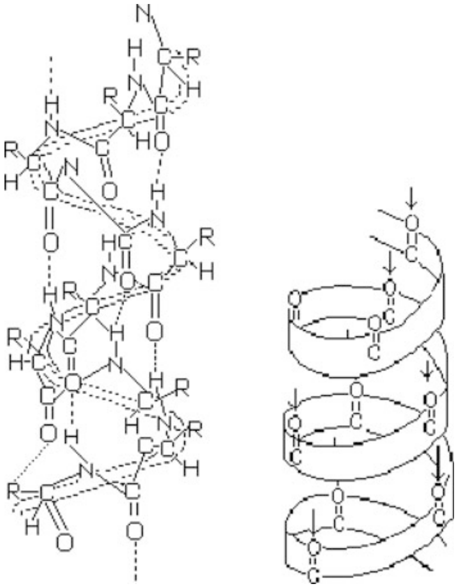
Fig. 8.2 Prostate group **heme**

also occur in water solutions. This is due to van der Waal interactions [25], because water molecules interfere with hydrogen bonding that holds the helix together, as shown in Fig. 8.3.

Not all proteins, however, form helical structures. If the substituent groups on the amino acids are small, as found in silk fibroin, then the polypeptide chains can line up side by side and form sheet-like arrangements. The chains tend to contract to accommodate hydrogen bonding and form pleated sheets. This is called *β-arrangement*. Such an arrangement can be parallel and antiparallel. The identity period of the parallel one is 6.5 Å and that of the anti-parallel 7.0 Å.

The secondary structures of proteins do not describe completely the arrangement of these macromolecules. There may, for instance, be sections that may exhibit some irregularity. Or, some sections may be linked chemically by sulfur–sulfur bonds of cystine groups. There may also be areas

Fig. 8.3 α-Helix structure of proteins



where the folding of the helix is such that it allows hydrogen bonding between distant sites. The overall, three-dimensional picture of a protein structure is referred to as the ***tertiary structure***. Disruption of the tertiary structure in proteins is called ***denaturation***. When the protein is composed of more than a single peptide chain, the arrangement is called a ***quaternary structure***. This association results from non-covalent interactions.

There is a relationship between the primary structures, or the amino acid content of many proteins, and the secondary structures [27]. The helical contents are inversely proportional to the amount of serine, threonine, valine, cysteine, and proline in the molecule. Conversely [28], valine, isoleucine, serine, cysteine, and threonine are non-helix-forming amino acids. Proline, due to its specific configuration, actually disrupts the helical structure when it is present in the polypeptide [29]. In addition, proteins that are composed of low ratios of polar to nonpolar amino acids have a tendency to aggregate [30]. Also, the globular protein, will, in an aqueous environment, tend to form shapes with nonpolar groups located inside the structure. This is due to the thermodynamic nature of the hydrophobic side chains. The polar ones, on the other hand, tend to be located outside, toward the water [31].

To date, much more information is available on some proteins than on others. Some of the more thoroughly explored proteins will be mentioned below.

Keratins are proteins that are found in wool, hair, fur, skin, nails, horns, scales, feathers, etc. They are insoluble because the peptide chains are linked by disulfide bonds [32, 33]. Many keratins contain coils of α-helixes [34–36]. Some keratins, however, were found to consist of complicated β-helical structures. This apparently has not been fully explained. Wool keratin was shown to range in molecular weight from 8,000 to 80,000 [37]. The extensibility of α-keratins is believed to be due to the helical structures. The extent of keratin hardness (in claws, horns, and nails) is believed to be due to the amount of sulfur links.

Silk fibers, which are obtained from the secretion of the silkworm, are double filaments that are enclosed by a coating of a gum (sericin) as they are secreted [40]. The amino acid sequence of the silk protein was shown to be (glycine–serine–glycine–alanine–glycine–alanine)$_n$. The polypeptide chains are bound into antiparallel pleated β-sheet structures by hydrogen bonding [31, 39, 42]. The structures are also held together by van der Waal forces [31, 38].

The protein of skin and extracellular connective tissues in animals is *collagen*. The polymer is rigid and cross-linked. Mild hydrolysis disrupts the rigid secondary valence forces and produces gelatin [26]. The fundamental unit of collagen exists as a triple helix [41]. Three left-handed helices twist together to form a right-handed threefold super helix [31]. Collagen is composed mainly of glycine, proline, and hydroxyproline. Some other amino acids are also present in minor amounts.

A protein that is similar to collagen is ***elastin***, which is present in elastic tissues, such as tendons and arteries. Hydrolyses of elastin, which has rubber-like properties, however, do not yield gelatin. Mildly hydrolyzed elastin can be fractionated into two proteins [26].

Among the most studied globular proteins **are *myoglobin*** and ***hemoglobin***. Myoglobin consists of a single chain of 153 amino acid residues and a prosthetic group that contains iron, called *heme*. Myoglobin polypeptides have eight helical segments that consist of right-handed α-helices that are interrupted by corners and non-helical regions. The overall shape resembles a pocket into which the heme group just fits. The pocket is hydrophobic because all but two side groups are nonpolar. The heme group's two carboxylic acids protrude at the surface and are in contact with water [43]. The hemoglobin is similar to myoglobin but more complex [44]. There are four heme groups enclosed in the hemoglobin structure. Detailed conformational analysis has shown that hemoglobin is build up from 2 × 2 myoglobin-like subunits, α_2 and β_2 [45, 46].

Casein is present in several animal and vegetable sources. Commercially, however, casein is primarily obtained from milk that contains about 3% of this protein. The polymer is isolated either by acid coagulation or with the help of enzymes obtained from animal stomachs. It is very heterogeneous. The molecular weight of a large portion of bovine casein is between 75,000 and 100,000. It consists of two components, α and β. Casein belongs to groups of proteins that are identified as ***phosphoproteins*** because the hydroxyl residues of the hydroxy amino acids are esterified with phosphoric acid.

One other group of proteins that has so far not been fully identified is ***glycoprotein***. This group of proteins contains a prosthetic group that is either a carbohydrate or a derivative of a carbohydrate. Glycoproteins are found in mucous secretions.

Very special proteins are called ***enzymes***. These are biological catalysts. Their primary function is to increase the rate of reactions in organisms and they are found in all living systems. Many enzymes, like *pepsin* or ***trypsin***, are relatively simple proteins. Others are conjugated proteins containing prosthetic groups often known as ***coenzymes***. Because of their extreme importance to biochemists, enzymes and their actions are being investigated extensively. The full structures of several enzymes have been determined. One such enzyme is ***lysozyme***.

Lysozyme enzymes occur in many species of plants and animals and the chemical behavior may differ. The enzyme found in egg white has a peptide chain consisting of two sections, approximately equal in size. The two sections are separated by a deep cleft. This enzyme performs its function by binding the substrates within this cleft with hydrogen bonds. The substrate is then hydrolyzed with the aid of glutamine (35th amino acid) and aspertine (52nd amino acid). Egg lysozymes primary structure contains 129 amino acid residues. The polymer is a single polypeptide chain that is cross-linked at four places by disulfide bonds [47].

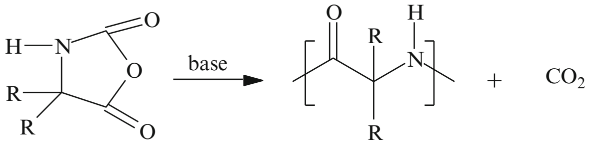
In addition, it was demonstrated [72] that the secondary structure of an enzymic protein is essential to protein's catalytic activity. Also, it was shown that this structure remains intact in neat organic solvents [72]. The molecules, however, are denatured in water–organic solvent mixtures. The α-helix of lysozyme, for instance, when the enzyme is crystalline or dissolved in neat acetonitrile, 35% of it is an α-helix, but in pure water that value is 23%. In a 60:30 mixture by volume of acetonitrile and water, it is reduced to 13% [72].

Some of the uncertainty about the transition state of the reaction of some enzymes, like β-phosphoglucomutase-catalyzed transfer of a phosphoryl group to a substrate in sugar metabolism, was resolved recently. Allan and Dunaway demonstrated that by means of ^{19}F nuclear magnetic resonance that the transition state involved a bipyramidal oxyphosphorane intermediate [72].

8.5.3 Synthetic Methods for the Preparation of Polypeptides

Studies of protein structures and their functions in nature or mode of actions, as in the case of enzymes, are only part of various investigations. Much effort is also put into syntheses of different polypeptide. Such polymers can actually be formed from mixture of various amino acids by simply heating them together. The products, however, are complex polymeric materials with random distribution of amino acids and do not resemble any naturally occurring materials.

Base catalyzed ring opening polymerization reactions of *N*-carboxy-α-amino acid anhydrides also result in formations of polypeptides:

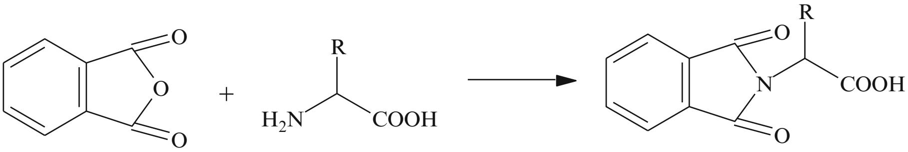


(for the mechanism of reaction see Chap. 5) [48]. Over the years, many polypeptides were synthesized by this reaction. These, however, were homopolymers of individual amino acids. Copolymerization leads only to block copolymers. Ability to form random copolymers with controlled sequences of amino acids, which would match naturally occurring proteins, appears to be beyond reach by this reaction [49, 50].

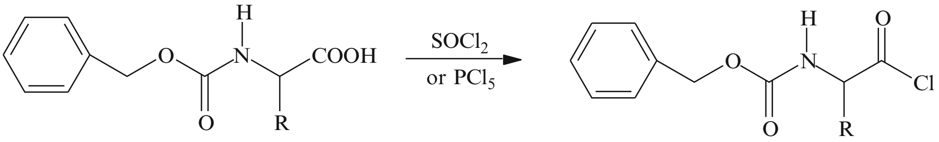
Duplication of naturally occurring polypeptides is needed, however, to understand the details of structures that lead to biological activities. One of the early works consisted of assembling 23 amino acids to form synthetic pig corticotropin [43]. The molecules were built stepwise [43].

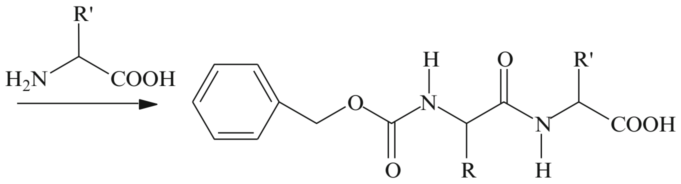
One technique used in these syntheses is to protect the terminal amino nitrogen by forming protective derivatives that can subsequently be easily cleaved. This is often done by converting them to amide groups:

p-Toluenesulfonyl chloride is used in the same manner. It is also possible to form imides by reactions with phthalic anhydride:

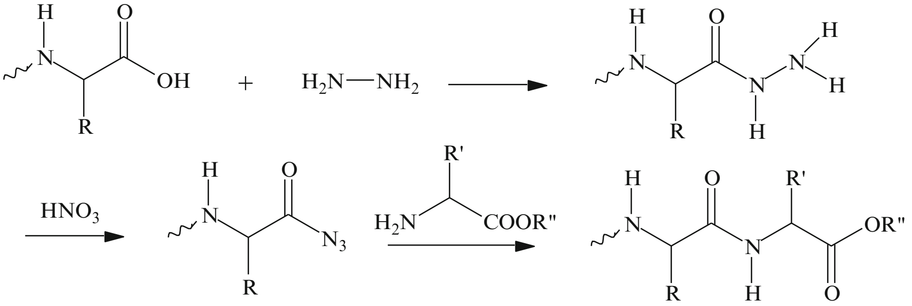


The condensations can be carried out by a number of different techniques [26, 28]. A few of them will be shown below. One is to carry out amino acyl halide reactions:

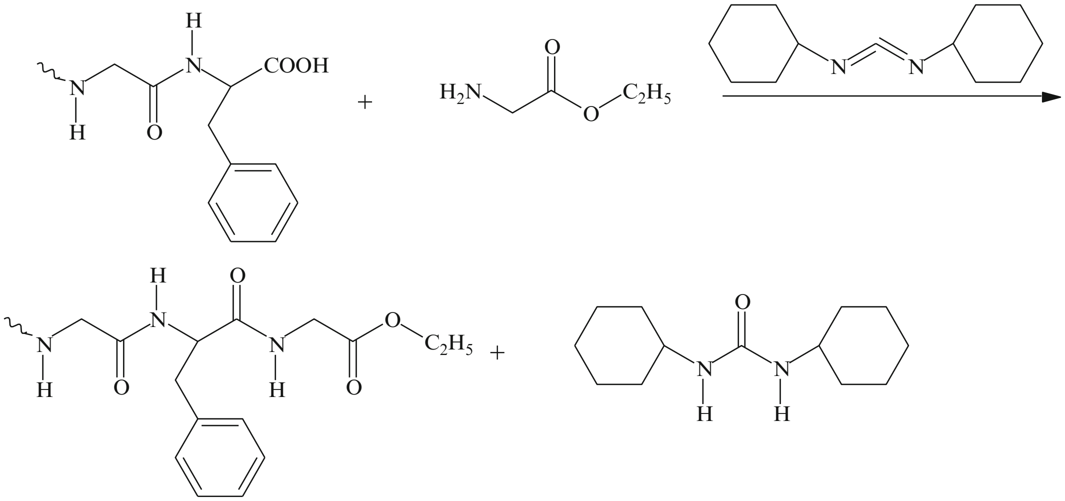




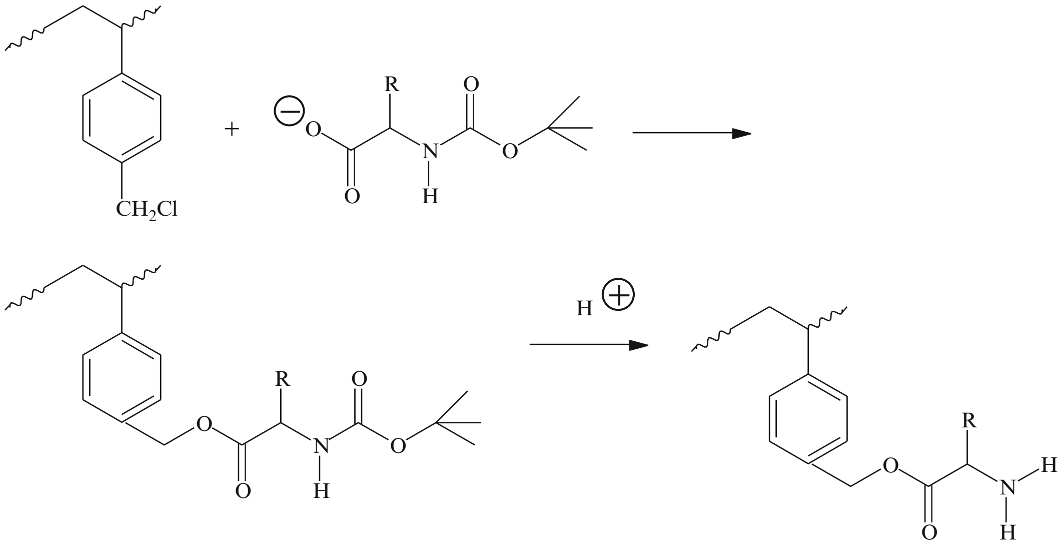
The Schotten–Baumann reaction is used in many peptide syntheses. It is usually carried out in the presence of common bases to remove the halogen acid. Another reaction that is also utilized often is an acid azide condensation:



A unique way of coupling carboxylic acids with an amine groups is by using an *N*,*N*′-dicyclohexyl carbodiimide method. This can be illustrated as follows:



In addition to the above mentioned, rather painstaking, techniques of polypeptide syntheses, a very elegant technique was developed by Merrifield [53]. This ***solid phase peptide synthesis*** automates the reaction sequences. The method makes use of an insoluble cross-linked polymer substrate with pendant reactive groups for attachment of peptide chains. Chloromethylated polystyrene microgels are often used (see Chap. 9 for more discussions on the use of chloromethylated polystyrene for reactions of polymers). The chloromethyl moieties serve as the initiating sites for formation of the polypeptides:

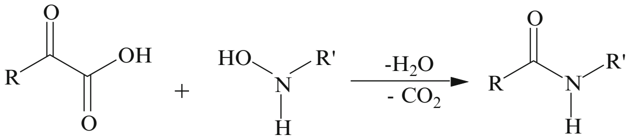


A new amino acid with a protective group can now be added. The sequence of additions can be controlled and repeated many times to build up the desired polypeptide chain. Unwanted by-products of the syntheses are washed away or filtered off before each new step.

This method lends itself so well to automation that automatic peptide synthesizers are now available commercially. One automatic peptide synthesizer was employed, for instance, in the synthesis of ribonuclease, an enzyme. In another instance, an enzyme, ferredoxin that consists of 55 amino acid residues was synthesized [26].

Most recent approaches to protein syntheses include use of templates for spontaneous self-assembly of multiple copies of a derivatized peptide [70]. The resultant structure, however, is not a conventional linear-chain protein. Instead, oxime bonds are formed between amino-oxyacetyl groups on the peptides and aldehyde groups on the template. The method is claimed to have many potential applications.

Bode et al. [70] reported a new method for synthesis of peptide oligomers. The reaction creates aide linkages between α-keto carboxylic acids and *N*-alkylhydroxylamines.



8.5.4 Chemical Modification of Proteins

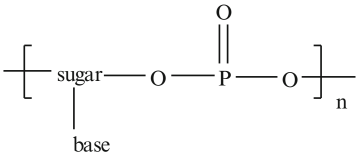
Proteins have been utilized commercially from ancient times, either in their naturally occurring form or modified in some manner. Use of silk and wool fibers, for instance, goes back a very long time. Many animal glues, prepared from bones and hides of cattle or sheep, have also been around for a very long time. Today such glues are being replaced rapidly by synthetic materials. Those that are still manufactured are usually formed by steaming the bones and the hides under pressure and then treating them with hot water in several cycles. This degrades the collagen and make is soluble. The aqueous solution is concentrated by vacuum evaporation of the water. The material that gels is dried and pulverized. Milder hydrolysis yields gelatin that is used commercially in foods.

Casein, the milk protein (less readily available casein from vegetable sources is hardly ever used), is also used in adhesives. Here too, synthetics are gradually taking over. At one time it was used to produce a fiber and a plastic that was formed by cross-linking with formaldehyde. The cross-linking reaction was carried out by immersing the proteins in a formaldehyde solution (4–5%) at 55–65°C for long periods of time, such as days and even months, depending upon the size of the article. The cross-linking reaction involved pendant amino groups and is quite similar to the reactions of urea- and melamine-formaldehyde resins (see Chap. 7). Some condensation and formation of methylene bridges may also involve amide nitrogens. It does not appear likely that casein fibers or plastics are still being produced anywhere.

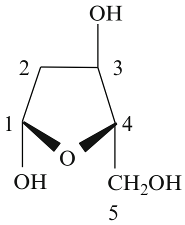
Extensive research work has gone into modification of proteins, not for commercial applications but for academic reasons. Thus, for instance, Frances et al. developed a new reaction that introduces single reactive ketones or aldehydes at the N-terminal groups of protein when the proteins are mixed with pyridoxal phosphate [44]. The researchers also developed a palladium-catalyzed allylic alkylation that attaches long lipid tails to proteins, a process that can be used to customize the solubility of enzymes, antibodies, viral capsids, and other proteins.

8.6 Nucleic Acids

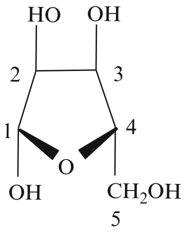
These are protein-bound polymers that are essential in many biological processes. They perform such functions as directing the syntheses of proteins in living cells and constitute the chemical basis of heredity [56, 57]. The polymers are polyphosphate esters of sugars that contain pendant heterocyclic amines, called “bases”:



There are two principle types of nucleic acids with two different sugars. One is ***D-2-deoxyribose*** found in ***deoxyribonucleic acid*** (**DNA**):

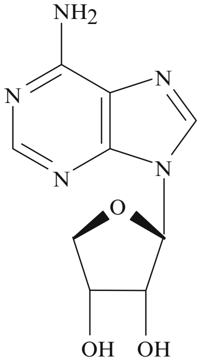


The other one D-***ribose*** is found in ***ribonucleic acids*** (**RNA**):

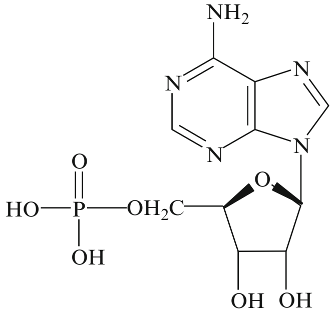


The sugars are in the furanose form. They are linked through the hydroxyl groups on carbons 3 and 5 as phosphate esters. The heterocyclic amine "bases" are attached at carbon 1, replacing the hydroxyl group.

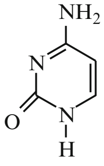
A sugar molecule with a base attached to it is referred to as a ***nucleoside***:



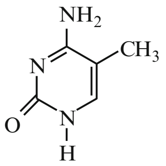
A nucleoside esterified with phosphoric acid is called a ***nucleotide***:



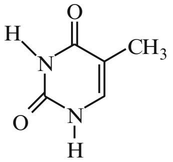
All the heterocyclic amines that occur in nucleic acids (DNA and RNA) are derivatives of either pyrimidine or purine. These are:



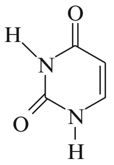
cutosine

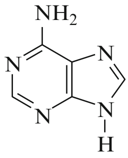


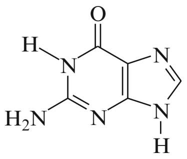
5-methylcytosine



thymine


uracil


adenine

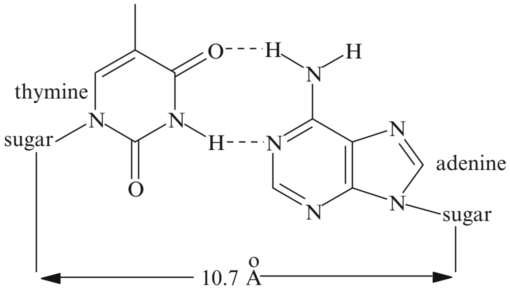

guanine

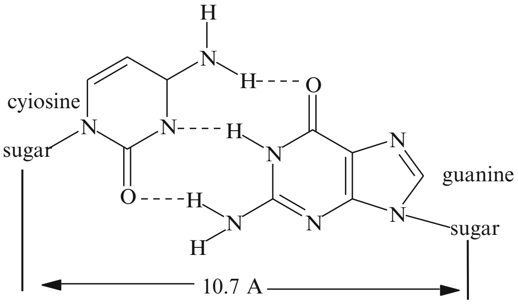
The naming of nucleosides depends upon the sugars. Thus, adenine attached to ribose is called adenosine. When it is attached to deoxyribose, it is called deoxyadenosine.

Hydrolysis of nucleoproteins separates the acids from the proteins. Further hydrolysis yields the components of nucleic acids, namely sugars, bases, and phosphoric acid. The nucleic acids differ from each other, depending upon the source, in chain lengths, sequences, and distributions of bases. Just like in the proteins, the primary structure of nucleic acids is determined by partial and sequential hydrolysis.

8.6.1 DNA and RNA

Deoxynucleic acids have been isolated from all types of living cells and it was established that their main function is to carry genetic information [57]. These are very high molecular weight polymeric materials. Some were found to be as high as 100 million. Analyses of DNA structures show that the numbers of adenine bases are always the same as the number of thymine bases. Also, the numbers of guanine bases always equal the numbers of cytosines. Based on the information from various analyses and an X-ray investigation of the structure, Watson and Crick concluded that the secondary structure of DNA must be a double helix [58]. Two separate right-handed helical chains wind around each other and are held together by hydrogen bonding between base pairs. The bases that are paired off are adenine with thymine and guanine with cytosine:



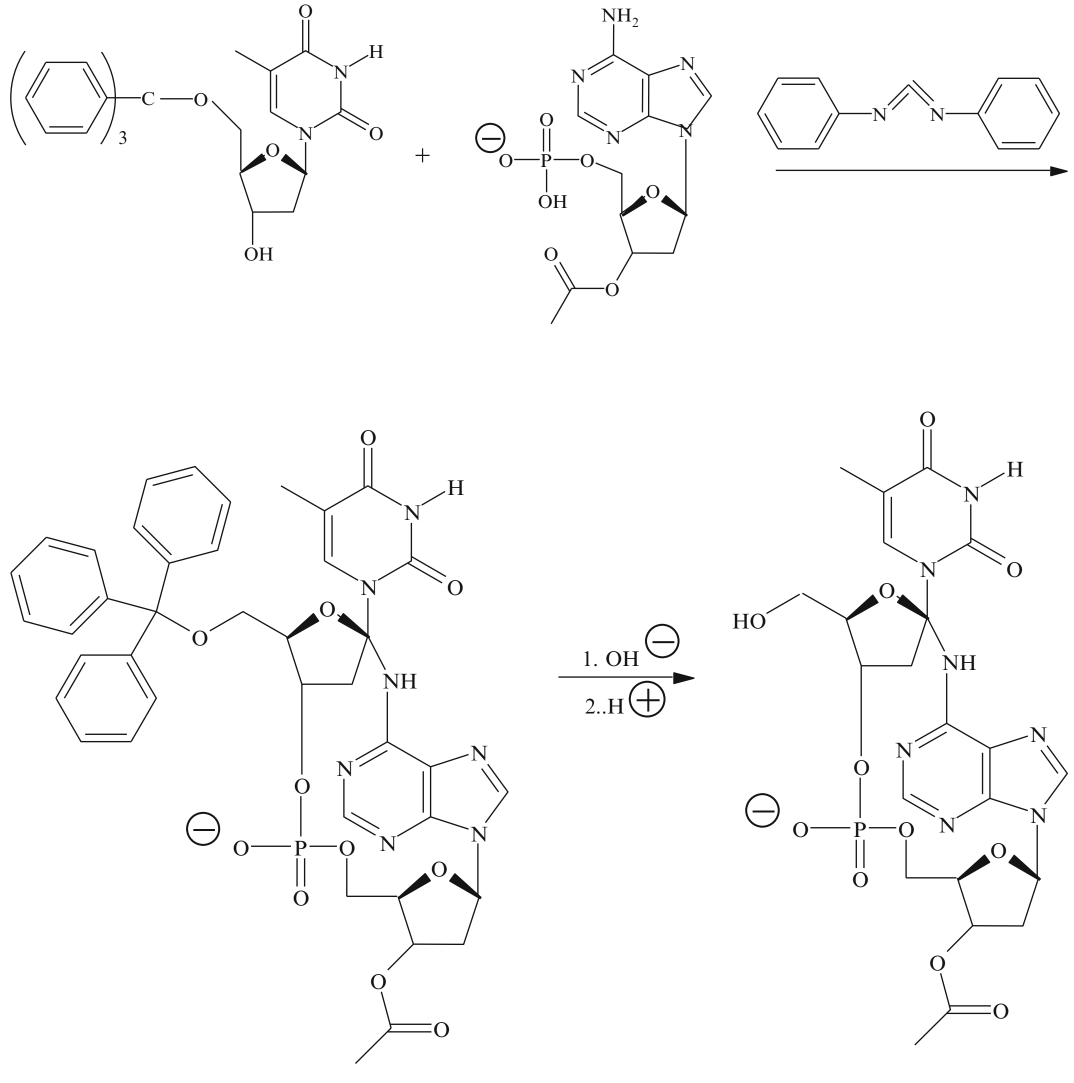


The base pairs are extended perpendicularly toward the center and the deoxyribose–phosphate ester chains are located on the outside of the helix. The two strands are antiparallel to each other. One turn of the helix corresponds to ten nucleotide pairs, 34 Å in length. The width of the helix is 20 Å. Evidence was presented that some DNAs in their native forms are cyclic [59] and may even occur as two interlocking rings. While most known DNA molecules form a right-handed helix, a left-handed helix can be prepared synthetically in the laboratory [52]. It was speculated that in some instances left-handed helixes may exist in nature and have a biological function [53]. These DNA conformations were named Z-DNAs because the backbones zigzag down the molecule.

There is less information about the secondary structures of RNAs. It is known that the RNA molecules are lower in molecular weight than are the DNA molecules. In addition, it is known that there are three main types of RNAs in living cells. These are *ribosomal* RNA (r-RNA), *transfer* RNA (t-RNA), and *messenger* RNA (m-RNA). The molecular weights of the three forms on the average are about 1,000,000, 25,000, and 500,000, respectively. RNA molecules, with the help of hydrogen bonding, take three-dimensional cloverleaf structures [54]. The molecule's three-dimensional shape also assumes an L-shape, into which the cloverleaf is bent.

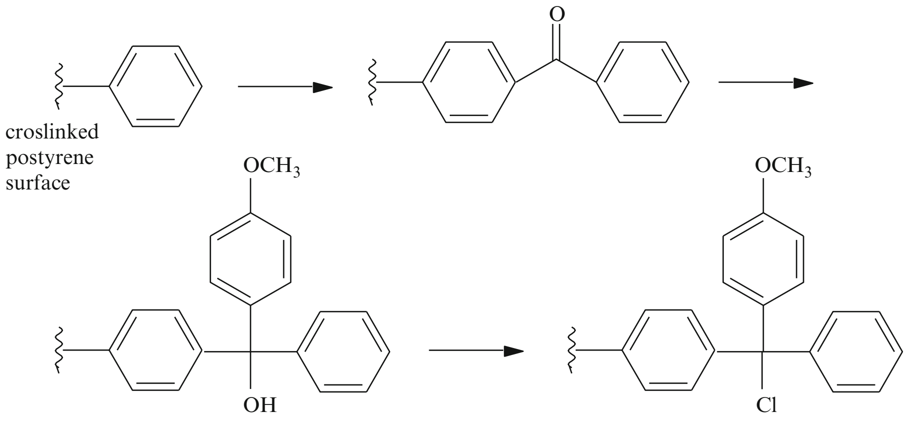
8.6.2 *Synthetic Methods for the Preparation of Nucleic Acids*

Over the last 20–30 years, methods were developed to synthesize short deoxyribonucleotide chains [57]. One synthetic procedure can be illustrated as follows:



The bulky triphenylmethyl moiety functions to block the 5′ hydroxyl groups and is removed when necessary. The same is true of the acetyl portion that also serves to block the 3′ hydroxyl position. The product can be used for further expansion of the chain.

Another approach to the syntheses of nucleic acids is to use polymeric supports as in the syntheses of polypeptides. The preparation of protecting groups for attachment to carbon 5 of deoxyribose on the surface of cross-linked polystyrene can be illustrated as follows [57]:

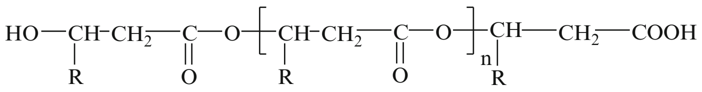


Another protective group that has been used is dimethoxy trityl. The carbon 3 of deoxyribose has been protected with phosphoramide. Benzoyl groups are used to protect the adenine and guanine bases. Lately, in place of cross-linked polystyrene, controlled pore glass supports have become popular.

Commercial synthesizing machines are available today for polynucleotide syntheses. These are similar to the synthesizers used in polypeptide syntheses.

8.7 Polyalkanoates

Many bacteria are a potential source of naturally occurring polyesters, mainly *poly (β-hydroxyalkanoate)s* with a general structure



$$\mathrm{HO{-}}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH_2{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}O}\left[\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH_2{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}O}\right]_n\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH_2{-}COOH}$$

when the polymer is poly(β-hydroxybutyrate) R = CH_3 [69]. The material is found in the form of hard crystalline granules in many bacterial cells. The most common one, poly(β-hydroxybutyrate), was discovered back in the 1920s and identified as a polymer of D-(−)-β-hydroxybutyric acid. In the native state this polymer may reach molecular weights of 1,000,000 or higher. It forms a compact right-handed helix with a twofold screw axis and a repeat unit of 5.96 Å. Because poly (β-hydroxybutyrate) is stereoregular, it is highly crystalline. The substitution in the β-position makes it thermally unstable. This limits its use in plastics. It was found, however, that oxygen starvation of bacterial cultures results in formation of a copolymer of β-hydroxybutyric acid with β-hydroxyvaleric acid instead of a homopolymer. Further investigations showed that as many as 11 different β-hydroxy acid constituents are present in different naturally occurring polyalkanoates, depending upon the bacterial source and conditions of growth. Today, a family of products, marketed under the trade name of Biopol, is available commercially with a range of properties, such as melting point, toughness, flexibility, and others. The melting points range from 80 to 180°C.

It was reported that *Pseudomonas oleovorans* microorganism can be forced to produce a thermoplastic elastomer by growing it on a substrate containing sodium octanoate [71]. The product is poly (β-hydroxy octanoate). It contains crystalline regions that act as physical cross-links.

Also, addition of poly(ethylene glycol) of molecular weight 200 to cultivation media of *Alcaligines eutrophus* during polymer formation, where the carbon source used is 4-hydroxybutyrate, affects the type of ester that it produces [73]. Addition of this glycol in amounts from 0 to 2% by weight results in increased amounts of 4-hydroxybutyrate incorporation from 66 to 86 mol.% into the produce, poly(3-dydroxyalkanoate). When, however, the amount of the glycol is increased to 4%, the amount of incorporation of the 4-hydroxybutyrate decreases to 64%. The product then also contains a diblock copolymer of poly(3-hydroxyalkanoate) and poly(ethylene glycol) [73].

Review Questions

Section 8.1

1. List the six main categories of naturally occurring polymers.
2. Draw the chemical structures of the repeat units of each category of naturally occurring polymers.

Section 8.2

1. Describe hemicellulose. This should include an explanation of what xylan, galactan, araban, and plant gums.
2. In discussing starches, explain what are amylose and amylopectin. Explain and draw structures.
3. Discuss cellulose. How does cellulose differ from starch?
4. What is cellobiose? Draw the structure and give the chemical name.
5. What is regenerated cellulose? Explain what is Chardonnet silk, Cuprammonium rayon, and viscose rayon and how they are prepared.
6. Discuss the chemistry of cellulose nitrates. How are they prepared and used?
7. Discuss the chemistry of cellulose acetate. How is it prepared and used? Describe mixed cellulose esters.
8. Discuss the chemistry of cellulose ethers.
9. Show the reaction of cellulose with acrylonitrile.
10. Iodocellulose can be dehydrohalogenated to form double bonds in the polymer. This can be used to form new derivatives. Give two examples.
11. Draw the structures of alginic acid and chitin.

Section 8.3

1. Discuss the chemistry of lignin, drawing the structure of coniferyl alcohol. Can you think of a useful product from lignin?

Section 8.4

1. Describe natural rubber. How is it obtained? What is the chemical structure?
2. What are gutta-percha, balata, and chicle? Explain.

Section 8.5

1. Explain what is meant by polypeptides.
2. Explain the difference between fibrous proteins and globular proteins.
3. What are nucleoproteins? What is a prosthetic group? Give an example.
4. Explain what is meant by a secondary structure of a protein and an α-helix.
5. What is meant by a tertiary structure of a protein?
6. What is an enzyme? How does it function?
7. Discuss with the aid of chemical equations the synthetic routes to polypeptides.
8. Discuss chemical modifications of proteins for commercial purposes.

Section 8.6

1. What is the basic structure of a unit in nucleic acids?
2. How do the sugars differ in DNA from RNA?
3. Draw the structures of a nucleoside and a nucleotide.
4. Discuss the syntheses of nucleic acids.

Recommended Reading

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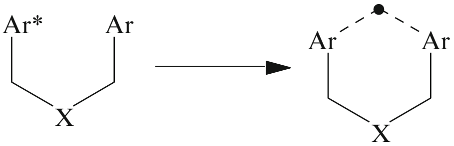
Chapter 9
Organic Reactions of Polymers

9.1 Reactivity of Macromolecules

In consideration of various chemical reactions of macromolecules, the reactivity of their functional groups must be compared to those of small molecules. The comparisons have stimulated many investigations and led to conclusions that functional groups exhibit equal reactivity in both large and small molecules, if the conditions are identical. These conclusions are supported by theoretical evidence [1, 2]. Specifically, they apply to the following situations [1]:

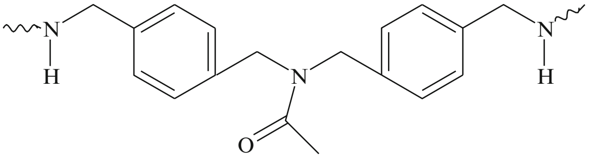
1. Reactions that take place in homogeneous fluid media with all reactants, intermediates, and end products fully soluble. These conditions exist from the start to the end of the reactions.
2. All elementary steps involve only individual functional groups. The other reacting species are small and mobile.
3. The steric factors in the low molecular weight compounds selected for comparison must be similar to those of the large molecules.

The above can be illustrated by a few examples. For instance, the rates of photochemical *cis–trans* isomerization of azobenzene residues on the backbones of flexible polymeric chains are analogous to those of small molecules [3]. Another example is the activation energy for *cis–trans* isomerization of azo-aromatic polymers. It is the same for low molecular weight analogs [4]. A third example is an experiment in comparing conformational transitions of some eximers in large and small molecules. A sandwich complex forms between an excited aromatic chromophore, *Ar,* and a similar chromophore in the ground state when irradiated with light of an appropriate wavelength. The conformation required by such an excimer can correspond to a prohibitive energy requirement for the unexcited molecule. All conformational transitions must take place during the lifetime of the excited state of the chromophore that is of the type [5]:



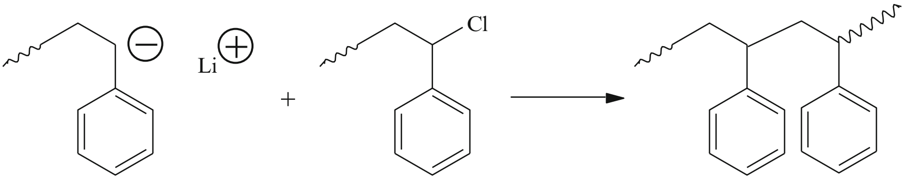
A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_9,

The ratio of the fluorescence intensity of an excimer and a normal molecule is a measure of the probability that the conformational transition takes place during the excited lifetime. A polyamide with only a small proportion of the following units was used for comparison:

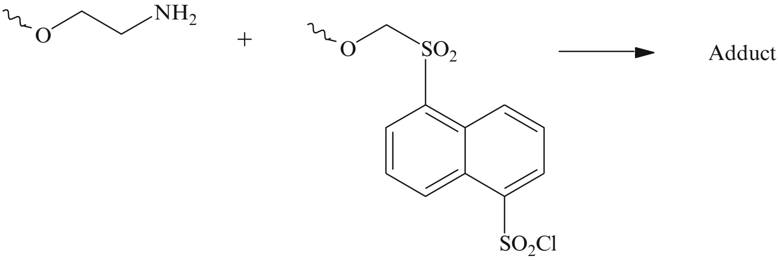


Emission spectra of dilute solutions of the above polyamide and its low molecular weight analog were measured over a range of temperatures. They showed that the activation energies of the conformational transitions required for excimer formations are essentially the same for both materials [5].

In addition, all bimolecular activation-controlled reactions are independent of the degree of polymerization [6]. Simple S_N2 reactions between reactive groups attached to chain ends of monodisperse macromolecules in a wide range of molecular weights are independent of the DP [7, 8] in the range of 20–2,000 [7]. This was shown on three different reactions. In the first one, the reactivities of chlorine-terminated low and high molecular weight polystyrenes towards polystyryllithium are equal in benzene and cyclohexane solvents:



In the second one, the reactivity of primary amine-terminated polyoxyethylenes with sulfonyl chloride-ended polyoxyethylenes in chloroform is also the same:



In the third one, chain length dependence of the propagation rates was measured in polymerizations of methyl methacrylate. In the range of DPs from 130 to 14,200, the propagation constant was shown to be independent of the chain length [8].

On the other hand, unequal reactivity was observed:

1. In bimolecular reactions that are diffusion-controlled.
2. When neighboring group participations become significant.
3. When the properties of the polymers in solution are altered by gelation.
4. When the tacticities of the polymers affect neighboring group interactions.
5. When heterogeneous conditions affect accessibility to the reactive sites.

There are special situations that can occur. For instance, electrostatic charges carried by the polymers may extend over long distances in solutions and may manifest themselves in reactions with charged reagents. Sometimes, chain flexibility or folding can cause functional groups to come together and interact, though they may be located well apart on the polymer backbone. Polymer solutions of this type are comparable to dispersions of individual droplets of concentrated solutions.

Some statements above may require additional clarification. An elaboration, therefore, follows.

9.1.1 Diffusion-Controlled Reactions

Reactions that are bimolecular can be affected by the viscosity of the medium [9]. The translational motions of flexible polymeric chains are accompanied by concomitant segmental rearrangements. Whether this applies to a particular reaction, however, is hard to tell. For instance, two dynamic processes affect reactions, like termination rates, in chain-growth polymerizations. If the termination processes are controlled by translational motion, the rates of the reactions might be expected to vary with the translational diffusion coefficients of the polymers. Termination reactions, however, are not controlled by diffusions of entire molecules, but only by segmental diffusions within the coiled chains [10]. The reactive ends assume positions where they are exposed to mutual interaction and are not affected by the viscosity of the medium.

9.1.2 Paired Group and Neighboring Group Effects

When *random*, *irreversible*, and *intramolecular* reactions occur on polymeric backbones with the functional groups adjacent to each other, they can be expected to react. There is, however, an upper limit to conversions. This upper limit is due to statistical probability that some functional groups are bound to become isolated. The limit for conversion was calculated to be 86.5% [11].

Theoretically, quantitative conversions should be possible with *reversible* reactions of paired functional groups on macromolecular backbones. The ability, however, of isolated reactive groups to find each other and then pair off depends either upon particularly high driving forces, or upon the time required to accomplish complete conversions [12]. For reactions initiated randomly, at different sites, the probability is high that two groups on the terminal units will eventually meet and react. Since the reactions are reversible, at least in theory, very high conversions are possible.

Neighboring group participation can usually be deduced from three types of evidence:

1. If the reactions occur more rapidly during the rate-determining step than can be expected from other considerations.
2. If the stereochemistry of the reactions suggests neighboring group involvement.
3. If molecular rearrangements occur and the groups remain bonded to reaction centers, but break away from the atoms to which they were originally attached on the substrates.

There are many examples in the literature that describe neighboring group effects in reactions of polymers. One example is hydrolysis of poly(*p*-nitrophenyl methacrylate-co-acrylic acid). The high reaction rate at a neutral pH is due to attacks by the carboxylic moieties upon the neighboring carbonyl carbons [13–15]. Decomposition rates of *t*-butyl acrylate-styrene copolymers [16] can serve as an another example. Experimental data show pronounced acceleration for all samples. This is interpreted in terms of both intra and intermolecular interactions of the esters and the carboxylic groups. It follows a suggestion of Cherkezyan and Litmanovich [16, 17] that the instantaneous reactivity of any group depends on its microenvironment. That includes (for reactions of polymer in molten condition) two nearest units on the same chain (internal neighbors) and two units belonging to two different chains (external neighbors).

Another example of the neighboring group effect is the behavior of polyacrylamides in hydrolyses. There are two distinct and successive rates [18]. After conversions of up to 40–50% are reached, the reactions slow down. This is due to accumulations of negative electrostatic charges on the polymeric backbones [18]. In alkaline media, the increasing negative charges along the chains exert electrostatic repulsions toward the hydroxyl ions. This results in rate decreases.

9.1.3 Effect of Molecular Size

An example is the effect of DP on the rates of alkaline hydrolyses of poly(vinyl acetate)s. Rapid increases in the rates can be seen [19] in large, but not in small molecules, as the reactions progress. Solvents that are good for the products, like acetone–water mixtures, are used in these reactions. These are, however, poor solvents for the staring materials with high DP. Low molecular weight molecules are more soluble. This means that, at the start of the reaction, the large molecules are coiled up and the reactive sites not readily available. As the reactions progress, the chains unravel and the sites became more accessible with accompanying increases in the reaction rates. Because the small molecules are more soluble, the reactive sites are accessible from the start of the reactions, and the rates are constant.

There are many report in the literature on the *effects of chain conformation* [19–25]. One example is radical bromination of poly(methyl styrene) [20] with *N*-bromosuccinimide-benzoyl peroxide or Br_2-K_2CO_3-light. ^{13}C NMR spectroscopy shows differences in reactivities of the methyl groups in the 3 and 4 positions on the benzene rings between isotactic and atactic polystyrenes [20].

The differences in reactivities in poly(vinyl alcohol)s between isotactic (*meso*) and syndiotactic (*dl*-diol) portions of the polymers and between *cis* and *trans* acetals [26–28] is another example. In extending this to model compounds, reactions of stereo isomers of pentane-2,4-diol and heptane-1,4,6-triol with formaldehyde take place much faster for the meso than for the *dl*-diol portions [26–28]. Even more important are the steric effects imposed by restricted rotations. For instance, quaternizations of chloromethylated polyether sulfones exhibit decreasing rates at high degrees of substitution. This can be attributed to restricted rotations of the polymeric chains, because this phenomenon is not observed with more flexible chloromethylated polystyrene under identical conditions [23, 24].

9.1.4 Effects of Changes in Solubility

Changes in solubility can occur during the courses of various reactions. Such changes are observed, for instance, during the chlorination of polyethylene in aromatic and chlorinated solvents [29]. There is an increase in the solubility until 30% conversion is reached. After that, solubility decreases and reaches a minimum at 50–60% chlorine content. Following that it increases again. This, however, is not typical of many reactions of polymers in solutions. More common is that the starting material is soluble, but not the product or the opposite is true. Higher conversions are, usually, expected when the polymers are solvated and the chains are fully extended. In such situations, the reagents have ready access to the reactive sites [29]. If the products are insoluble in the reaction medium and tend to precipitate as the reaction progresses, the sites become increasingly less accessible. This can result in low conversions and premature terminations. If the opposite is true and the product is more soluble than the starting material, homogeneous limited reactions can be controlled. When the starting material is incompatible with the product, mutual precipitation or coiling of the chains can take place. This can also result in limited reactions. In addition, only minor differences in the constitutions of two polymers can cause incompatibility. For instance, among methacrylate polymers, there are incompatibilities in benzene solutions that result from differences only in the amount of branching of the alkyl groups [29].

Problems with solvent incompatibility can sometimes be overcome by using mixtures of solvents. Those that are good for the starting materials can be combined with those that are good for the products. With careful experimentation, it may be possible to develop a mixture of solvents that will keep all components in solution [30]. In some instances, however, insolubility of the products might be an advantage. This is the case in alcoholysis reactions of poly(vinyl acetate), where the polymer precipitates during the reactions and in doing so absorbs the catalyst with it. The phenomenon permits complete alcoholysis, particularly with the higher molecular weight species that precipitate first.

Secondary reactions, like cross-linking and gelation, can result in precipitations from solution. The extent of the reactions, however, is not necessarily limited, because diffusions of low molecular weight species are still possible. Isolation of useful products, however, often becomes very difficult.

9.1.5 Effects of Crystallinity

Crystallinity can only affect reactivity when the reactions are carried out on polymers in the solid state and at heterogeneous conditions. The differences in accessibility to the reactive sites vary with the amount of crystallinity. Cellulose, for instance, is often reacted in the solid state and the degree of crystallinity is expressed in terms of reactivity to various reagents [31]. The progress of a reaction can sometimes be monitored by a loss of crystallinity. What is more significant, however, is that greater accessibility to amorphous regions results in reaction products with special properties. An example is heterogeneous and homogeneous chlorination of polyethylene. Two different products are obtained [32]. The material from heterogeneous chlorination is much less randomly substituted and remains crystalline up to a chlorine content of 55%. The products from the homogeneous reactions, on the other hand, are amorphous after 35% substitution.

9.1.6 Reactions That Favor Large Molecules

Hydrophobic interactions play important roles in many polymeric reactions. They are, for instance, significant in the hydrolyses of low molecular weight esters when catalyzed by polymeric sulfonic acid reagents, like poly(styrene sulfonic acid). In these reactions, the hydrogen ions are located close to the macromolecules [19]. The hydrolytic cations are located in the regions of the macromolecules and not in the bulk of the solution. The rates of the reactions are high. Low molecular weight catalysts, on the other hand, like HCl, have all the hydrogen ions distributed evenly throughout the reaction medium. As a result, the rates are lower. Adsorption of the ester groups to the polymeric sites is accompanied by an increase in the apparent rate constant, as compared to reactions with HCl.

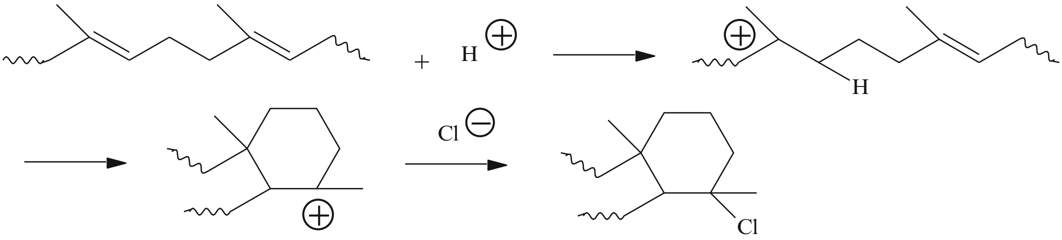
Examples are hydrolyses of methyl and butyl acetates [19]. Another example is formation of eximers and exiplexes in polyesters and methacrylate polymers that always favor large molecules over small ones [33]. Proton transfer reaction of poly(vinyl quinoline) [34] can serve as a third example. The emission, excitation, and absorption spectra of this polymer in a mixture of dioxane and water can be compared to that of 2-methylquinoline. The emissions coming from the protonated heterocyclic rings in the polymer occur sooner than from the low molecular weight compound [34].

9.2 Addition Reactions

Polymers with double bonds in the backbones or in the pendant groups can undergo numerous addition reactions. Some are discussed in this section.

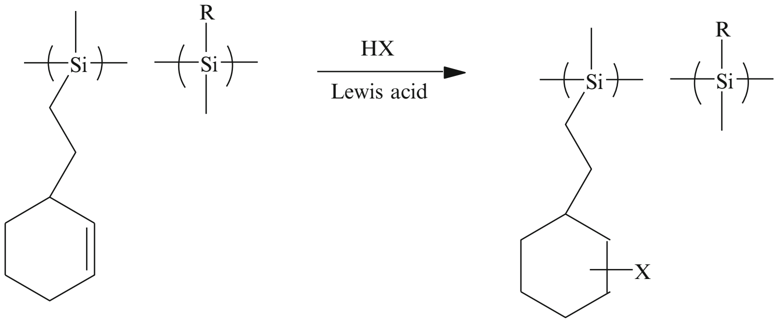
9.2.1 Halogenation

Hydro chlorination of natural rubber is often accompanied by cyclization [35, 36]:

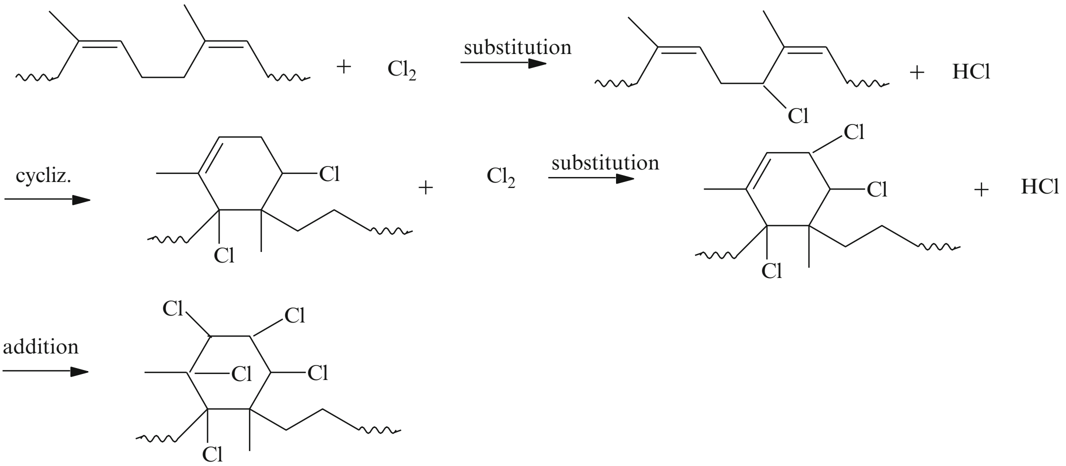


trans-1,4 and 1,2-Polybutadiene can be hydro halogenated under mild conditions with gaseous HCl [51]. The same is true of copolymers of butadiene with piperylene and also of isotactic *trans*-1,4-piperylene. The addition of HCl to the asymmetric double bond is *trans* for polypiperylene and occurs in a stereoselective way, judging from the ^{13}C NMR [51] spectra.

Polysilanes with alkene substituents add HCl and HBr in the presence of Lewis acids [58]. The products are the corresponding chlorine and bromine containing polymers with little degradation of the polysilane backbone:



Chlorinations of rubber, however, are fairly complex, because several reactions occur simultaneously. These appear to be: (1) additions to the double bond; (2) substitutions; (3) cyclizations; and (4) cross-linkings. As a result, the additions of halogens to the double bonds are only a minor portion of the overall reaction scheme [37, 38]. In CCl_4, the following steps are known to occur:

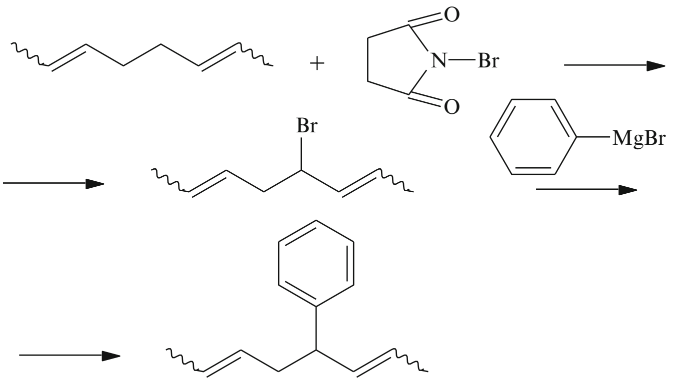


Halogenation reactions of unsaturated polymers follow two simultaneous paths, ionic and free radical. Ionic mechanisms give soluble products from chlorination reactions of polybutadiene [42]. The free-radical mechanisms, on the other hand, cause cross-linking, isomerization, and addition products. If the free-radical reactions are suppressed, soluble materials form. Natural rubber can be chlorinated in benzene, however, with addition of as much as 30% by weight of chlorine without cyclization [39, 40]. Also, chlorination of polyalkenamers both *cis* and *trans* yields soluble polymers. X-rays show that the products are partly crystalline [43, 44]. The crystalline segments obtained from 1,4-*trans* polyisoprene are diisotactic poly(erythro dichlorobutamer)s, while those obtained from the 1,4-*cis* isomer are diisotactic poly(threo 1,2-dichlorobutamer)s [45].

Additive type chlorination of natural rubber can also be carried out with phenyl iododichloride or with sulfuryl chloride [39, 40]. Traces of peroxides must be present to initiate the reactions. This suggests a free-radical mechanism. Some cyclization accompanies this reaction as well [40]. In CCl_4, for the first 25 chlorine atoms that add per each 100 isoprene units, 23 double bonds disappear and only a small quantity of HCl forms. Subsequent 105 chlorinations, however, cause a loss of only 53 double bonds.

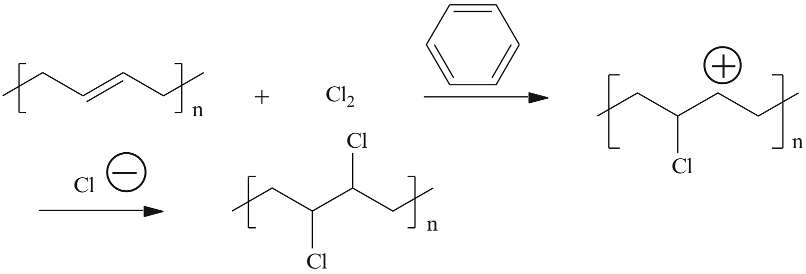
Rubber can be ***brominated*** at 30°C. If traces of alcohol are present, the reaction appears to go on entirely by addition [39, 40]. Without alcohol, substitutions take place rapidly and simultaneously with the additions to the double bonds [41]. Exomethylene groups and intramolecular cyclic structures form in the process. Slow additions of bromine to vinylidene double bonds result in formations of tri bromides, $–C_5H_7Br_3$. Also, ***cis*** and ***trans*** isomers of polyisoprene [41] brominate differently. Substitution reactions take place in brominations with *N*-bromosuccinimide. They are accompanied by cyclizations [39].

Brominations of polybutadienes with *N*-bromosuccinimide yield α-brominated polybutadienes [46, 47] that may also contain butane diylidene units. The products act as typical alkyl halides and can undergo Grignard-Wurz reactions:



The bromination reaction is accompanied by shifts of the double bonds that are coupled with the sites of substitution. Several different substituents can form. The polymers may contain pentane diylidene, hexane diylidene, and heptane diylidene units [46, 47].

By contrast, chlorination of polybutadiene in benzene is a straightforward addition reaction of the halogens to the double bonds [48, 49]:



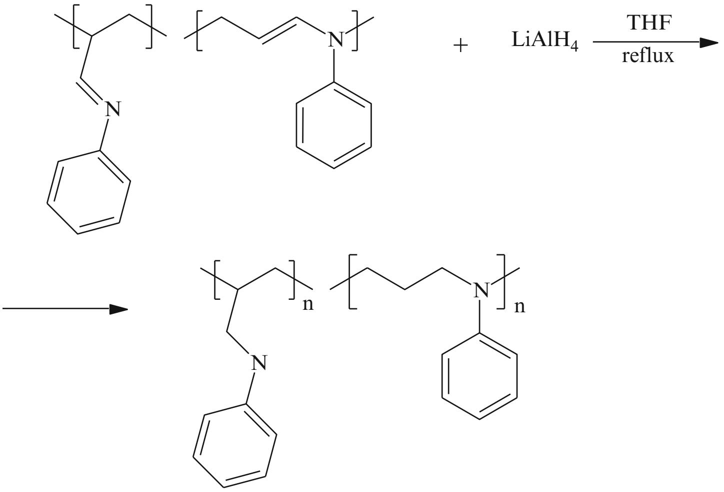
Very little HCl is liberated until all the double bonds are consumed. When CCl_4 is used in place of benzene, some substitutions occur during the latter stages of the reactions. If cross-linking occurs at the same time, the substitutions may not be extensive. The cross-linking reactions are believed to involve carbocationic intermediates.

Polybutadiene can be halogenated readily in tetrahydrofuran with iodine chloride or bromine [49]. The products are glassy polymers. These products dehalogenate in reactions with organolithium compounds, like *n*-butyllithium, *sec*-butyllithium, and polystyryllithium in tetrahydrofuran solution. Dehalogenation of poly(iodo-chlorinated butadiene) with *n*-butyllithium yields product with different *cis*/*trans* ratios. Also, this is accompanied by partial cross-linking. The reactions may involve [49] halogen-metal exchanges that are followed by intra- and intermolecular elimination of lithium halide. In brominations of polybutadienes, both couplings and eliminations take place. Both iodo-chlorinated and brominated polybutadienes form graft copolymers when reacted with polystyryllithium in tetrahydrofuran [50]. Gel formation, however, accompanies the grafting reaction.

9.2.2 Hydrogenation

Atactic 1,4-polybutadiene and syndiotactic 1,2-polybutadiene can be hydrogenated at 100°C and 50 bar pressure of hydrogen with a soluble catalyst $\{[(Ph)_3\text{-}P]_3RhCl\}$. Complete saturation of double bonds results [52]. Butadiene acrylonitrile copolymers can also be hydrogenated quantitatively with this rhodium catalyst under mild conditions [53]. The kinetics are consistent with a mechanism where the active Rh-catalyst interacts with the unsaturation at the polymer in the rate-determining step. The nitrile group, however, appears to also interact with the catalyst and inhibit the rates [53].

Hydrogenation of carbon-to-nitrogen double bonds in polymer backbones and in the pendant groups can be carried out with lithium borohydride [86]:

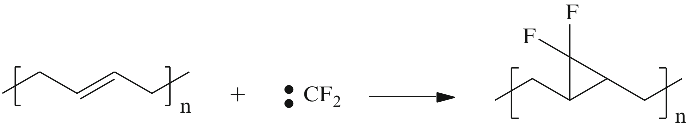


It was reported [485] that syndiotactic polystyrene can be hydrogenated over Ni/SiO_2 and Pd/$BaSO_4$ catalysts. The Ni catalyst yields complete hydrogenenation when low molecular weight polymer is used. Hydrogenation of high molecular weight polystyrene, however, is incomplete. On the other hand, the Pd catalyst yields completely hydrogenating material. The hydrogenated syndiotactic polystyrene is a crystalline material with good heat resistance [485].

9.2.3 *Addition of Carbenes*

Polyisoprenes and polybutadienes can also be modified by reactions with carbenes. Dichlorocarbene adds to natural rubber dissolved in chloroform in a phase transfer reaction with aqueous NaOH [54]. A phase transfer reagent must be used with the aqueous NaOH. Solid sodium hydroxide can be used without a phase transfer reagent. There is no evidence of *cis–trans* isomerization and the distribution of the substituents is random [54].

Difluorocarbene, generated under mild neutral conditions, adds to 1,4-*cis*- and 1,4-*trans*-polybutadienes to give materials containing cyclopropane groups [55]. The addition takes place randomly, to give atactic stereo sequence distributions [55]:

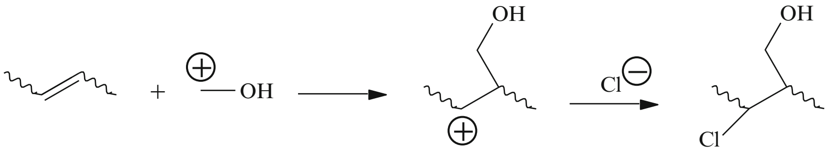


Fluorocarbene, formed from phenyl(fluoro,dichloromethyl)mercury by thermolysis in situ, also adds to 1,4 *cis*- and *trans*-polybutadienes. The carbene can add at various levels [57]. The addition is stereospecific and preserves the alkene geometry of the parent polybutadiene. Also, the addition is random, showing that the reactivity of the double bonds is independent of the sequence environment [57].

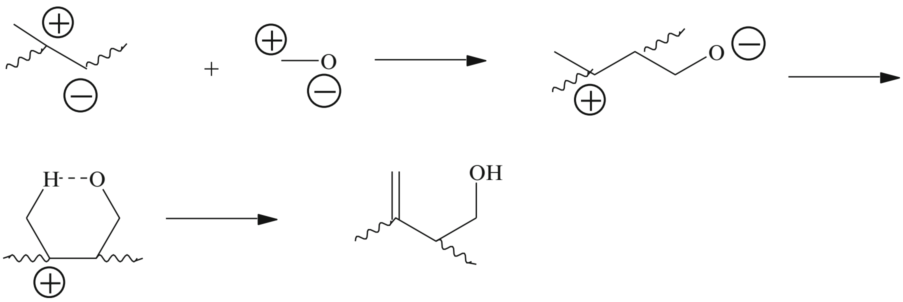
Dichlorocarbene, generated in situ from an organomercury precursor, phenyl(bromo, dichloromethyl)mercury (Seyferth reagent), adds to polybutadiene in a similar manner [56]. The reactions take place under homogeneous conditions. They can be carried out on 1% solutions of the polymer in benzene, using 10–20% mol excess of the reagent.

9.2.4 *Electrophilic Additions of Aldehydes*

These are additions to double bonds, like the *Prins reaction*, and they can be carried out on natural and synthetic rubbers [59, 60]. They take place rapidly in the presence of acid catalysts. Aqueous formaldehyde [61], or paraform in CCl_4 [62], can be used. The catalysts are inorganic acids or anhydrous Lewis acids, like boron trifluoride in acetic acid solution [63]:

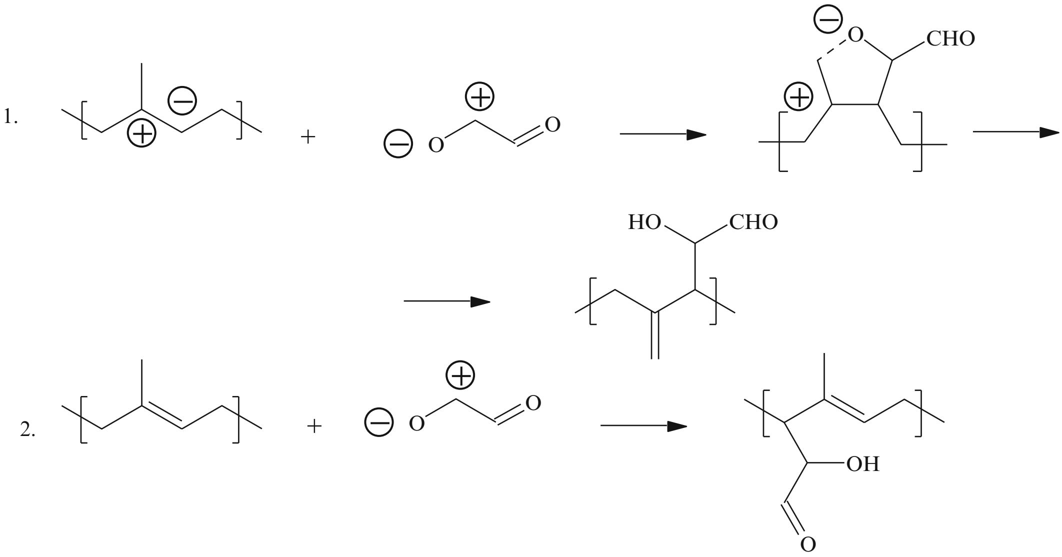


The reaction takes a different path in the absence of a catalyst [62]:



The products of the Prins reaction with rubbers are thermoplastic polymers that possess fair resistance to acids and bases. Free hydroxyl groups in the products are available for cross-linking with diisocyanates [64] or by other means. The Prins reaction can be carried out directly on rubber latexes [65]. It is also possible to just mill the rubber together with formaldehyde and then heat the resultant mixture in the presence of anhydrous metal chlorides [64] to get similar results [66].

Higher aldehydes also react with natural rubber [67]. The reaction works best with purified rubber. Additions take place without a catalyst at 180°C or in the presence of $AlCl_3$–NaCl at 120°C. These reactions can be carried out in the solid phase by milling the rubber with an aldehyde, like glyoxal [68]. Heating in a pressure vessel at above 175°C is required to complete the reaction. Infra-red spectra of the products from reactions in solution show presence of ether, carbonyl, and hydroxyl groups [69]. Two types of additions appear to take place [69]:



Products from reactions of rubber with glyoxal have a strong tendency to become spontaneously insoluble. This is probably due to a presence of residual aldehyde groups, because a treatment of the product with 2,4-dinitrophenyl-hydrazine eliminates spontaneous gelation.

Chloral adds to polyisoprene similarly. The reaction is catalyzed by Lewis acids [70]. Both $AlCl_3$ and BF_3 are efficient catalysts. Less cross-linking is encountered with aluminum chloride. Infra-red spectra of the products shows presence of hydroxyl groups, chlorine atoms, and vinylidene unsaturation [70].

9.2.5 Polar Additions

A number of polar additions to unsaturated polymers are known. These include Michael addition, hydroboration, 1,3-dipolar additions, ene reaction, the Ritter reaction, Diels–Alder additions, and others.

9.2.5.1 Michael Addition

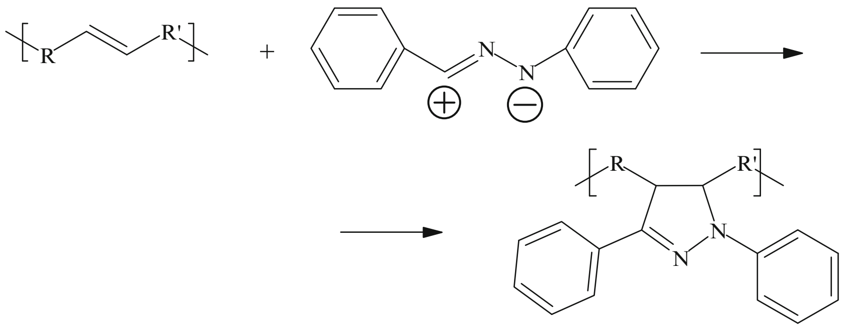
Among polar additions to unsaturated polymers are reactions of amines and ammonia with unsaturated polyesters in a form of a Michael condensation. Thus, for instance, additions to poly(1,6-hexanediol maleate) and poly(1,6-hexanediol fumarate) [71] show a difference in the reactivity of the two isomers. The maleate polyester reacts with ammonia to yield a cross-linked product at room temperature, when stoichiometric quantities or excess ammonia in alcohol is used. At the same reaction conditions, the fumarate isomer only adds a few percent of ammonia [71]. In a 1:1 mixture of chloroform and ethanol, however, approximately half of the fumarate double bonds react. Also, the maleate polyester reacts differently with piperidine or cyclohexylamine. In butyl alcohol at 60°C, the polymer initially isomerizes and precipitates. After the isomerization is complete and the temperature is raised to 80°C, the polymer redissolves. An exothermic reaction follows and Michael type adducts form [71].

9.2.5.2 Hydroboration

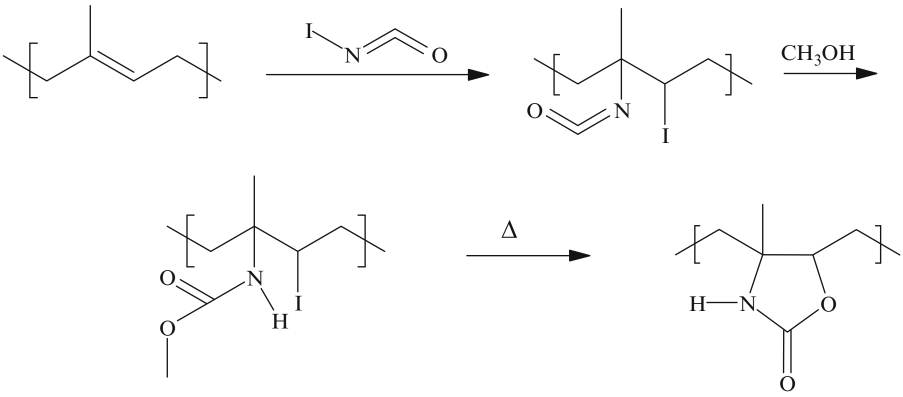
Polymers and copolymers of butadiene or isoprene with styrene can react with diborane [72]. A suitable solvent for this reaction is tetrahydrofuran. Subsequent hydrolyses result in introductions of hydroxyl groups into the polymer backbones. The reactions with diborane are very rapid. Some side reactions, however, also occur [72].

9.2.5.3 1,3-Dipolar Additions

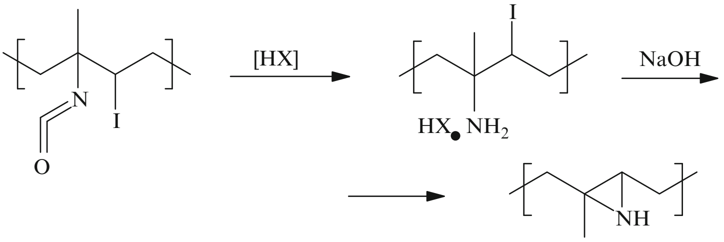
Cyclic structures form on polymer backbones through 1,3-dipolar additions to carbon to carbon or carbon to nitrogen double bonds [73]. Because many 1,3-dipoles are heteroatoms, such additions can lead to formations of five-membered heterocyclic rings. An example is addition of nitrilimine to an unsaturated polyesters [73]:



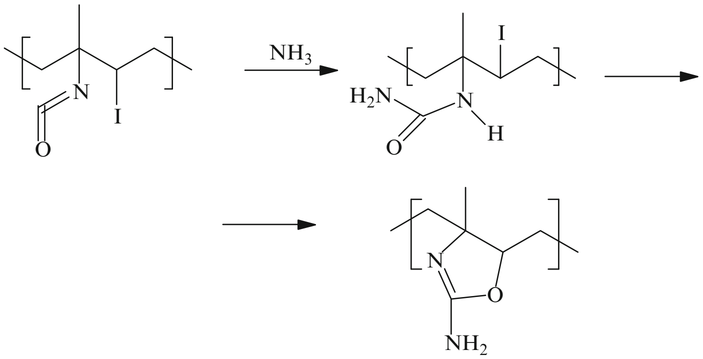
Also, iodine isocyanate adds to polyisoprene. The product can be converted to methyliodocarbamate or to iodourea derivatives [74]:



Iodine isocyanate additions result in approximately 40% yields. The products can undergo typical reactions of the isocyanate group [74], as for instance:

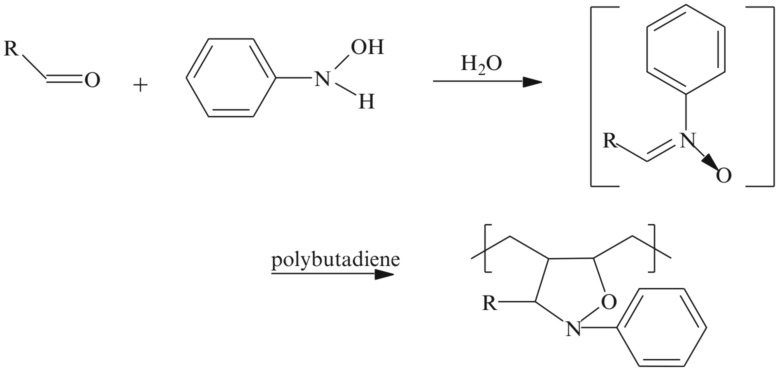


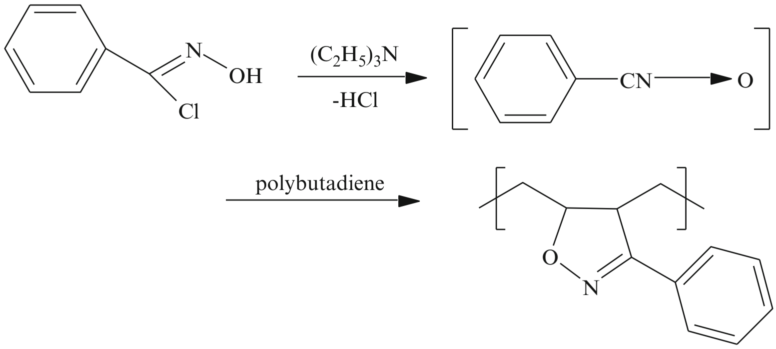
as well as:



where HX is a halogen acid. The products exhibit enhanced heat stability [74].

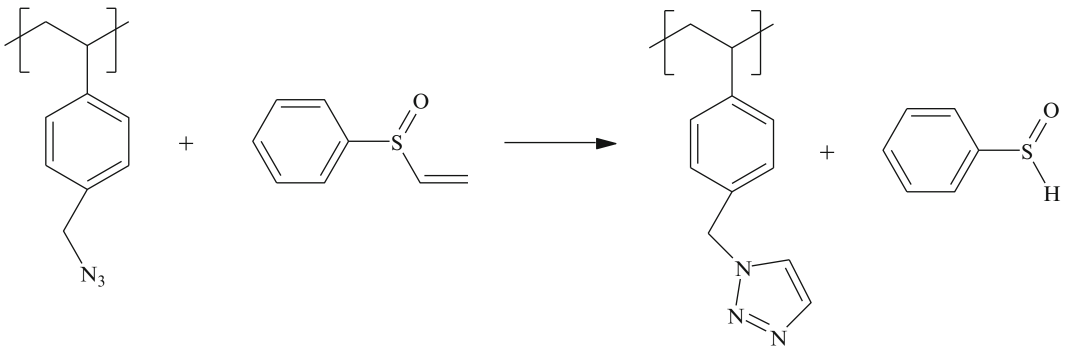
Dipolar cycloadditions take place when nitrones or nitrile oxides add to butadiene rubber. Some of the products contain isoxazolidine rings [75]:





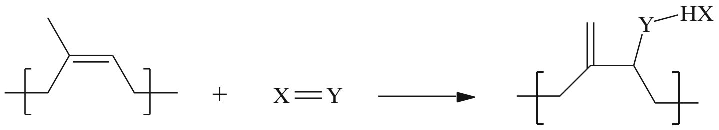
The above modification of butadiene rubber can be carried out to the extent of 3.1 mol.%. The product is higher in tensile modulus values and is greater in strength than the parent compound [75].

A final example is a 1,3 dipolar addition to pendant azide groups [87]. The reaction takes place with phenyl vinyl sulfoxide in dimethylformamide. Forty-eight hours at 110°C are required for the azide groups to become undetectable by infra-red spectroscopy. The product precipitates out with addition of ether [87]:

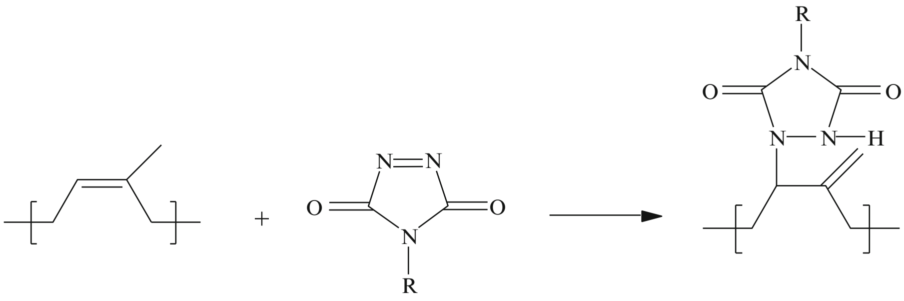


9.2.5.4 The Ene Reaction

The polymers of conjugated dienes can also be modified via the ene reactions [76], as for instance:

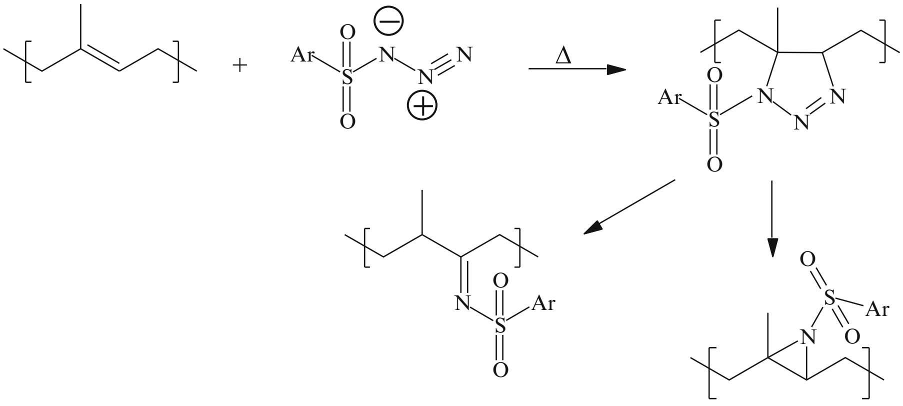


where, X=Y can be O=N–, –N=N–, >C=S, >C=O, or>C=C<. An example of this is an addition of triazolidones [76]:

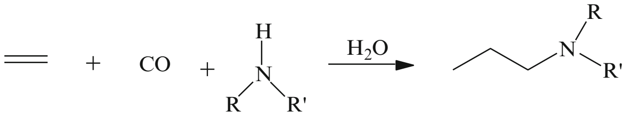


This results in formation of pendant urazole groups. The exact structure of the products, however, has not been fully established. The tensile strength of polymers improves considerably, but it is accompanied by a dramatic loss in molecular weight [76]. Nevertheless, ene reagents like C-nitroso and activated azo compounds are very efficient in adding to rubber. They add in a few minutes at temperatures between 100 and 140°C. In the case of the azo compound, the addition can be greater than 90%.

Substituted aryl sulfonyl azides decompose at elevated temperatures to nitrenes and add to natural rubber:

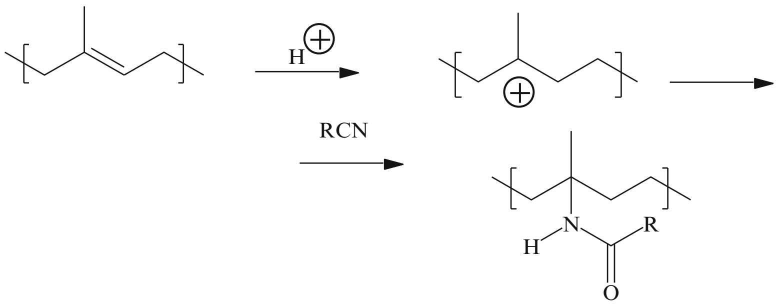


Novel types of polyamines and cationic polyelectrolytes form from polymers of conjugated dienes [77] in reactions with carbon monoxide, amines, and water at 150°C and 1,000–1,500 psi pressure. The reaction can be illustrated as follows [77]:



9.2.5.5 The Ritter Reaction

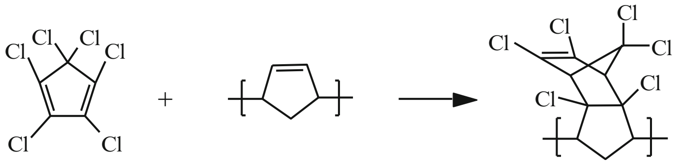
This reaction can be carried out on natural rubber and on synthetic polyisoprenes [78]:



The carbon cation, apparently, reacts with any nucleophile present. When the reaction is carried out in dichloroacetic acid, chlorine atoms can be detected in the product [78].

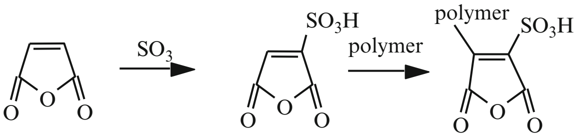
9.2.5.6 Diels–Alder Condensations

Crotonic acid esters of cellulose undergo addition reaction with cycloaliphatic amines, like morpholine or piperidine and with aliphatic primary amines [79]. Unsaturated polymers can also undergo Diels–Alder reactions. One example is a reaction of hexachlorocyclopentadiene with polycyclopentadiene [80]:



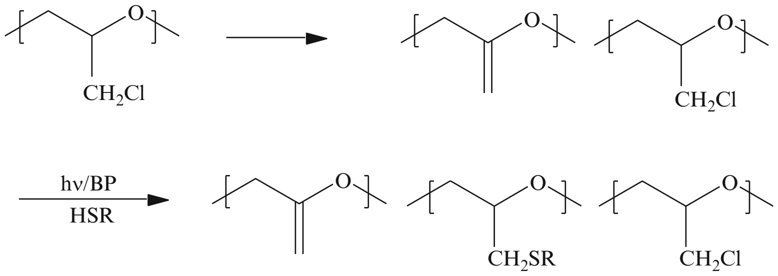
The addition takes place in an inert atmosphere at 140–150°C. Over 90 mol.% conversion is achieved in 6 h.

Diels–Alder condensations of fumaric and maleic acids polyesters with various dienes [81] can serve as another example. These reactions require 20 h at room temperature. Diels–Alder condensations can also be carried out on polymers of 1,3,5 hexatriene, 1,3,5-heptatriene, and 2,4,6-octatriene [82]. Sulfonate-substituted maleic anhydride adds to low functionality hydrocarbon elastomers, like EPDM, presumably via an Alder-ene type reaction [83]:



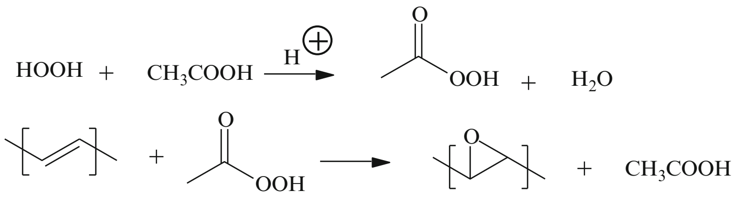
Thiols add to diene rubbers by a free-radical mechanism [84]. Thus, antioxidants, like 4-(mercaptoacetamido)-diphenylamine, add –SH groups to the double bonds of *cis*-polyisoprene and polybutadiene in the presence of free-radical initiators [84].

Thiol compounds also add photochemically to polymers containing double bonds. For instance, unsaturation can be introduced into polyepichlorohydrin by a partial elimination reaction. The product then reacts with mercaptans, aided by a photosensitizer (like benzophenone) and ultraviolet light [85]:

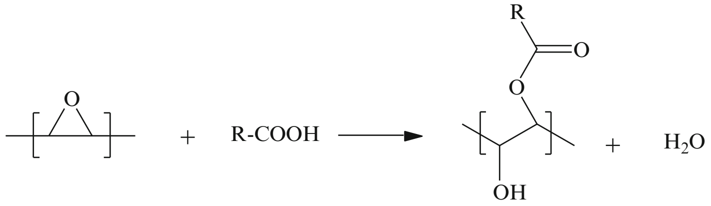


9.2.5.7 Epoxidation Reactions

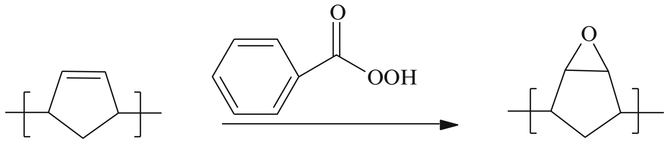
These addition reactions of unsaturated polymers, like liquid polybutadiene, developed into preparations of useful commercial materials [88–94]. Patent literature describes procedures that use hydrogen peroxide in the presence of organic acids or their heavy metal salts. Reaction conditions place a limitation on the molecular weights of the polymers, because it is easier to handle lower viscosity solutions. A modification of the procedures is to use peracetic acid in place of hydrogen peroxide [95–97]. The most efficient methods rely upon formations of organic peracids in situ with cationic exchange resins acting as catalysts [98]. This can be illustrated as follows:



The reaction is accompanied by formations of by-products:

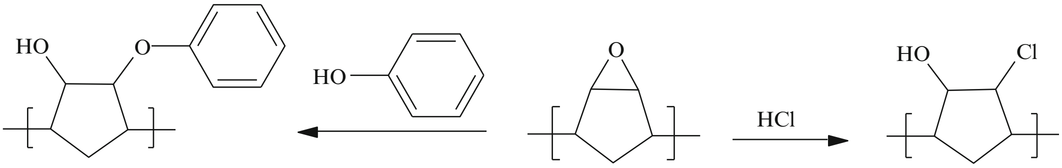


Polybutadienes that are high in 1,4-structures tend to epoxidize more readily and yield less viscous products [100, 101]. The epoxidation reaction can also be carried out on poly(1,4-cyclopentadiene) [99]:

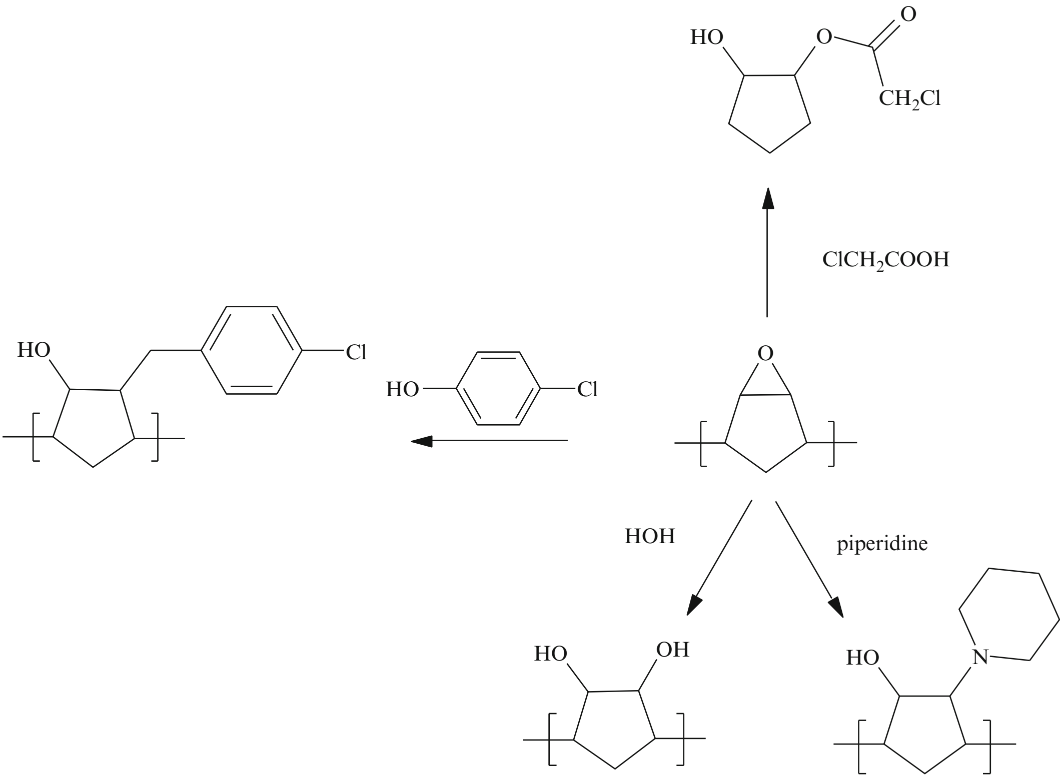


Perbenzoic acid is an effective reagent in chloroform and in methylene chloride solutions at 0–20°C. The conversions are high, yielding brittle materials soluble in many solvents. The products can be cast into transparent films [99].

Monoperphthalic and *p*-nitroperbenzoic acids are also efficient epoxidizing agents. They can, however, cause cross-linking, as is the case in epoxidation of polycyclopentadiene [99]. The products react like typical epoxy compounds [99]:



Some other reactions of the epoxy groups are [99]:

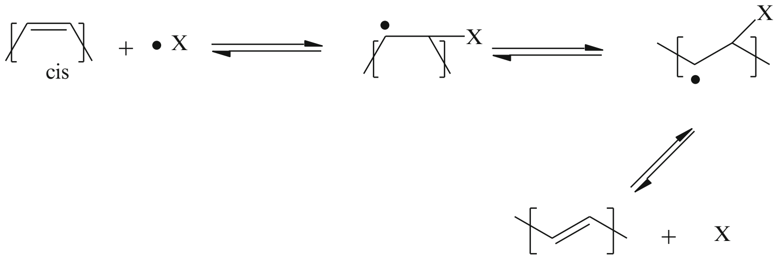


9.3 Rearrangement Reactions

There are different types of polymeric rearrangements. One of them is isomerizations of polymers with double bonds. Others can be intramolecular cyclizations in the polymeric backbone.

9.3.1 Isomerization Reactions

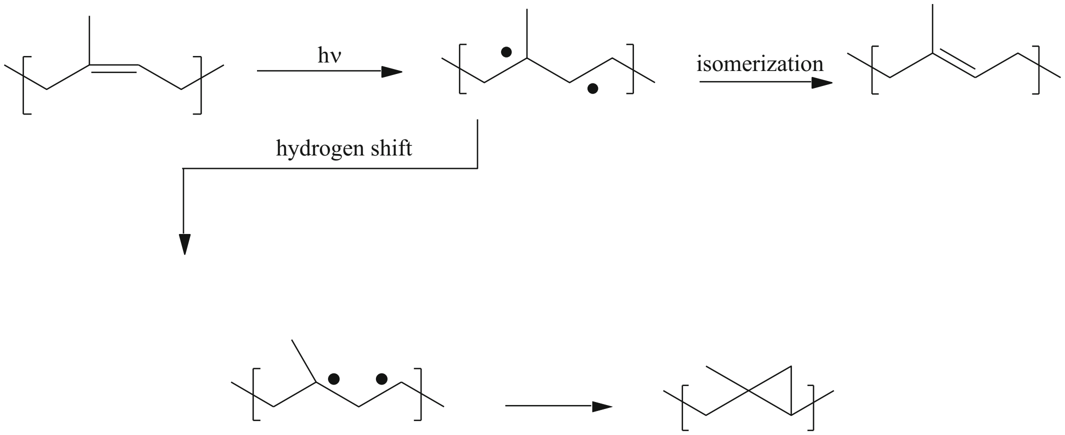
The isomerization of *cis*-polybutadiene can be carried out with the aid of ultraviolet light or with gamma radiation. When light is used, the free-radical reaction requires photoinitiators [102, 103]. The mechanism involves freely rotating transitory free-radicals on the polymer backbone. These form from additions of photoinitiator fragments to the double bonds. The adducts break up again, releasing the attached initiator fragments and reestablishing the double bonds. The new configurations are *trans* because they are more thermodynamically stable [102, 103]. This can be shown as follows:



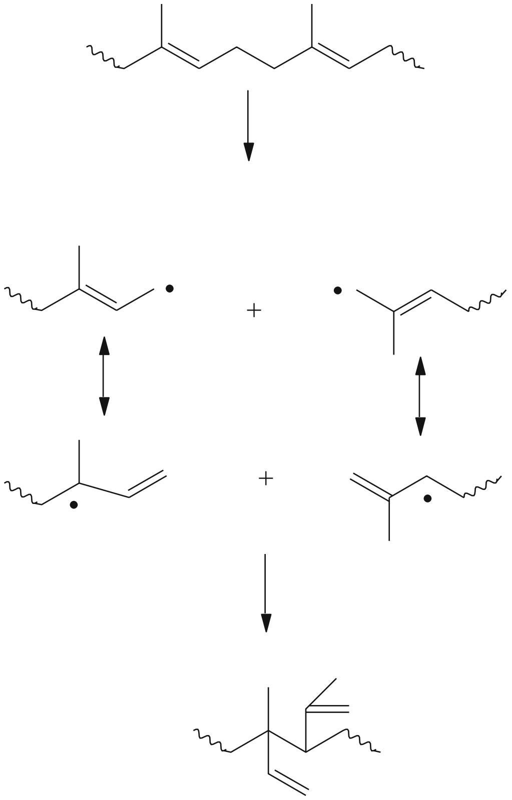
where, X• represents a free-radical fragment from a photoinitiator.

With gamma radiation, there is no need for any additives [104, 105]. Here, the mechanism of isomerization is believed to involve direct excitation of the π-electrons of the double bonds to anti-bonding orbitals where free and geometric interconversions are possible. In benzene solutions, energy transfers take place from excited benzene molecules to the polymer double bonds.

When 1,4-polyisoprene films are irradiated with light [122], *cis–trans* isomerizations occur. In the process, the quantities of 1,4-unsaturations decrease. Also, vinyl and vinylidene double bonds and cyclopropyl groups form. This can be illustrated as follows:



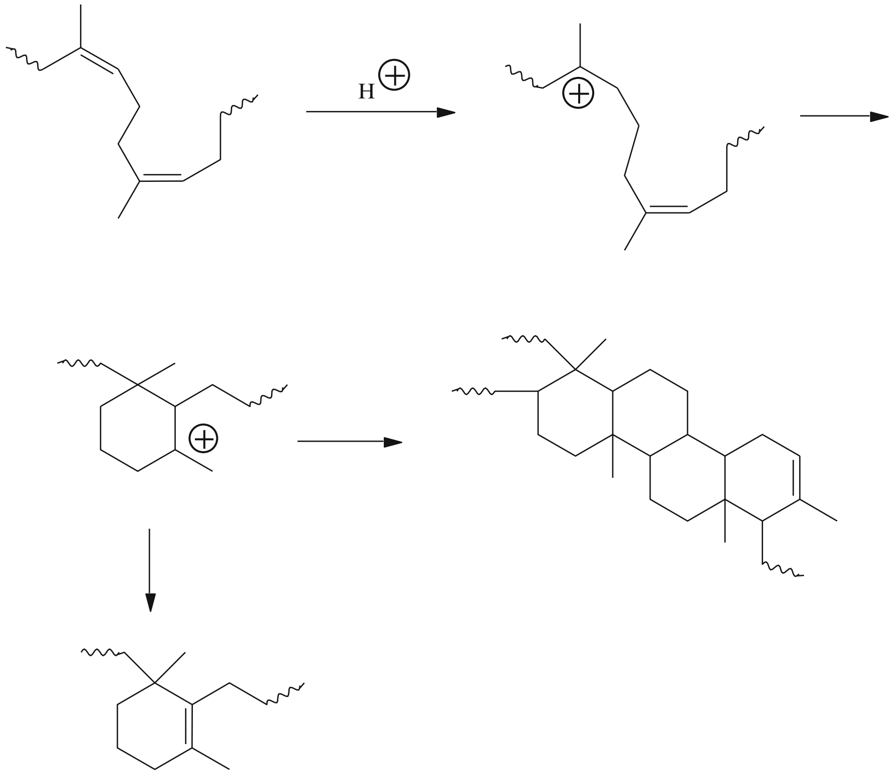
and



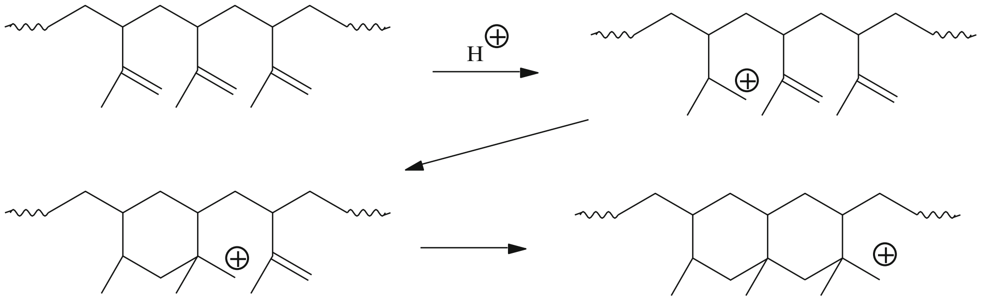
Polybutadiene can also isomerize *cis–trans* and lose unsaturation when irradiated in the solid state. This must be done in vacuum with ultraviolet light of 1,236 or 2,537 Å [106, 107]. Both free-radical and ionic mechanisms are suspected to operate simultaneously.

9.3.2 Cyclizations and Intramolecular Rearrangements

Cyclization reactions of natural rubber and other polymers from conjugated dienes have been known for a long time. The reactions occur in the presence of Lewis and strong protonic acids. They result in loss of elastomeric properties and some unsaturation. Carbon cations form in the intermediate step and subsequent formation of polycyclic structures [108, 109]:



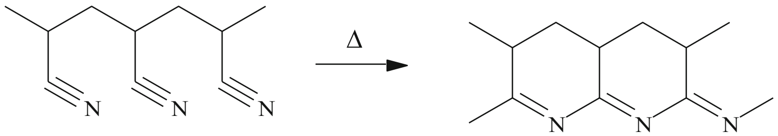
In a similar manner, polymers with pendant unsaturation undergo cyclization reactions in benzene in the presence of BF_3 or $POCl_3$, yielding ladder structures. The exact nature of the initiation process is not clear. Water may be needed for the initiation step [110, 111]:



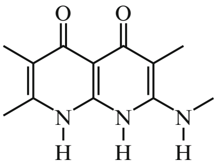
The reactions result in formations of six-membered monocyclic and fused polycyclic units. These reactions of carbon cations should also lead to molecular rearrangements, like 1,2 shifts of protons, resulting in formations of five-membered rings and spiro cyclopentane repeat units [111].

Cyclization reactions of polyisoprene can be catalyzed by $TiCl_4$ [112] and by sulfuric acid [113–115, 117]. The products appear similar in the infra-red spectra [110] with only a few minor differences. Also, there are only a small number of fused rings in the product.

Polyacrylonitrile converts to a red solid when heated above 200°C [116]. Only a small amount of volatile material is given off. Further heating of the red residue to about 350°C or higher converts it to a black brittle material. This black material has a ladder structure:

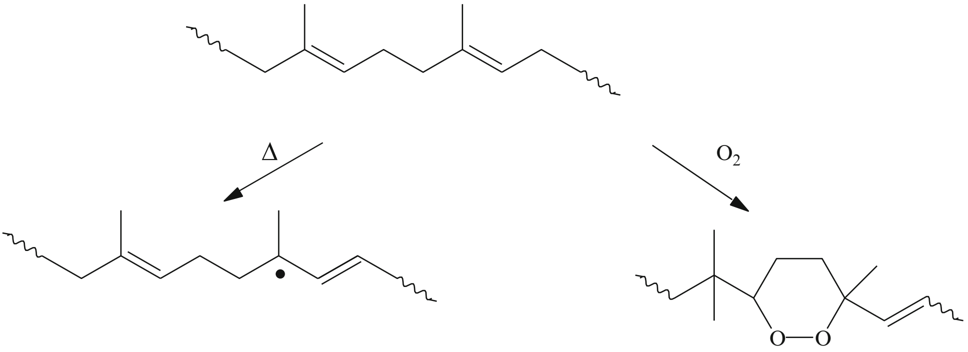


Heating of polyacrylonitrile in the presence of oxygen yields some quinone-type structures:

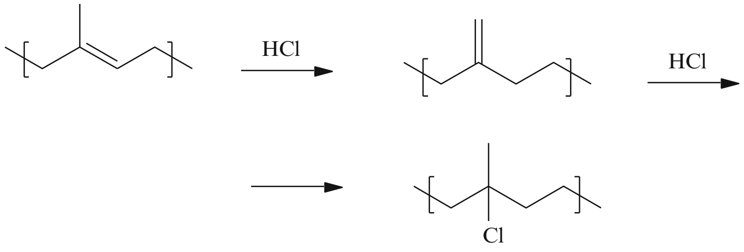


Further heating of the polymer, at very high temperatures, in excess of 2,000°C, results in formation of graphite-like structures [116]. All, or almost all nitrogen is lost, probably as HCN and N_2.

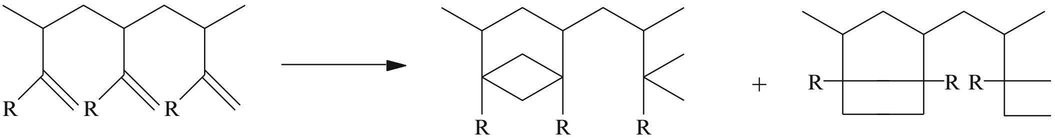
Migration of double bonds is a well-established phenomenon in polymers from conjugated dienes. It occurs, for instance, during vulcanization of rubber (discussed in a later section). It also occurs upon simply heating some polymers [117–119]. Thus, the double bonds shift in natural rubber when it is heated to temperatures of 150°C or above [120]:



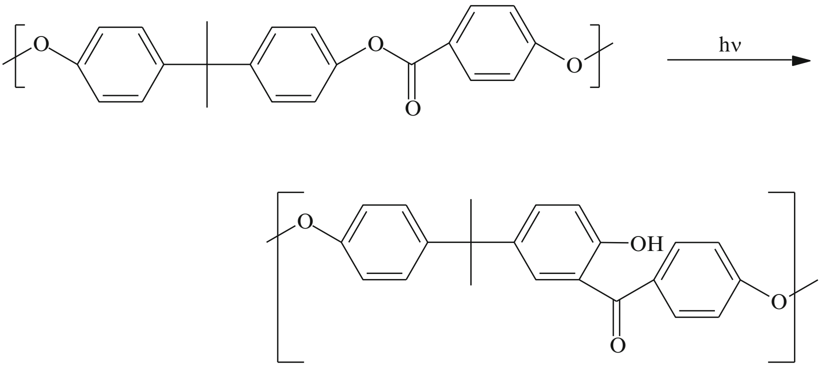
Hydro chlorination of rubber in solution causes a different kind of double bond shirt [121]:



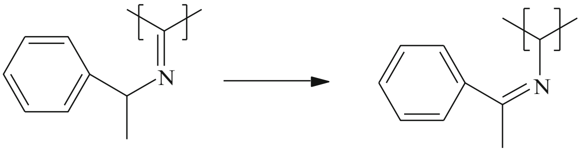
In polymers with pendant double bonds, facile cycloadditions occur upon heating [123–125]:



Many other polymeric structures can rearrange under proper conditions. For instance, poly(4,4′-diphenylpropane isophthalate) rearranges upon irradiation with UV light to a structure containing *o*-hydroxybenzophenones [126]:

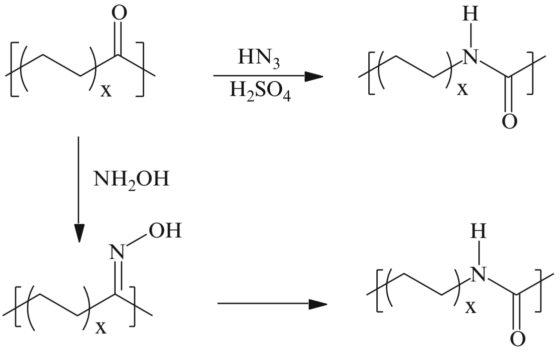


The mechanism is believed to be that of a photo-induced *Fries rearrangement*. It may be similar to one catalyzed by Lewis acids. Another example is a spontaneous rearrangement in the solid state of poly(α-phenylethylisonitrile) [128]:



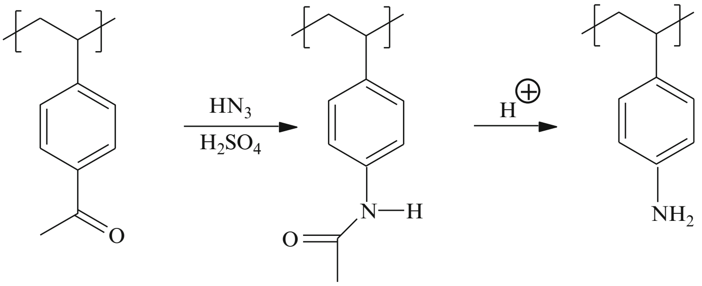
Based on studies of molecular models, it was concluded [128] that the substituents force progressive, one-handed twisting of the helix shape of the molecules. This occurs to such an extent that the vicinal imino double bonds are out of conjunction with each other. As a result, each benzylic hydrogen atom becomes localized over the electrons of the imino groups. It proceeds in a constant screw direction around the axis of the helix. Such steric confinement causes tautomeric rearrangements, as shown above, which results in some relaxation of the compression. An additional driving force is a gain in conjugation between the imino double bonds and the aromatic rings of each substituent.

Intramolecular rearrangements of polymers with ketone groups were subjects of several studies. The *Schmidt* and *Beckmann rearrangements* were carried out on copolymers of ethylene and carbon monoxide [129]:

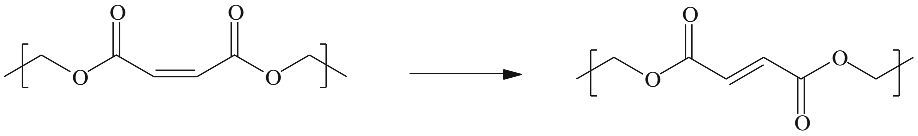


The starting materials were low and medium molecular weight copolymers. Infra-red spectra of the products from the Schmidt reaction show a high degree of conversion [129]. The yields of the oximes and subsequent Beckmann rearrangements are also high.

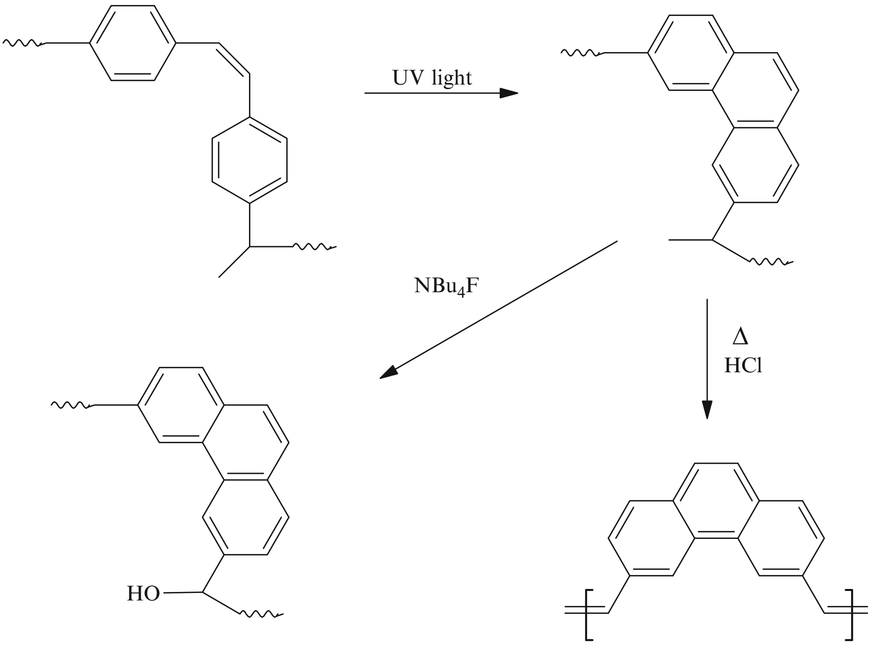
A Schmidt reaction on poly(*p*-acetyl styrene) yields a product containing acetyl amino styrene groups in high yields and the products are surprisingly pure [130]. The solvent is acetic acid and the converted material precipitates out as a sticky mass:



Another rearrangement reaction is isomerization of unsaturated polyesters upon heating. Thus, for instance, maleate polyesters rearrange to the fumarate analogs at elevated temperatures [131]:



It was reported that polymers with *cis*-stilbene moieties in the backbone can undergo photocylization that is almost quantitative [473]:



9.4 Substitution Reactions

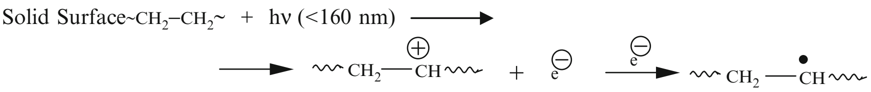
Many substitution reactions are carried out on polymers in order to replace atoms in the backbones or in the pendant groups with other atoms or groups of atoms. These reactions do not differ much from those of the small molecules.

9.4.1 Substitution Reactions of Saturated Polymeric Hydrocarbons

It is often desirable to replace hydrogens with halogens. *Fluorination of polyethylene* can be carried out in the dark by simply exposing the polymer, either in sheet or in powder form, to fluorine gas. The reaction is exothermic and it is best to dilute the gas with nitrogen 9:1 to allow a gradual introduction of the fluorine and avoid destruction of the polymer [132, 133]. In this manner, however, only the surface layers are fluorinated and the substitutions occur only a few molecular layers deep.

In surface fluorination with vacuum ultraviolet glow discharge plasma, the photon component of the plasma enhances the reactivity of the polymer surfaces toward fluorine gas [134]:

$$\text{Gas phase}: F_2 + h\nu(210\text{–}360\,\text{nm}) \rightarrow 2F^{\bullet}$$



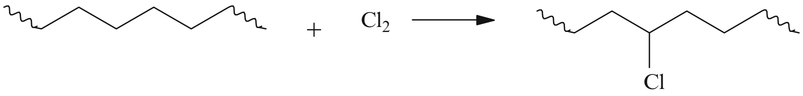
The surface free-radicals can also cause elimination of hydrogen radicals and formation of double bonds. Whether as free-radicals or through unsaturation, the units are now more reactive toward fluorine.

A film that is 3 mil thick can be completely fluorinated on a 100-mesh phosphor bronze gauze, if the reaction is allowed to proceed for several days [135]. Fluorination can also be carried out with mercuric or cupric fluorides in hydrofluoric acid. The reaction must be carried out at 110°C for 50 h. As much as 20% of fluorine can be introduced [136].

In direct fluorination of powdered high-density polyethylene with the gas, diluted with helium or nitrogen, the accompanying exotherm causes partial fusion. In addition, there is some destruction of the crystalline regions [137]. On the other hand, fluorination of single crystals of polyethylene can result in fluorine atoms being placed on the carbon skeleton without disruption of the crystal structure. The extent of cross-linking, however, is hard to assess [138]. The reaction has all the characteristics of free-radical mechanism [139]:

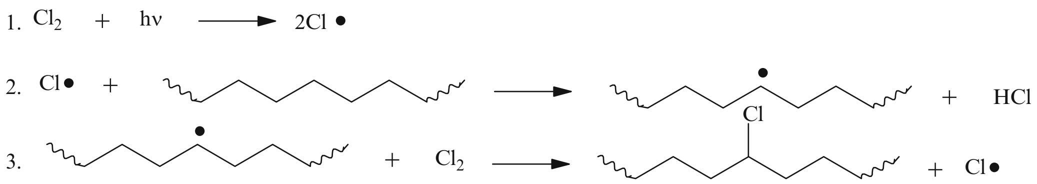
$$F_2 \rightarrow 2F^{\bullet}$$
$$\mathrm{RH} + F^{\bullet} \rightarrow \mathrm{R}^{\bullet} + \mathrm{HF}$$
$$\mathrm{R}^{\bullet} + F_2 \rightarrow \mathrm{RF} + F^{\bullet}$$

Chlorinations of polyethylene can be carried out in the dark or in the presence of light. The two reactions, however, are different, though both take place by free-radical mechanism. When carried out in the dark at 100°C or higher, no catalyst is needed, probably because there are residual peroxides from oxidation of the starting material. Oxygen must be excluded because it inhibits the reaction and degrades the product [140]. The reaction is catalyzed by traces of $\mathrm{TiCl_4}$ [141]. Such trace quantities can even be residual titanium halide from a Ziegler-Natta catalyst left over in the polymer from the polymerization reaction. When it is carried out at 50°C in chlorobenzene, –CHCl– groups form [142]:



This slows the chlorination of adjacent groups.

Trace amounts of oxygen catalyze chlorinations in the presence of visible light [140]. The same reaction in ultraviolet light is accompanied by cross-linking. The photochemical process can be illustrated as follows:



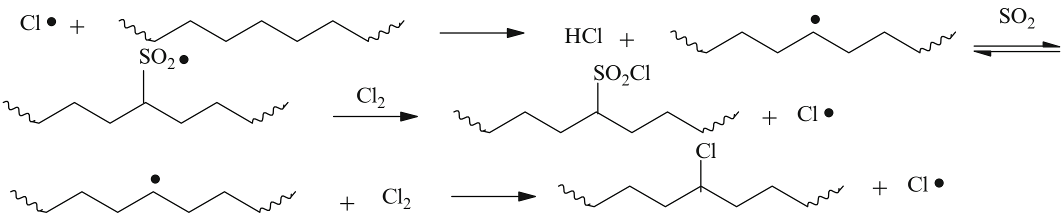
etc.

Chlorination of polyethylene can result in varying amounts of hydrogen atoms being replaced by chlorine. It is possible to form a product that contains 70% by weight of chlorine. The amount of chlorination affects the properties of the product. At low levels of substitution, the material still resembles the parent compound. When, however, the level of chlorine reaches 30–40%, the material becomes an elastomer. At levels exceeding 40%, the polymer stiffens again and becomes hard.

Commercial chlorinations of polyethylene are usually conducted on high-density ($D > 0.96$) linear polymers. The molecular weights of the starting materials vary. High molecular weight polymers form tough elastomers. Low molecular weight materials, however, allow easier processing of the products. The reactions are carried out in carbon tetrachloride, methylene dichloride, or chloroform at reflux temperatures of the solvents and at pressures above atmospheric to overcome poor solubility. The solubility improves with the degree of chlorination. Industrially, two different procedures are used. In the first one, the reactions are conducted at 95–130°C. When the chlorinations reach a level of about 15%, the polymers become soluble and the temperatures are lowered considerably [143]. In the second one, the reactions are conducted on polymers suspended in the solvent. When the chlorine content reaches 40% and the polymers become soluble, chlorinations are continued in solution. By continuing the reaction, a chlorine content of 60% can be reached. The products from the two processes differ. The first one yields a homogeneous product with the chlorine atoms distributed uniformly throughout the molecules. Chlorination in suspension, on the other hand, yields heterogeneous materials with only segments of the polymeric molecules chlorinated. Some commercial chlorinations are conducted in water suspensions. These reactions are carried out at 65°C until approximately 40% levels of chlorine are achieved. The temperatures are then raised to 75°C to drive the conversions further. In such procedures, agglomerations of the particles can be a problem. To overcome that, water is usually saturated with HCl or $CaCl_2$ [144]. Problems with agglomeration are also encountered during suspension chlorinations in solvents, like CCl_4. Infra-red spectra of chlorinated polyethylenes show presence of various forms of substitutions. There are –CHCl–CHCl– as well as $–CCl_2–$ groups present in the materials [145, 146]. Surface photo chlorination of polyolefin films [146] considerably improves the barrier properties of the films to permeations of gases.

Chlorinations of polypropylene usually result in severe degradations of the polymer. When $TiCl_4$ is the chlorination catalyst, presumably, less degradation occurs [140]. Studies of *bromination of polypropylene* (atactic) show that when the reaction is carried out in the dark, in CCl_4 at 60°C, the substitution reactions proceed at the rate of 0.5%/h [147].

Chlorosulfonation or polyethylene is a commercial process. The reaction resembles chlorination in the step of hydrogen abstraction by chlorine radicals. It is catalyzed by pyridine [148–150] and can be pictured as follows [147]:



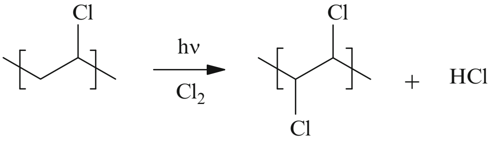
The amount of SO_2 vs. chlorine in the reaction mixture affects the resultant ratios of chlorosulfonation vs. chlorination of the polymer. These ratios and the amounts of conversion vary with the temperature [149].

Commercially produced chlorosulfonated polyethylene contains approximately 26–29% chlorine and 1.2–1.7% sulfur [151]. The material is an elastomer that remains flexible below −50°C. It is commonly cross-linked (vulcanized) through the sulfonyl chloride groups. Heating it, either as a solid or in solution, to 150°C results in loss of SO_2 and HCl. If the material is heated for 2 h at 175°C, all SO_2Cl groups are removed. In gamma radiation-induced chlorosulfonations and sulfoxidations of polyethylene powders [153] at room temperature, the ratios of SO_2Cl groups to Cl groups decrease with increases in radiation.

Polypropylene can be chlorosulfonated to the extent of containing 6% chlorine and 1.4% sulfur without embrittlement. The reaction can be done in CCl_4 at 55°C. There is apparently less degradation than in a direct chlorination reaction [148, 152].

9.4.2 Substitution Reactions of Halogen-Bearing Polymers

Procedures for commercial *chlorinations of poly(vinyl chloride)* vary. Low temperature chlorinations are done on aqueous dispersions of the polymers that are reacted with chlorine gas in the presence of swelling agents, like chloroform. These are light catalyzed reactions, usually carried out at about 50°C. They result in substitutions of methylene hydrogens [158, 159].



Some breakdown of the polymers accompanies the reactions in suspension [154]. Irregularity in the structures and the release of HCl significantly contribute to this. It appears that the degradations are initiated by HCl that is released as a result of the chlorination. In the process, double bonds form. Immediately upon their formation, they become saturated with chlorines.

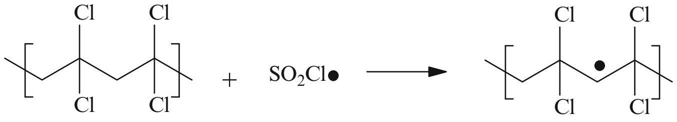
A study was conducted on solution chlorination of poly(vinyl chloride) in the presence of free radicals [155] generated from azobisisobutyronitrile. The reaction appears to proceed in two stages. The first one takes place until 60% of all the CH_2 groups have reacted. After that, in the second stage the original –CHCl groups are attacked. Some unreacted $–CH_2–$ groups, however, remain [155].

Photo chlorination can achieve 90% conversion [156, 157]. Typical commercially chlorinated poly (vinyl chloride), however, has a chlorine content of 66–67%. The material contains methylene groups and is in effect a copolymer of vinyl chloride and 1,2-dichloroethylene.

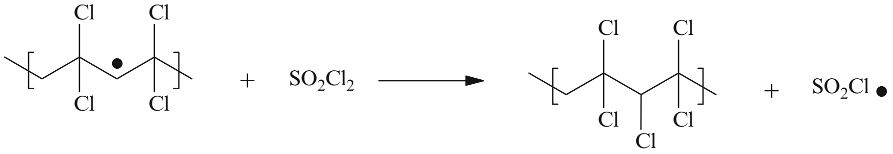
Chlorination raises the softening temperature of poly(vinyl chloride). The products exhibit poorer heat stability than the parent material and are higher in melt viscosity. High-temperature chlorinations in chlorinated solvents at 100°C result in extensive substitutions of the methylenic hydrogens as well. The reactions, however, are accompanied by extensive chain scissions. The products are soluble in solvents like acetone and methylene chloride and have low softening points, low impact strength, and poor color stability.

Chlorination of poly(vinylidene chloride) can be carried out with sulfuryl chloride using azobisisobutyronitrile [155]. The reaction appears to proceed in three steps:

1. Formation of SO_2Cl• free radicals by abstraction.
2. Formation of free radicals on the polymeric backbones:

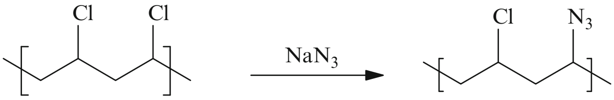


3. Transfer reactions of the active sites:

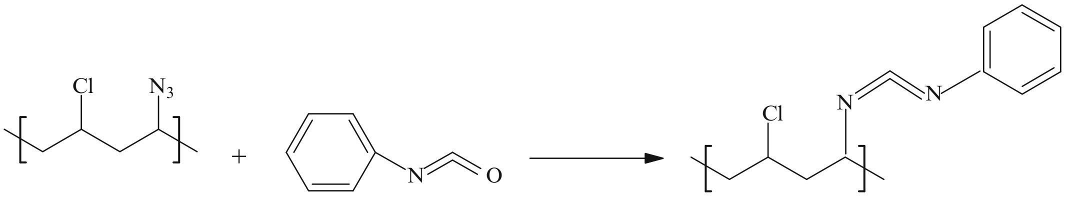


Chlorination of poly(vinyl fluoride) yields a product with 40–50% chlorine content [158]. *Fluorination* of poly(vinylidene fluoride) was reported [160]. When mixtures of fluorine and nitrogen gases are used, the reactions are limited by the amount of diffusion of fluorine into the polymer network. X-ray photoelectron spectroscopy shows presence of $-CF_2-$, –CHF–, and $-CH_2-$ groups in the product [161].

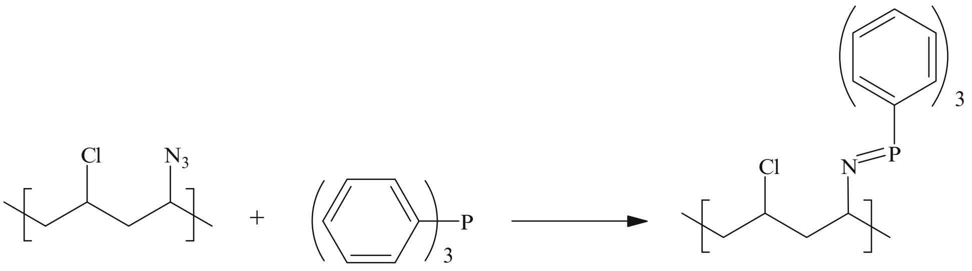
Many attempts at other modifications of poly(vinyl chloride) were reported in the literature. Often the reactions are based on expectations that the polymers will react like typical alkyl halides. Unfortunately, in place of nucleophilic substitutions, the polymers often undergo rapid and sequential eliminations of HCl along the chains. Nevertheless, many substitution reactions are still possible and can be successfully carried out. One example is a replacement of 43% of the chlorine atoms with azide groups [162]:



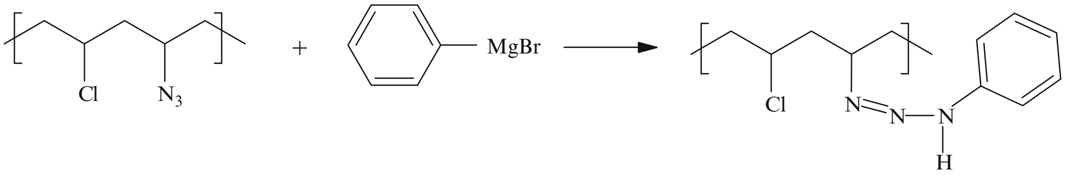
The reaction can be carried out at 60°C for 10 h and the polymer does not cross-link. It proceeds faster in DMF than in other solvents. Once substituted, the polymer becomes photosensitive and cross-links when irradiated with ultraviolet light. The presence of azide groups allows further modifications. One such modification is a reaction with an isocyanate [162]:

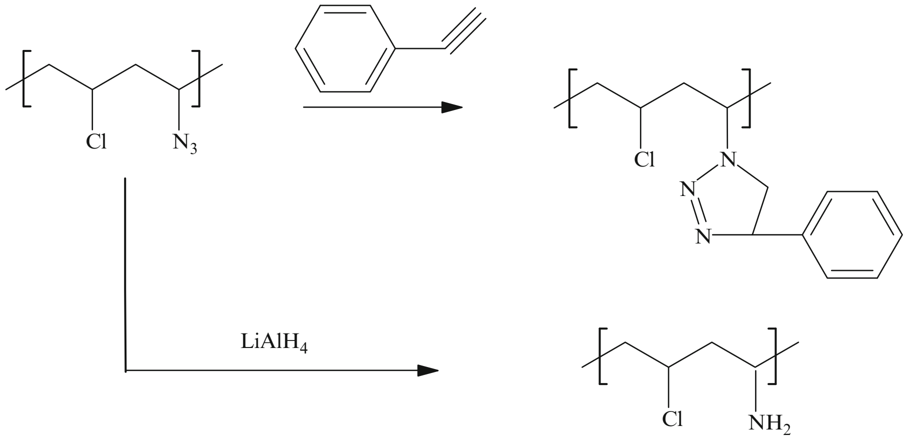


By a similar reaction, phosphinimine groups can be formed on the polymer backbone [162]:



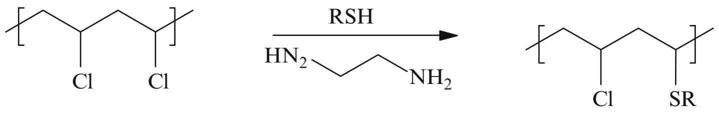
Some other modifications of the azide group containing polymers are [163, 164]:



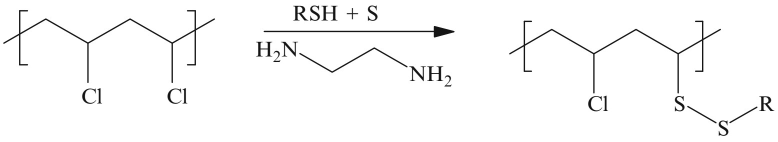


Note: The illustration of the reactions with $LiAlH_4$, as shown above, implies that all chloride atoms remain intact on the polymer backbones. It appears likely, however, that some of them might get removed and double bonds might form instead in the backbone.

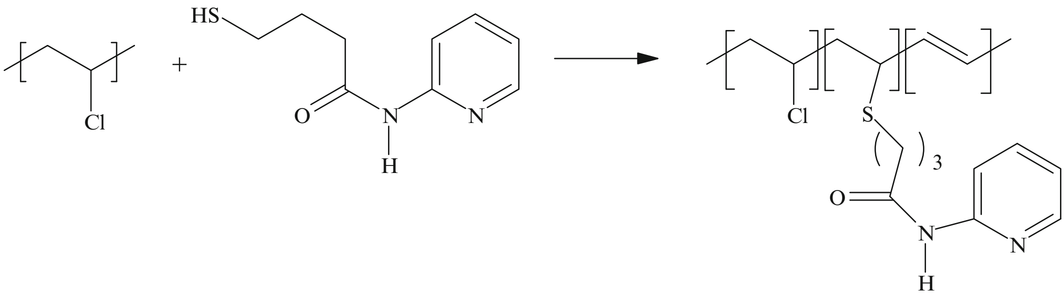
Poly(vinyl chloride) reacts with various thiols in ethylene diamine to produce monosulfide derivatives [165]:



When sulfur is added to the reaction mixture, disulfides form instead [165]:

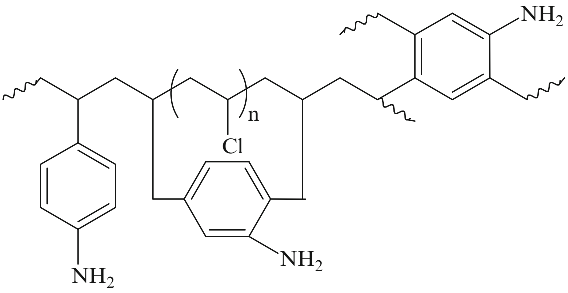


The thiolate ions can serve as strong nucleophiles and also as weak bases [166]. When poly(vinyl chloride) is suspended in water in the presence of swelling agents and phase transfer catalysts, it reacts with mercaptans, like 3-[*N*-(2-pyridyl)carbamoyl]-propylthiol:

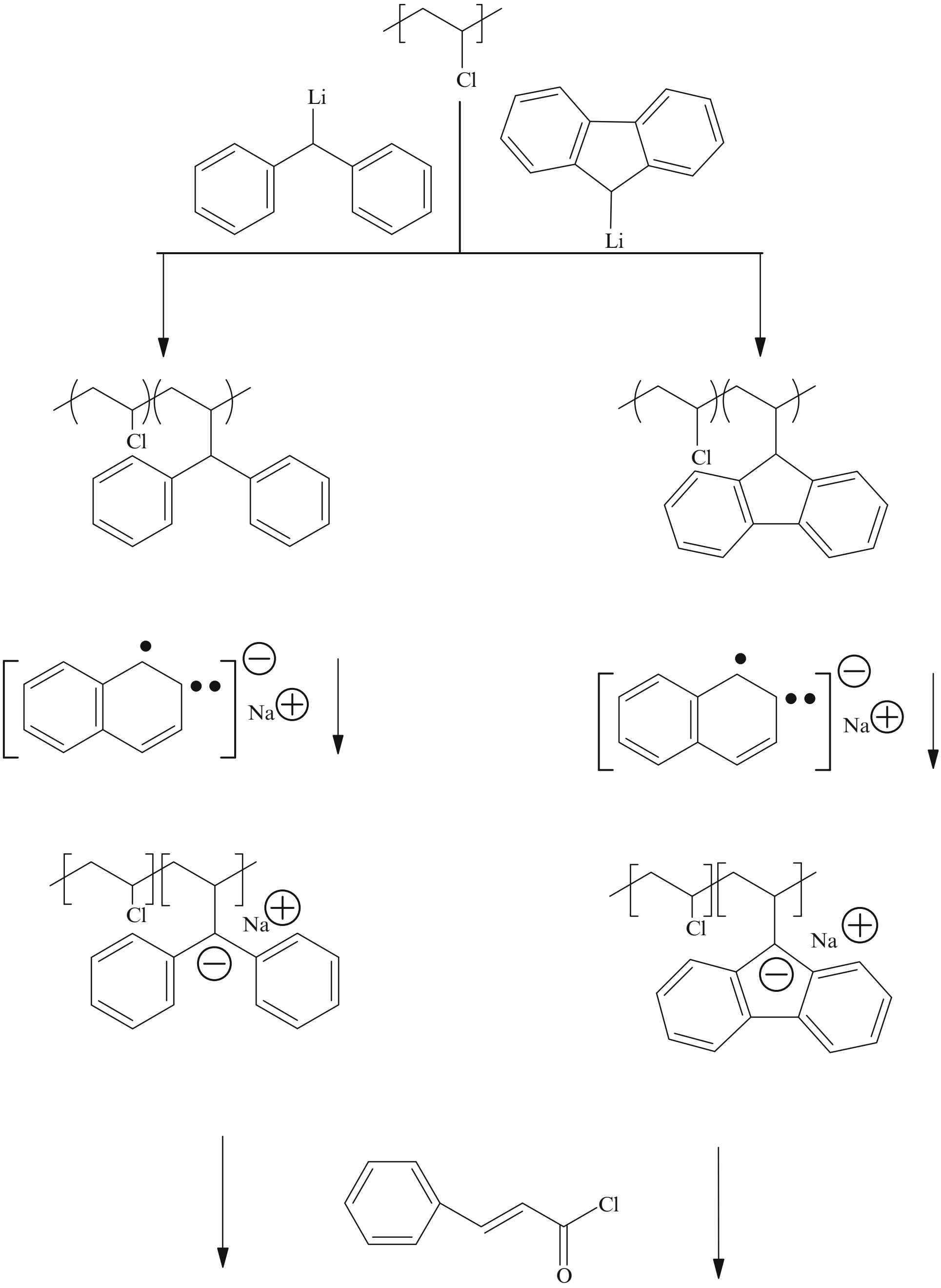


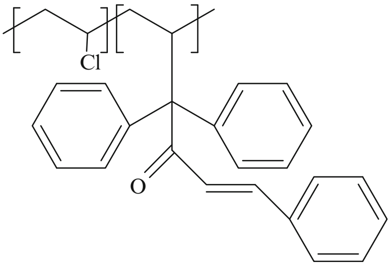
Acetoxylation of poly(vinyl chloride) can be carried out under homogeneous conditions [167]. Crown ethers, like 18-crown-6, solubilize potassium acetate in mixtures of benzene, tetrahydrofuran, and methyl alcohol to generate unsolvated, strongly nucleophilic “naked” acetate anions. These react readily with the polymer under mild conditions [167]. Substitutions of the chlorine atoms on the polymeric backbones by anionic species take place by S_N2 mechanism. The reactions can also proceed by S_N1 mechanism. That, however, requires formations of cationic centers on the backbones in the rate-determining step and substitutions are in competition with elimination reactions. It is conceivable that anionic species may (depending upon basicity) also facilitate elimination reactions without undergoing substitutions [167].

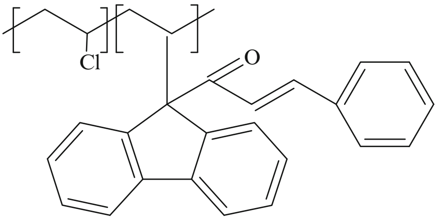
Reactions of poly(vinyl chloride) with aromatic amines, amino alcohols, or aliphatic amines in DMF solution result in both substitutions and in eliminations [168]. Reactions with aniline yield the following structure [168]:



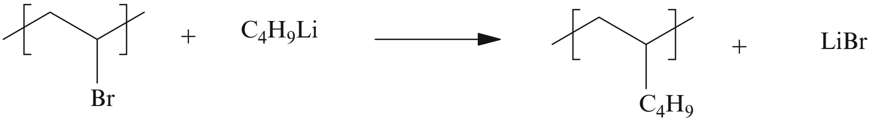
Carbanionic reaction sequences can be used to introduce various photosensitive groups [169]. The process consists of creating carbanionic centers on the backbone and then reacting them with various halogenated derivatives:



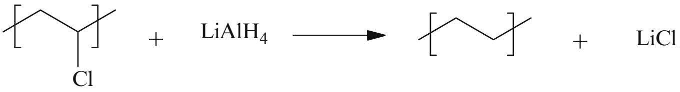




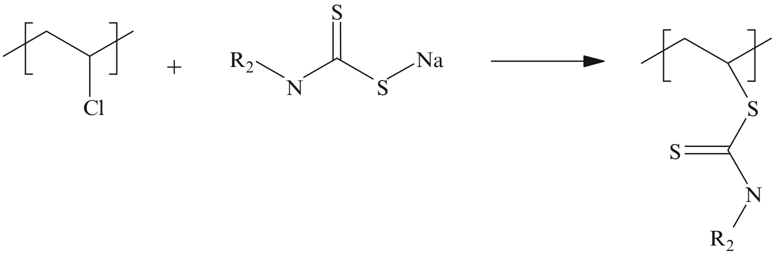
A redox cyclopentadienyl iron moiety can also be introduced into the poly(vinyl chloride) backbone by a similar technique [170]. Many other attempts were reported at replacing the halogens of poly(vinyl chloride), poly(vinyl bromide), and poly(vinyl iodide) with an alkali metal or with a hydrogen. For instance, in an effort to form poly(vinyl lithium), the polymers were reacted with organolithium compounds and with metallic lithium. The reactions with alkyllithium, however, resulted in substitutions by the alkyl groups, similarly to the reactions shown previously [171]:



Reactions with metallic lithium lead to formations of polyenes [171]. On the other hand, when poly(vinyl chloride) is reacted with metal hydrides, like lithium aluminum hydride in a mixture of tetrahydrofuran and decalin at 100°C, macroalkanes form [172]:



Replacement of the chlorine with *N*,*N*-dialkyl dithiocarbamate was reported to occur at 50–60°C in DMF solvent [173]:



The reaction is catalyzed with ethylene diamine [174].

9.4.3 Substitution Reactions of Polymers with Aromatic Rings

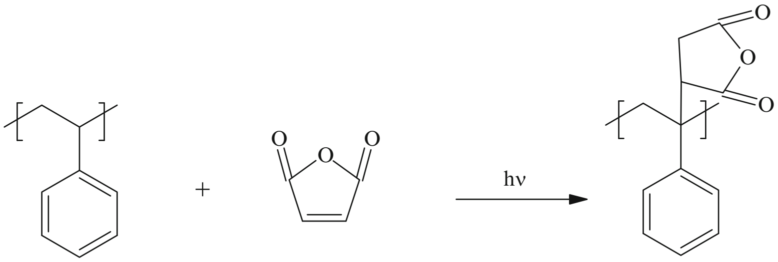
There are some interesting reports in the literature on reactions carried out on the backbones of polystyrenes. There are also many reports in the literature on aromatic substitution reactions of polystyrene. Only a few, however, are in industrial practice.

9.4.3.1 Reactions of Polystyrene

Photo chlorination of polystyrene involves replacement of hydrogens at the α and β positions [175, 176]. It was believed in the past that the chlorine atoms react preferentially at the α-position until the chlorine content of the product reaches 20% by weight. After that, it was thought that the chlorines are introduced into the other position. Later, however, this was contradicted [177]. In fact, when polystyrene is photo-chlorinated in carbon tetrachloride at low temperatures, like 13°C, it is substituted equally at both positions. At higher temperatures, like 78°C, substitutions at the β-position actually predominate [177].

Chlorinations of poly(*p*-methyl styrene) are somewhat more selective for the pendant methyl groups and result in di- and tri-substitutions at the *p*-methyl position. Only small amounts of chlorine are introduced into the polymer backbones [178]. Substitutions at the backbones, however, are possible with the use of SO_2Cl_2 as the chlorinating agent. In this case, half of the chlorines still replace the methyl hydrogens, but the other half replace hydrogens on the backbone.

Free radical additions of maleic anhydride to polystyrene backbones can be carried out with the help of either peroxides or ultraviolet light [164]. Approximately 2% of the anhydride can be introduced. If, however, the additions are carried out on α-brominated polystyrene, the anhydride content of the polymer can be raised to 15% [164]:



Note: the extra hydrogen shown above on the maleic anhydride moiety of the product presumably comes from chain transferring.

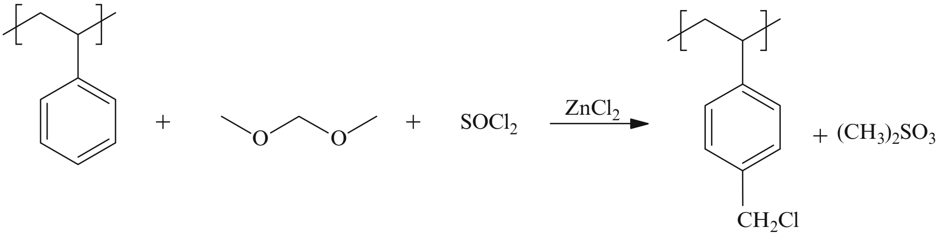
Bromination of polystyrene with *N*-bromosuccinimide and benzoyl peroxide in CCl_4 at room temperature can achieve a 61% conversion in 4 h. Considerable degradation, however, accompanies this reaction [180].

9.4.3.2 Chloromethylation Reactions

Chloromethylation reactions of the aromatic rings of polystyrene and styrene copolymers are being carried out extensively. Chlorodimethyl ether (a carcinogen) is a good solvent for these polymers. It is, therefore, commonly employed as the reagent [181, 182]. Laboratory preparations can be carried out in mixtures of carbon disulfide and ether, using zinc chloride as the catalyst. A 9-h reaction at room temperature yields 10% substitution [183]. The chloromethylation process [184] occurs in two steps. Benzyl methyl ether forms as an intermediate. Cross-linking reaction between the aromatic nuclei and the formed CH_2Cl group occurs as side reaction. There are strong indications that the chloromethylation takes place only at one position on the ring [185]. The same is true of bromomethylation [185].

Stannic chloride is a very effective catalyst for this Friedel-Craft reaction [186]. Iodomethylation can also be carried out in the same manner with similar results [179]. When the reactions are carried out on cross-linked styrene copolymers with chlorodimethyl ether and stannic chloride catalyst, they are accompanied by strong morphological changes [187]. If these reactions are carried out with low levels of chloromethylating agents or catalysts, they occur more or less homogeneously. Larger levels of either of them, however, result not only in greater levels of chloromethylation, but also in higher degrees of secondary cross-linkings and in uneven distributions of the chloromethyl groups [188].

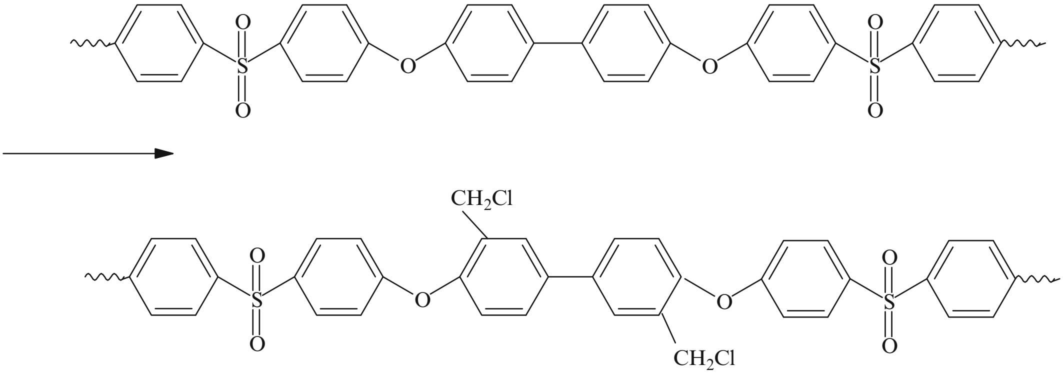
Another technique of chloromethylating polystyrene is to react it with methylal and thionyl chloride in the presence of zinc chloride [189]:



Chloromethyl-substituted polystyrenes can also be prepared from poly(*p*-methyl styrene)s by treating them with aqueous sodium hypochlorite in the presence of a phase transfer catalysts, like benzyltriethylammonium chloride [190]. The conversions of methyl to chloromethyl groups can be as high as 20% without any detectable morphological changes [187]. If these reactions are carried out with low levels of chloromethylating agents or catalysts, they occur more or less homogeneously. Larger levels of either of them, however, result not only in greater levels of chloromethylation, but also in higher degrees of secondary cross-linkings and in uneven distributions of the chloromethyl groups [188].

Another technique of chloromethylating polystyrene is to react it with methylal and thionyl chloride in the presence of zinc chloride [189].

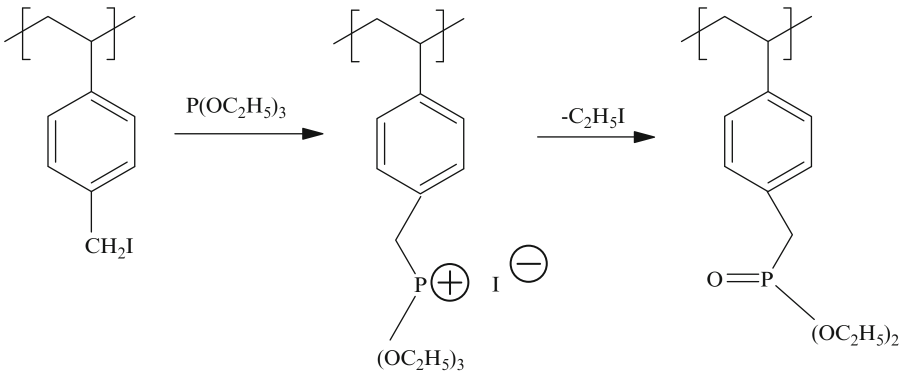
Techniques for chloromethylating polyarylether sulfones, polyphenylene oxide, phenolic resins, and model compounds were described recently [191]. When the subsequent products are converted to quaternary amines, there is a decrease in the quaternization rate with increase in degree of substitution. This may be due to steric effects imposed by restricted rotation of the polymeric chains [191]. This phenomenon was not observed in quaternization of poly(chloromethyl styrene). The chloromethylation reaction of a polysulfone with chloromethyl ether, catalyzed by stannic chloride, can be illustrated as follows:



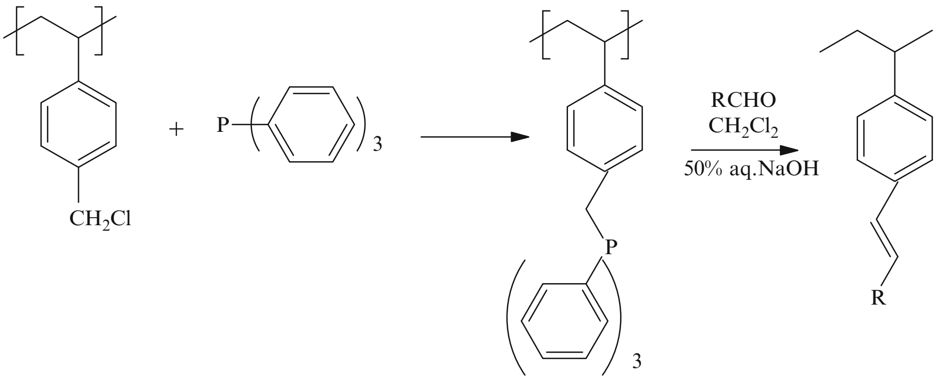
Vinyl benzyl chloride monomer is available commercially. It is possible, therefore, to simply prepare the chloromethylated polystyrene or copolymers from the monomer without the chloromethylation reactions.

9.4.3.3 Reactions of Halomethylated Polymers

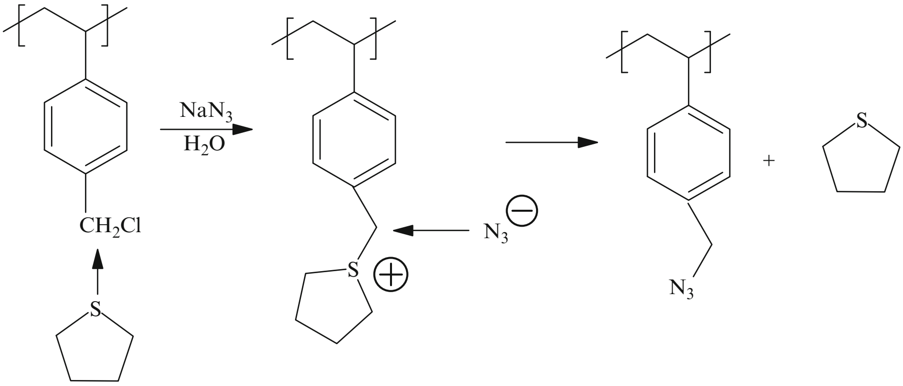
Many known reactions of the halomethyl groups on polymers are possible. One can, for instance, convert poly(chloromethyl styrene) to poly(hydroxymethyl styrene) [183]. Also, iodomethylated polystyrene can be treated with triethyl phosphite in order to carry out an *Arbuzov* reaction [192]:



Chloromethylated polystyrene can also be converted to a phosphonium salt for use in the *Wittig* reaction [193]:



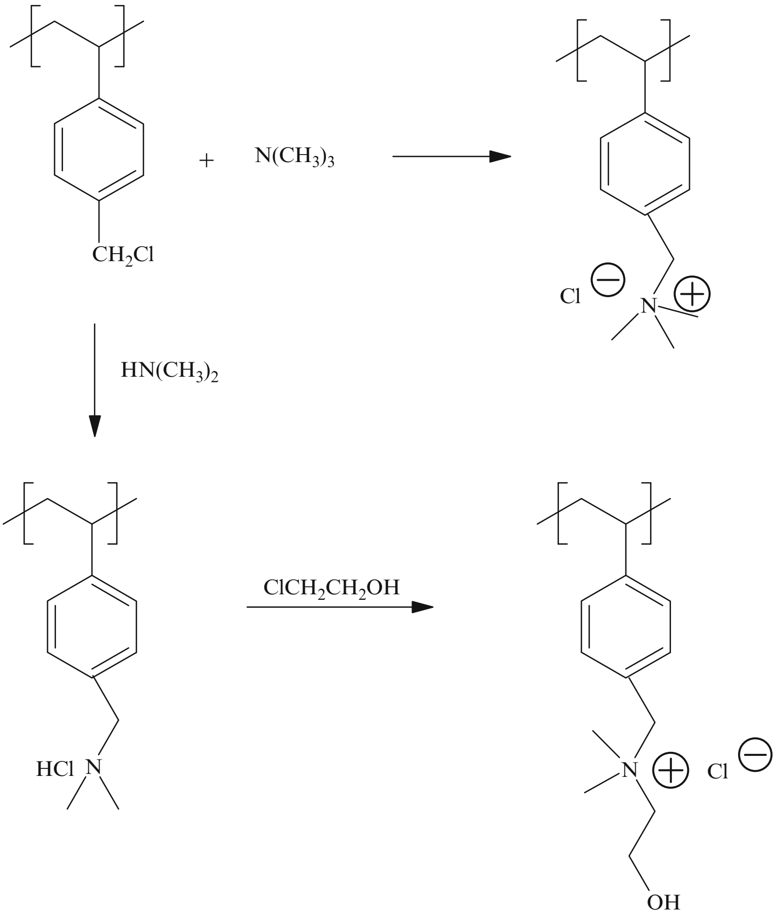
The product of a reaction of chloromethylated polystyrene and triphenylphosphine can also convert to nucleophiles [194]. In addition, use of a phase transfer catalyst converts soluble chloromethylated polystyrenes to phosphine oxides. Reactions with dioctylphosphine can serve as an example [195]. Sometimes phase transfer reactions are easier to carry out than conventional ones. This is the case with a Witting reaction. Both linear and cross-linked chloromethylated polystyrenes react smoothly with triphenylphosphine to give derivatives that react with various aldehydes [196, 197]. Phase transfer catalysts can also be used in carrying out nucleophilic substitutions with the aid of sulfides, like tetrahydrothiophine [198]:



When chloromethylated cross-linked polystyrene is reacted with potassium superoxide, the yield depends upon the type of solvent used. In dimethylsulfoxide, in the presence of 18-crown-6 ether, the conversion to hydroxymethyl groups is 45%. In benzene, however, it is only 25%. High conversions are obtained by catalyzing the reaction with tetrabutylammonium iodide in a mixture of solvents. This results in 85% conversions to hydroxymethyl groups, while the rest become iodide groups [199].

Quaternary salts are more effective than crown ethers in reactions with salts of oxygen-anions, such as carboxylate and phenolate [200]. On the other hand, lipophilic crown ethers, like dicyclohexyl-18-crown-6, exhibit higher catalytic activity than the quaternary salts in reactions with salts of the sulfur anions. Also, the catalytic activity of the phase transfer catalysts toward nitrogen anions is intermediate between that toward oxygen and that toward sulfur anions. Solid–liquid two-phase systems generally give higher degrees of conversion than do liquid–liquid systems. When, however, lipophilic phase transfer catalysts are used with lipophilic reagents, high degrees of substitutions are achieved in liquid–liquid two-phase systems [200].

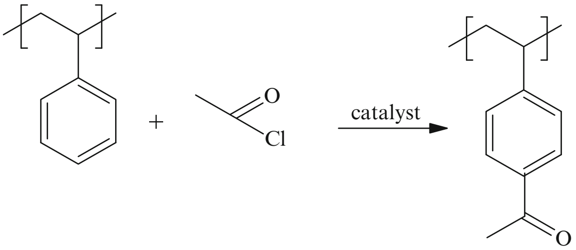
Conversion of chloromethylated styrene to anionic exchange resins is done commercially by amination reactions to form quaternary ammonium groups [201, 202]. This reaction can be illustrated as follows [203]:



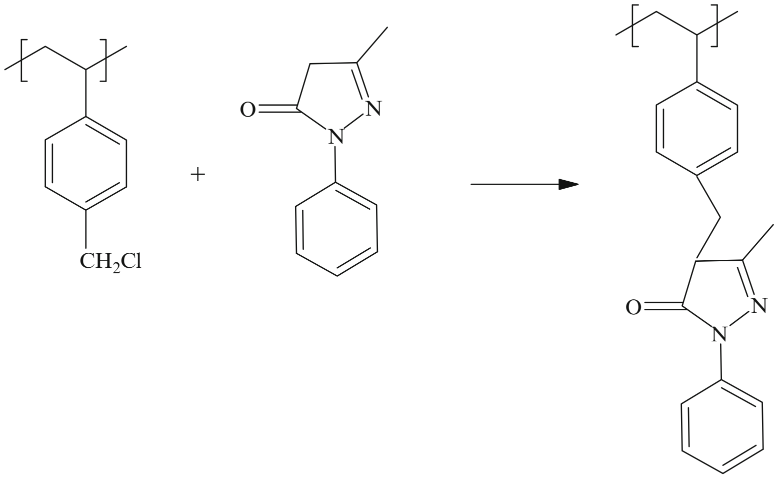
The kinetics of amination of chloromethylated polystyrene with monohydroxy dialkyl tertiary amines shows that the reactions proceed in two steps, at two different rates. The rate changes take place at conversions of 45–50% [205]. These rates are favorably influenced by increases in the dielectric constants of the solvents [204]. Two different rate constants also exist in reactions with 3-alkylaminopropionitrile.

9.4.3.4 Friedel-Craft Alkylation Reactions

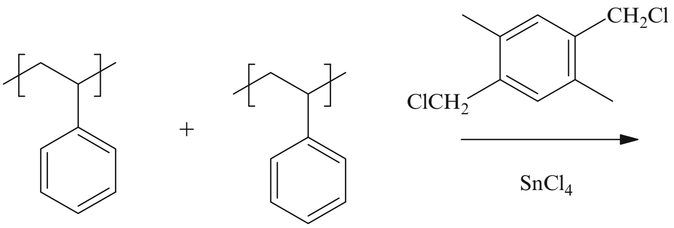
Friedel-Craft acylations of polystyrene can be carried out in CS_2 or in CCl_4 at reflux temperatures of the solvents. The yields are high [209]:

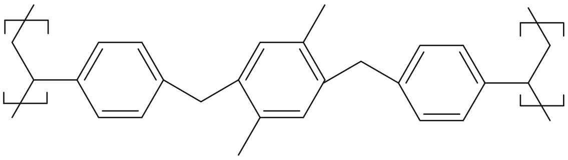


Chloromethylated copolymers of styrene with divinyl benzene undergo Friedel-Craft type reactions in condensations with 1-phenyl-3-methylpyrazolone or with 1-phenyl-2,3-dimethyl-pyrazolone-5 in the presence of either $ZnCl_2$, BF_3, or $SnCl_4$ [208]:



Polystyrene can also cross-link by a Friedel-Craft reaction [210]:





The above condensation takes place in dichloroethane, with stannic chloride catalyst at 50°C [210]. The maximum reaction rate varies with both, the initial concentration of 1,4-dimethyl-2,5-dichloromethylbenzene, shown above, and the initial concentration of $SnCl_4$. Cross-linked polystyrene particles, or beads also form by Friedel-Craft suspension cross-linking of polystyrene with 1,4-dichloromethyl-2,5 dimethyl-benzene [211]. The polymer is dissolved in nitrobenzene and a two-phase reaction occurs in 70% by weight of an aqueous suspension of $ZnCl_2$. Poly(vinyl alcohol) can be used as the suspending agent.

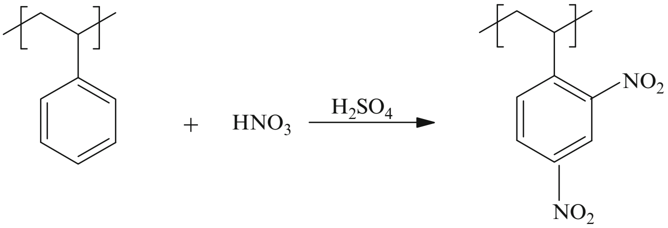
9.4.3.5 Sulfonation Reactions

Sulfonation reactions of polystyrene and its copolymers with divinyl benzene are carried out commercially to prepare ion exchange resins. Partial sulfonations of polystyrenes are achieved in the presence of ethers. When more than 50% of the aromatic rings are sulfonated, the polymers become water-soluble. At lesser amounts of sulfonation, 25–50%, the polymers are solvent-soluble [212, 213].

When polystyrene is sulfonated in chlorinated hydrocarbons with a complex of dioxane-SO_3, the polymer precipitates from solution at low concentrations [214, 215]. Complexes of ketones with SO_3 can also be used to sulfonate polystyrene in halogenated solvents [216]. The ratio of sulfonation is more favorable for poly(vinyl toluene) than it is for polystyrene at the same conditions [217]. Also, sulfur dioxide swells polystyrene. The polymer can be sulfonated in this medium with sulfur trioxide or with chlorosulfonic acid [218]. Polystyrene, sulfonated in CS_2 with aluminum chloride catalyst, is water-insoluble in a free acid form [219].

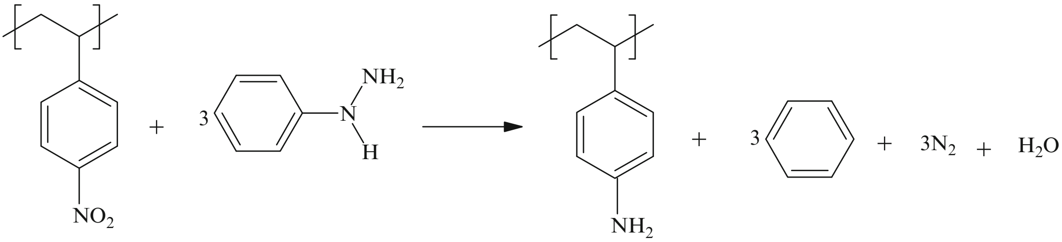
9.4.3.6 Nitration, Reduction, and Diazotization

Nitration of polystyrene was originally carried out a long time ago [220]. A nitrating mixture of nitric and sulfuric acids dissolves the polymer and a nitro derivative forms at 50°C within 3 h [221]:

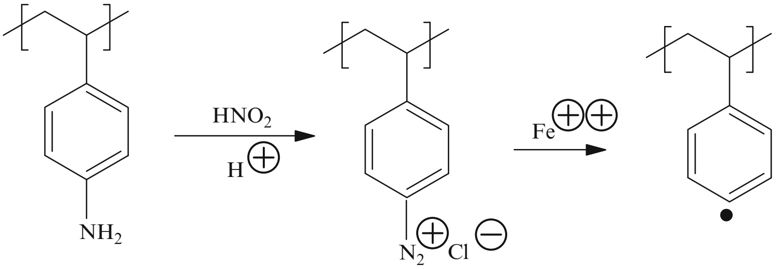


The reaction is accompanied by a loss of molecular weight. Nitration of isotactic polystyrene yields a more crystalline product (about 1.6 NO_2/ring) than the parent compound [222]. Here too, however, a loss in molecular weight accompanies the reaction [223]. Polystyrene can be nitrated under mild conditions using acetyl nitrate. The product contains approximately 0.6 nitro groups per each benzene ring [224].

The nitro groups of polynitrostyrene are reduced by phenyl hydrazine that acts as a hydrogen donor [225]:

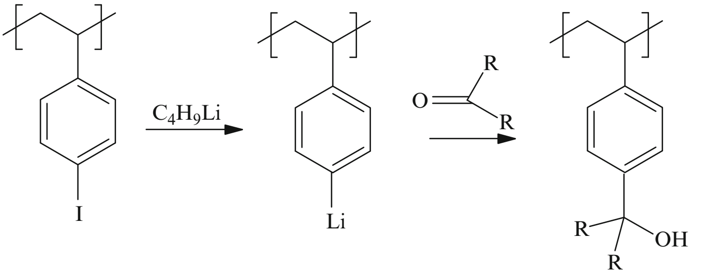


Polyaminostyrene can undergo typical reactions of aromatic amines, such as diazotization [226]. The diazonium salt decomposes with ferrous ions to yield polymeric free-radicals:

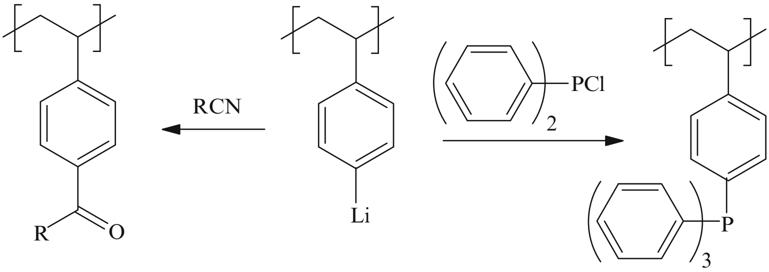


9.4.3.7 Metalation Reactions

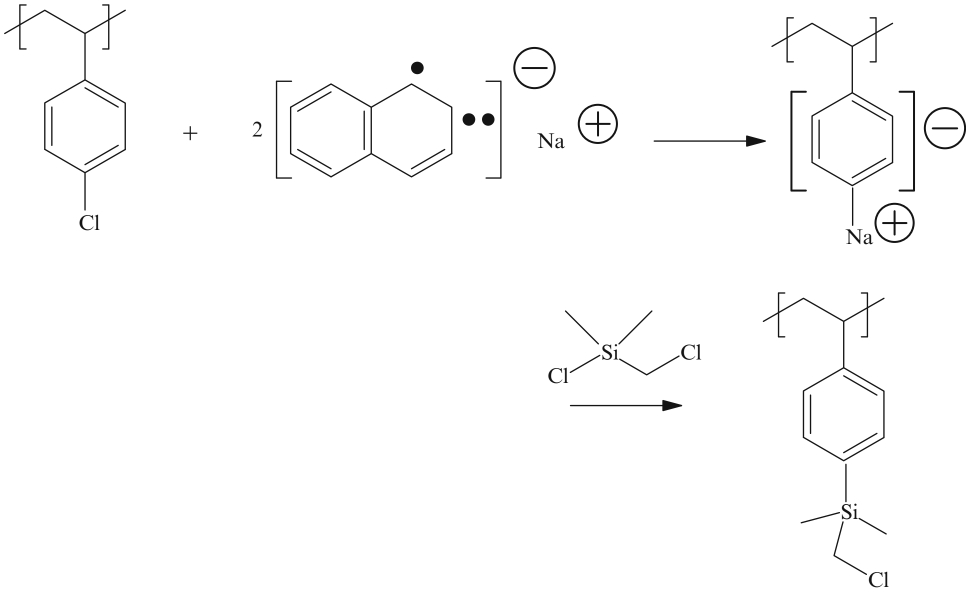
Functional polystyrene derivatives are starting materials for further reactions in many multistep syntheses. An example is a metalation of polystyrenes for use as intermediates [227]:



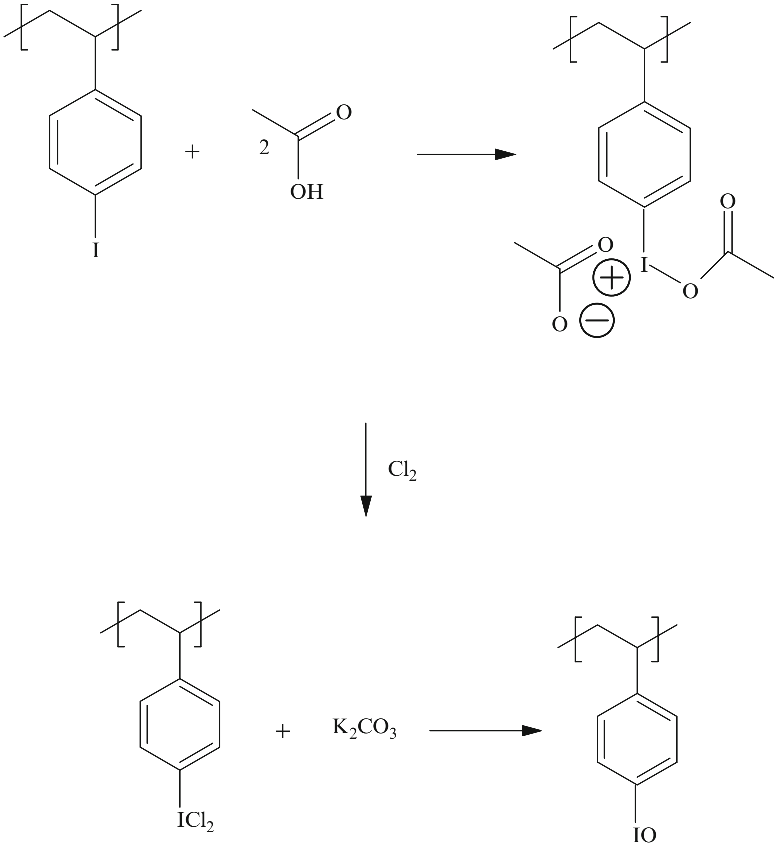
Some other reactions of lithiated polystyrene are [227]:



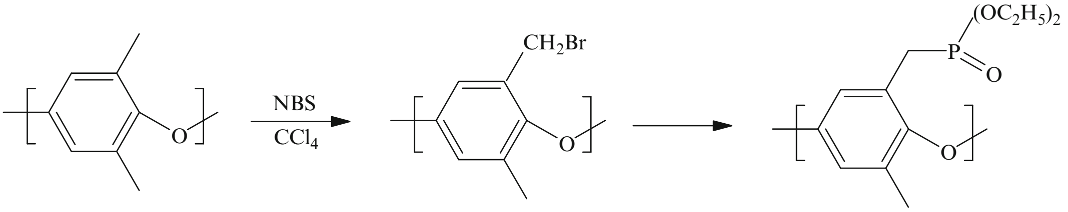
When polystyrenelithium is aminated by a reagent prepared from methoxyamine and methyllithium, two reaction mechanisms are possible. One may proceed via nitrene intermediates and the other one via electrophilic nitrenium ions [228]. Many other reactions of polystyrenelithium can be found in the literature [229–232]. Sodium metalated polystyrene reacts in a similar manner [228]:



Polyiodostyrene is a good starting material for many other reactions. Some of them are [233, 234]:



Poly(2,6-dimethyl-1,4-phenylene oxide) can be brominated with *N*-bromo-succinimide [235]. The product can also subsequently be used for further reactions [235], as, for instance, phosphorylation with triethyl phosphite:

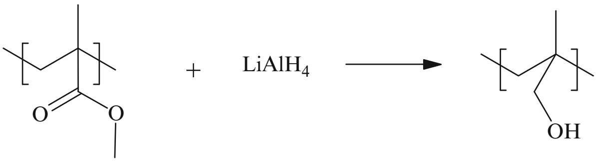


9.4.4 Reactions of Acrylic, Methacrylic, and Related Polymers

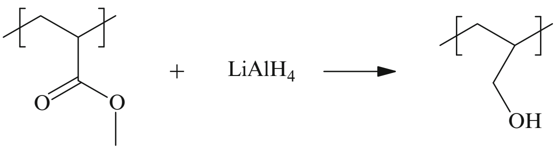
The functional groups of polymers from acrylic and methacrylic esters can undergo all the typical reactions of such groups. There are, therefore, numerous reports in the literature on such reactions.

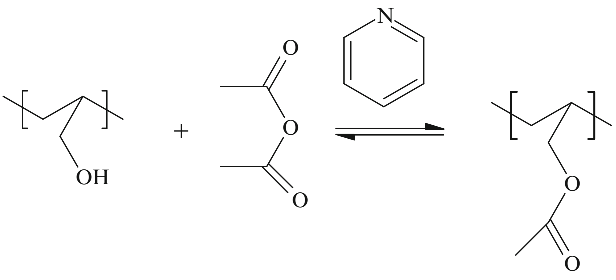
9.4.4.1 Reduction of the Ester Groups

Perhaps the most reported reactions of these polymers are *reductions* of the functional groups. Among them is the reaction with lithium aluminum hydride to reduce the ester groups. The success, however, depends upon the reaction medium. Poly(methyl methacrylate) can be reduced to poly(methallyl alcohol) in ether solvents [236]:



The results, however, are inconclusive, because combustion analyses fail to match the theoretical composition for poly(methallyl alcohol). It is impossible to tell to what extent the reduction takes place [236]. Inconclusive results are also obtained in similar reductions of poly(methyl acrylate) in mixtures of tetrahydrofuran and benzene. The product of such reduction is acetylated with acetic anhydride in pyridine [237] as follows:



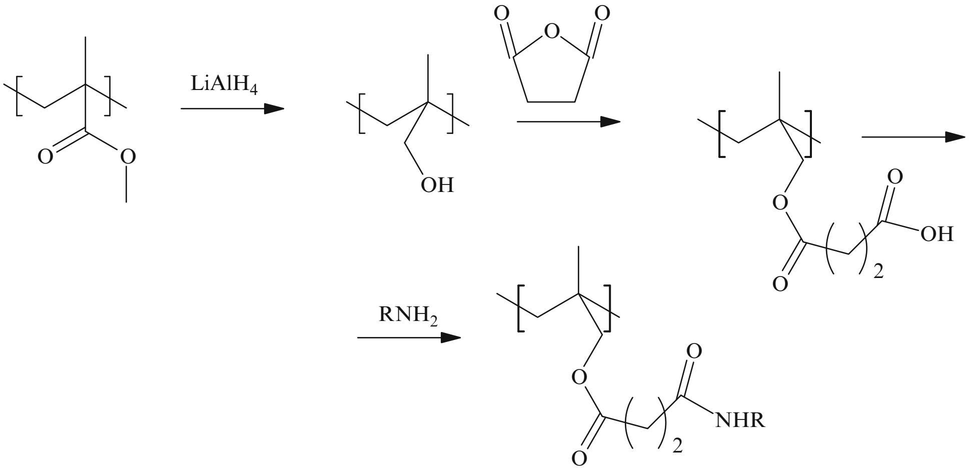


Hydrolysis in water of the product of acetylation, followed by treatment with hot *m*-cresol, and subsequent extraction with hydrochloric acid to remove the suspended inorganic matter [237], yields a material that is still only soluble in pyridine and *m*-cresol.

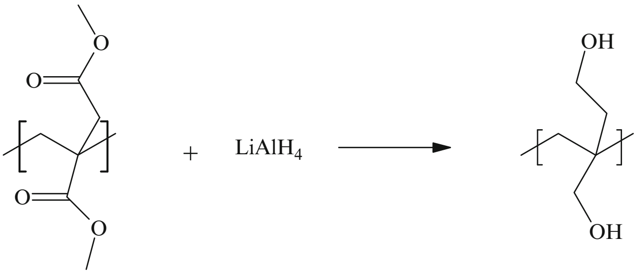
Somewhat similar results are obtained in reductions of high molecular weight poly(methyl acrylate) with lithium aluminum hydride [238] in tetrahydrofuran. The reaction yields a product that is only soluble in mixtures of hydrochloric acid with either methyl alcohol, dioxane, or tetrahydrofuran. The problem is apparently due to some residual aluminum that is hard to remove [239]. If, however, the reduction is carried out in a *N*-methylmorpholine solution, followed by addition of potassium tartrate, a pure product can be isolated [240]. *N*-methylmorpholine is a good solvent for reductions of various macromolecules with metal hydrides [236]. In addition, the solvent permits use of strong NaOH solutions to hydrolyze the addition complexes that form. Other polymers that can be reduced in it are those bearing nitrile, amide, imide, lactam, and oxime pendant groups. Reduction of polymethacrylonitrile, however, yields a product with only 70% of primary amine groups [241].

Complete reductions of pendant carbonyl groups with $LiAlH_4$ in solvents other than *N*-methylmorpholine, however, were reported. Thus, a copolymer of methyl vinyl ketone with styrene was fully reduced in tetrahydrofuran [242].

Reductions with metal hydrides are often preliminary steps for additional reactions. For instance, a product of $LiAlH_4$ reduction of syndiotactic poly(methyl methacrylate) can be reacted with succinic anhydride and then converted to an amide [243]:

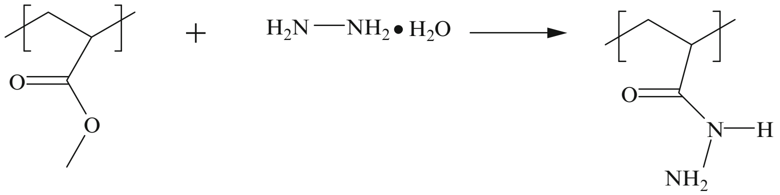


Substituted succinic anhydride can be used as well. When poly(dimethyl itaconate) is reduced with $LiAlH_4$ in THF, the product contains some ash, but 93% of the functional groups are reduced [239]:

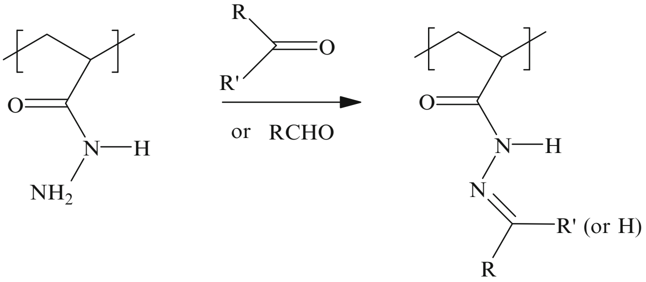


9.4.4.2 Nucleophilic and Electrophilic Substitutions

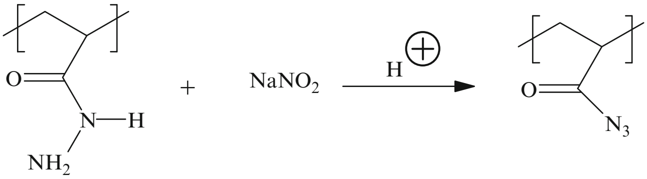
Many other conversions of functional groups of acrylic and methacrylic resins were reported. One of them is a conversion of methyl acrylate to a hydrazide by a direct reaction with hydrazine [244]:



The above reaction requires a 10:1 ratio of hydrazine to the ester groups. In the laboratory, it can be carried out on a steam bath over a period of 2–3 h. Approximately 60–80% of the ester groups convert [244]. The hydrazides can form various hydrazones through reactions with aldehydes and ketones:



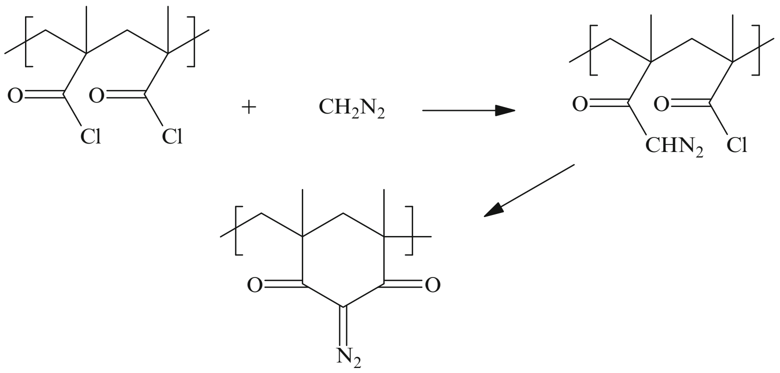
The hydrazide can also be converted to an azide [244]:



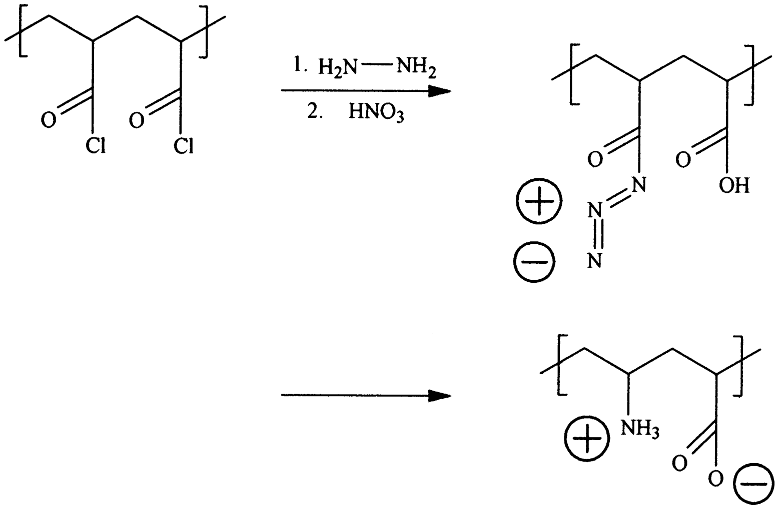
A *Hoffman reaction* of the azide yields a cross-linked polymer [244]. Syndiotactic poly(methyl methacrylate) converts to a hydrazide in a similar manner [245].

Nucleophilic substitution reactions can be carried out on poly(methyl methacrylate) with heterocyclic organolithium reagents [246]. The reactions are conducted in homogeneous solutions in tetrahydrofuran or in benzene combined with hexamethyl-phosphoramide. Copolymers will form with tautomeric keto-β-heterocyclic structures. Following heterocyclic reagents are useful [246]: 2-picolinyllithium, [(4,4-dimethyl-2-oxazole-2-yl)methyl]lithium, quinaldinyllithium, and [2-thiazole-2-yl-methyl]lithium.

In attempts to carry out *Arndt-Eister* reactions on poly(methacryloyl chloride), the polymer was reacted with diazomethane in various molar ratios and at different temperatures [247]. Initially, acid chloride groups do react with diazomethane as expected. The products, however, undergo subsequent reactions with neighboring acid chloride groups and form cyclic structures [247]:

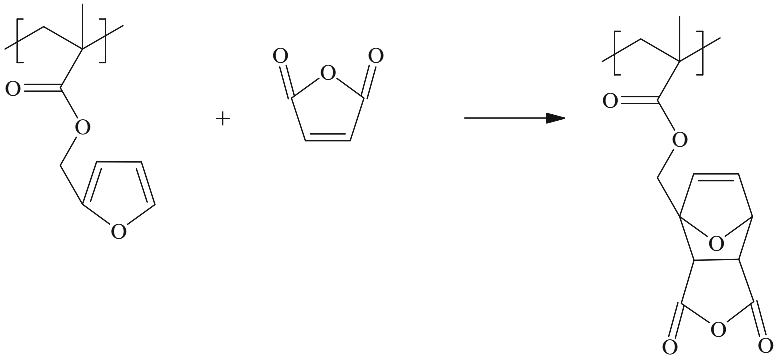


When *Curtius* and *Lossen* rearrangement reactions are attempted on poly(acryloyl chloride) [248], the products are fairly regular polyampholytes:



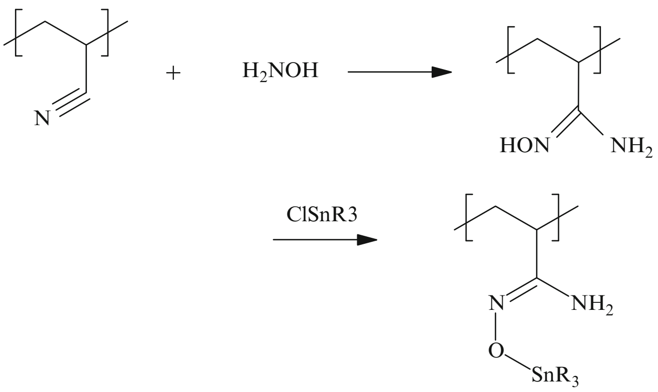
Somewhat similar results are obtained with a *Hoffman reaction* on polyacrylamide [279]. A *Schmidt reaction* on poly(acrylic acid) also yields mixed results [250]. When it is run in acetic acid, the intermolecular reactions appear to predominate over the intramolecular ones. Also, the products formed in acetic acid have higher nitrogen content that those formed in dioxane [250]. The NMR spectra show presence of some acid anhydride groups. This has an additional effect of lowering the yield.

Diels-Alder reactions can be carried out on poly(furfuryl methacrylate) with dienophiles like maleic anhydride or a maleimide [252]. Dilute solutions (10%) of the polymers in benzene can be used, requiring up to 30% molar excess of the dienophiles:



The additions take place at room temperature and the reactions take from 7 to 30 days [252] to complete.

Polyacrylonitrile reacts with hydroxylamine and the product can be metalated by elements from Group IV (Sn, Ge, and Si). This is a convenient route to formation of polymers with such pendant organometallic groups [253]:

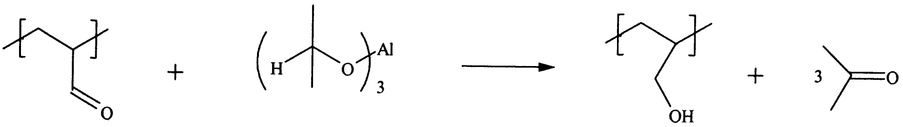


The yields are high when the reactions are carried out on dilute solutions of polyacrylonitrile in dimethylformamide at 75°C. The solutions must contain 1.5 mol each of hydroxylamine hydrochloride and sodium carbonate per mole of acrylonitrile groups [253].

A *Ritter* reaction can be carried out on atactic polyacrylonitrile with *N*-hydroxymethylamides of acetic, benzoic, and benzene-sulfonic acids [254]. When the same reactions are carried out with *N*-hydroxymethylimides of succinic or phthalic acids in tetramethylene sulfone, there is a stronger tendency toward cross-linking.

Copolymers of methacroyl chloride will undergo an *Arbuzov rearrangement* in reactions with triethyl phosphite in dimethylformamide, dioxane or benzene at 75°C [255]. The conversions are high, ranging between 96 and 98%.

The aldehyde groups of polyacrolein can be reduced by the *Meerwein-Ponndorf reaction*. There is a limit, however, to the amount of alcoholate that can be used and to the concentrations of free aldehyde groups in the starting material [256]. Also, ester condensations take place (*Tischenko* reaction) at the same time as the reductions occur [256].



9.4.5 Substitution Reactions of Poly(vinyl alcohol)

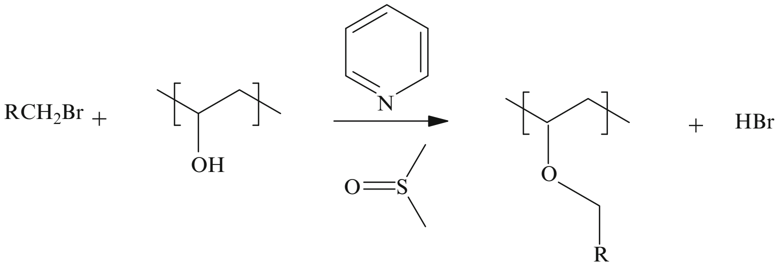
There are many practical uses for products from reactions of poly(vinyl alcohol). Among them are commercial preparations of poly(vinyl acetal)s formed through condensations with aldehydes. Two materials that are currently being marketed are poly(vinyl formal) and poly(vinyl butyral). The first one is formed from partially hydrolyzed poly(vinyl acetate) that is dissolved in aqueous acetic acid and excess formaldehyde. The mixture is heated, sulfuric acid is added, and the reaction is allowed to proceed at 70–90°C for 6 h. Sulfuric acid is then neutralized and the formal precipitates out.

Two different industrial processes are used for preparations of the butyral. In both of them, acetate free poly(vinyl alcohol) is used. In the first one, 10% solutions of the starting material are treated with butyraldehyde and sulfuric acid. The mixtures are heated to 90°C for 1½ h and the products precipitate. They are neutralized, washed, and dried. In the second one, poly(vinyl alcohol) is suspended in ethanol/ethyl acetate and butyraldehyde together with a strong mineral acid is added. The solutions are then neutralized. The butyrals separate out. They are neutralized and the resin are washed and dried.

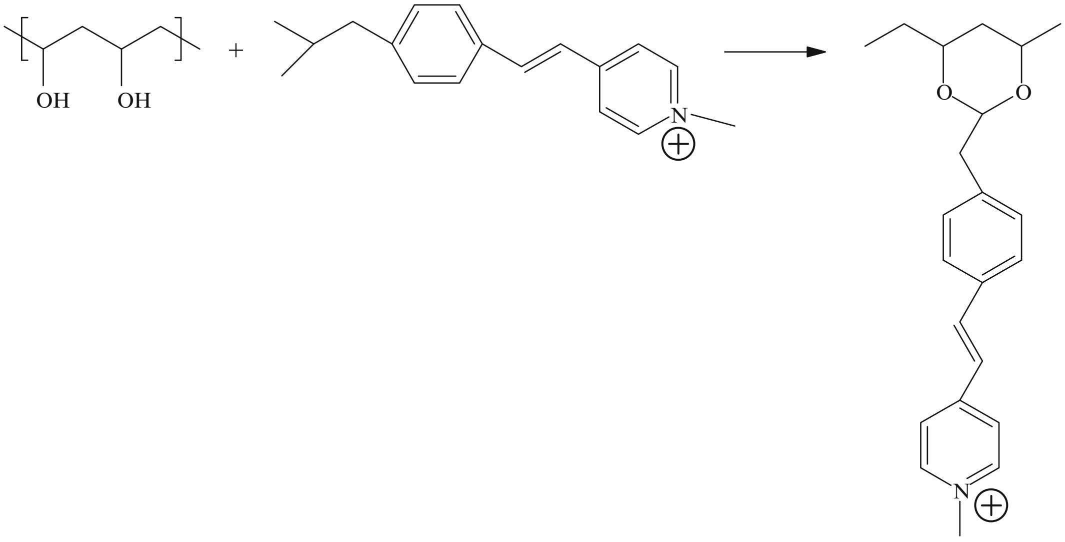
If poly(vinyl alcohol) films are reacted with formaldehyde in water containing salt and an acid catalyst (heterogeneous formalization), cross-linking occurs. The number of the cross-links increases with decreasing acid concentration and fixed amounts of formaldehyde and salt [257].

Direct reactions of poly(vinyl alcohol) with aldehydes in the *Kornblum reaction* result in formations of acetals that also contain residual hydroxyl group and often acetate groups. The acetate groups can be there from incomplete hydrolysis of the parent poly(vinyl acetate) that was used to form the poly(vinyl alcohol). Reactions of poly(vinyl alcohol) with ketones yield similar ketals. At present, no ketals are offered commercially.

Alkyl etherification of poly(vinyl alcohol) occurs when the polymer is combined with *n*-alkyl halides in dimethylsulfoxide combined with pyridine [258, 259]. It was suggested that the alkyl halides convert to aldehydes and acids and then act as intermediates in the dimethylsulfoxide-pyridine solution [258, 259]:



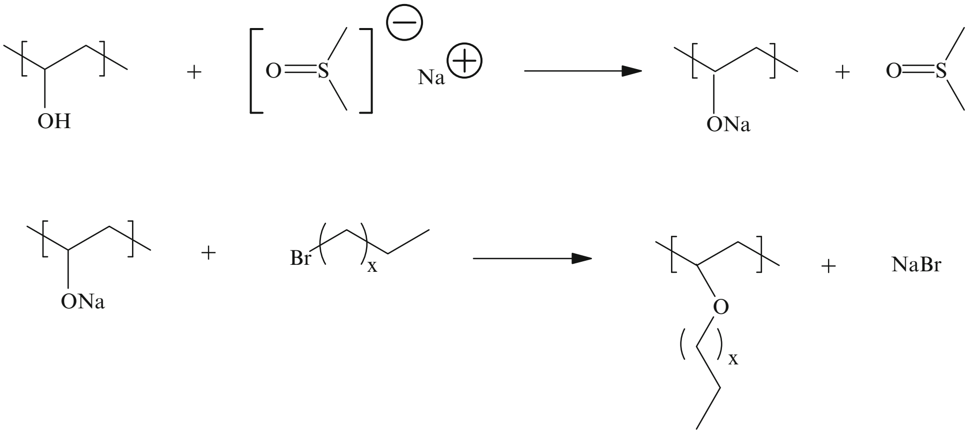
Many modifications of poly(vinyl alcohol) were carried out to form photosensitive materials. Thus, unsaturation was introduced into the pendant groups for photocross-linking. One example is a condensation with pyridinium and quinolinium salts [260]:



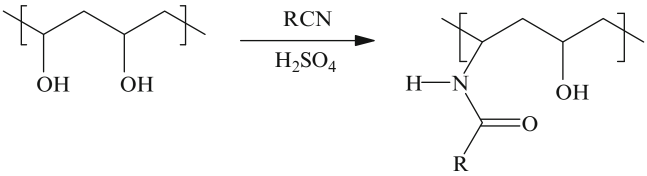
The material cyclodimerizes on exposure to light [261] (see Chap. 10 for additional discussion of this subject).

Schotten-Baumann esterifications of poly(vinyl alcohol) are used extensively in preparations of various derivatives. The reactions appear to proceed well when acid chlorides are employed in two-phase systems [262]. The polymers are dissolved in water and the solutions are blended in 1:1:1 equal volume with NaOH solutions and cyclohexanone. They are then mixed thoroughly with solutions of the acid chlorides in mixtures of cyclohexanone and toluene. The reaction mixture is stirred vigorously for about 90 min at −5 to 5°C to obtain the desired product.

Metalation of poly(vinyl alcohol) is used to form ether derivatives [263]:



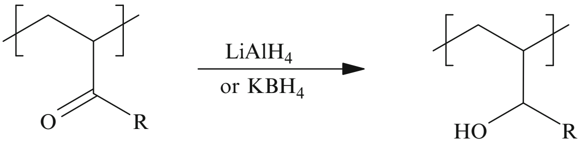
The *Ritter reaction* on poly(vinyl alcohol) yields soluble products. Only some of the hydroxyl groups, however, are converted to amide structures [264]:



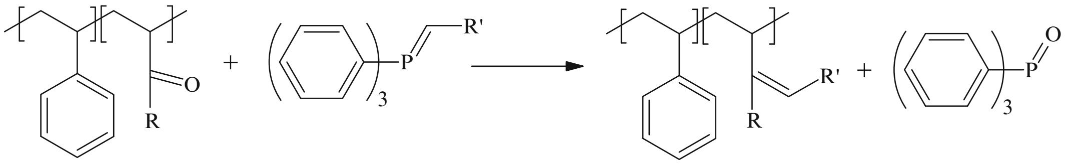
Also, it is possible that neighboring group interactions may lead to cyclizations and formations of 1,3-oxazines [264].

9.4.6 Miscellaneous Exchange Reactions

Many miscellaneous exchange reactions are reported in the literature. A few are presented here. One such reaction is reduction of pendant carbonyl groups of poly(vinyl methyl ketone) with metal hydrides [242, 265]:

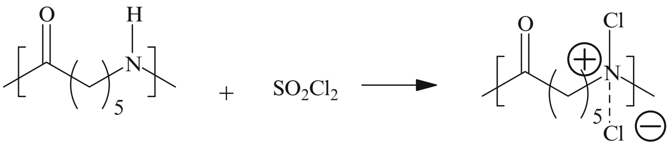


Another one is introduction of unsaturation into pendant groups by a Wittig reaction on pendant carbonyls [266]:

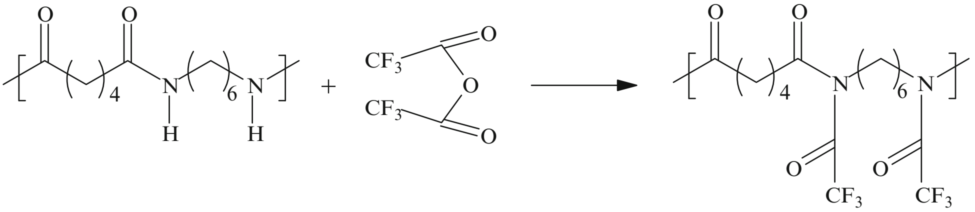


The same reaction can also be carried out on a copolymer of ethylene and carbon monoxide [266].

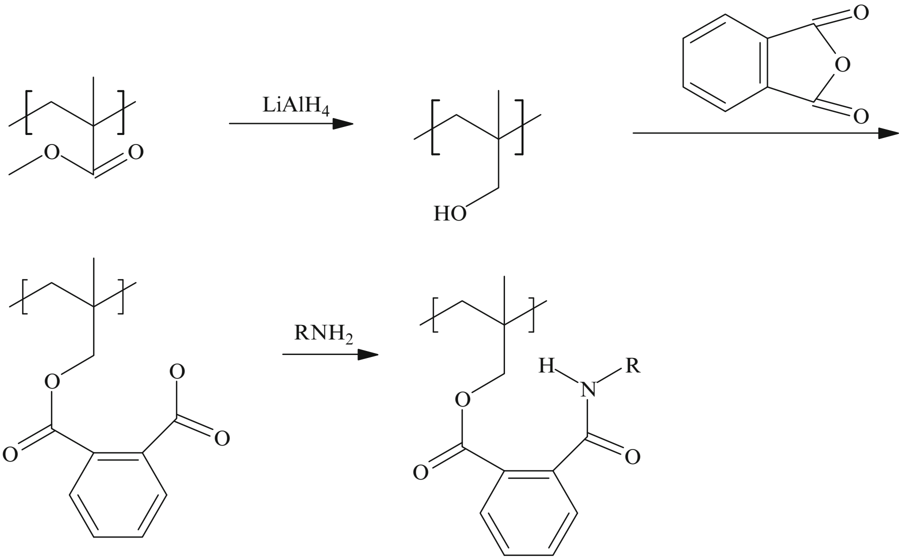
Polycaprolactam can be treated with either SO_2Cl_2, $POCl_3$, or PCl_5 at 70°C to introduce ionic chlorine groups [267]. The main product is poly(α,α-dichloro-caprolactam):



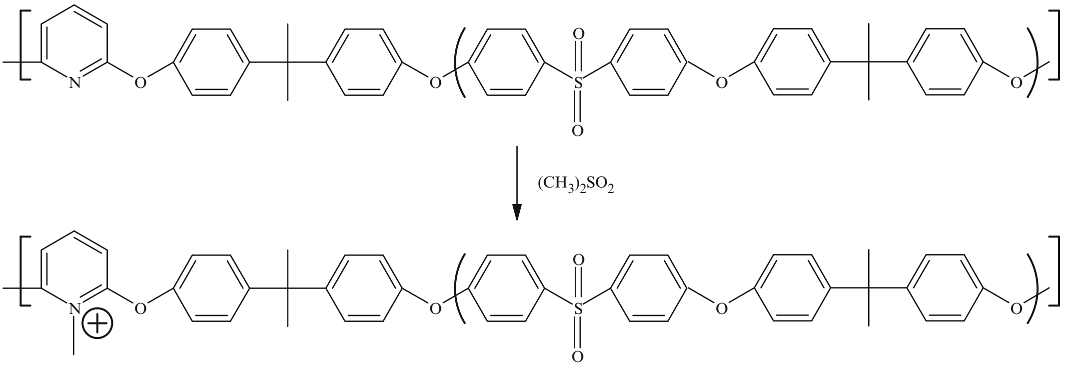
Also, when Nylon 6,6 is reacted with trifluoroacetic anhydride, trifluoroacetyl nylon forms [268]:



Syndiotactic poly(2-methallyl hydrogen phthalate) can be prepared and amidated according to the following scheme [269]:

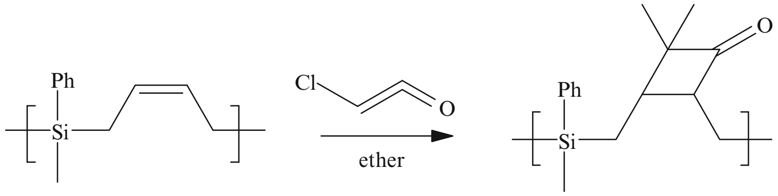


poly(pyridine ether sulfone)s in nitrobenzene [70]. The reaction can be illustrated as follows:



A 20% mol excess of the alkylating reagent is required and the reaction must be conducted for 6 h at 80°C.

Dichloroketene, generated by the ultrasound-promoted dechlorination reaction of thrichloroacetyl chloride with zinc, adds to the carbon–carbon double bonds of poly(methyl-1-phenyl-1-silane-*cis*-pent-3-ene) [271]. This can be illustrated as follows:

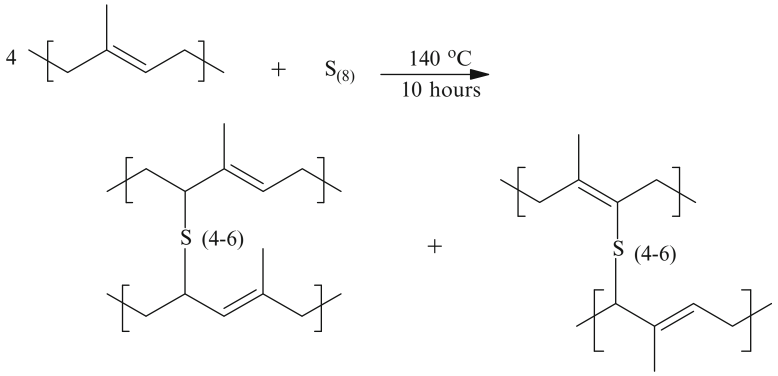


9.5 Cross-linking Reactions of Polymers

These reactions are quite numerous and have been utilized for a long time. They also include all thermosetting processes of polymers. Many are discussed in previous chapters.

9.5.1 Vulcanization of Elastomers

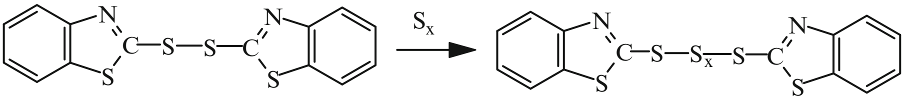
Cross-linking of natural rubber was discovered by Goodyear back in 1839. Sulfur, which was the original cross-linking agent, is still utilized today in many processes. Early studies demonstrated that the cross-links are mainly polysulfides:



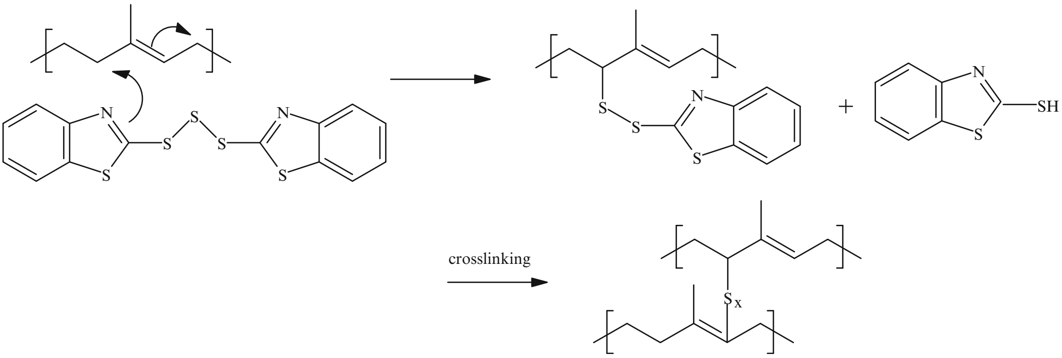
The reactions take place at all temperatures, but industrially they are carried out from 50 to 75°C and above. At lower temperatures, however, the process may take days to complete. At temperatures of 135–155°C, approximately 8% of sulfur (by weight of rubber) reacts [272]. Also, sulfur dissolves in unvulcanized rubber even at room temperature. The overall mechanism of the reaction is still being studied. Most evidence points to an ionic mechanism and a sulfonium ion intermediate [272]. It was shown [273] that a straightforward reaction of sulfur with rubber is insufficient. Somehow, between 40 and 100 atoms of sulfur must be combined in order to obtain one cross-link. Out of 40–100 atoms, only 6–10 are actually engaged in the formation of the cross-links. The rest of the atoms form cyclic sulfide units that become spread along the main chain [273].

To improve the efficiency of the vulcanization reaction, various accelerators were developed. Among them are zinc oxide combined with fatty acids, and/or amines. Zinc oxide forms zinc mercaptides like $(XS)_2ZnL_2$ where X is an electron withdrawing substituent and L is a ligand from a carboxyl or an amine group. The function of the ligand is to render the complex soluble. The mercaptide complexes are believed to react with additional sulfur to form zinc perthiomercaptides.

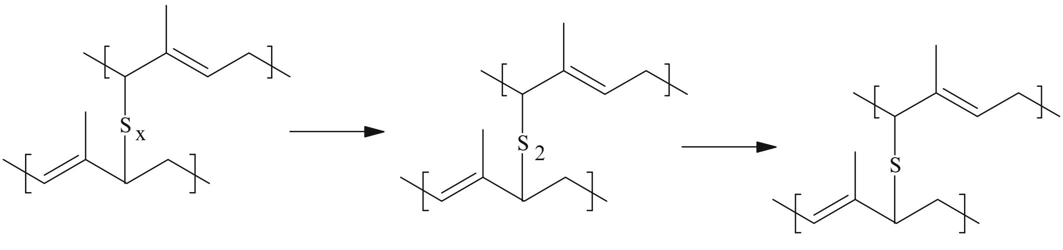
The accelerators that are most commonly used are derivatives of 2-mercaptobenzothiazole. They are very effective when used in combinations of metal oxides with fatty acids (referred to as *activators*). The favorite activators are zinc oxide combined with stearic acid. The combinations permit rapid vulcanizations that take minutes compared to hours when sulfur is used alone. In the process of vulcanization, 2,2′-dithiobisbenzthiazole forms initially and then reacts with sulfur to form polysulfides [273]:



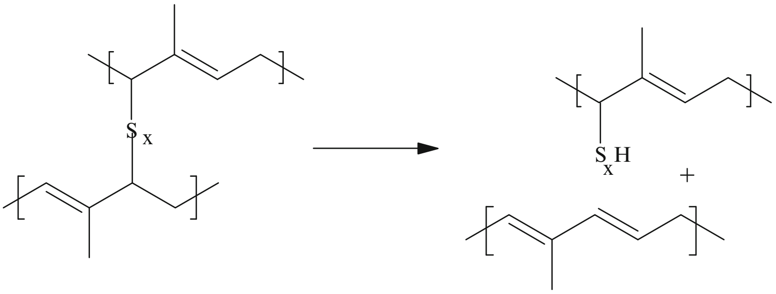
The products from reactions with sulfur in turn react with natural or synthetic rubber at any allylic hydrogen. This is a concerted reaction that results in formation of sulfur containing adducts of the polymers:



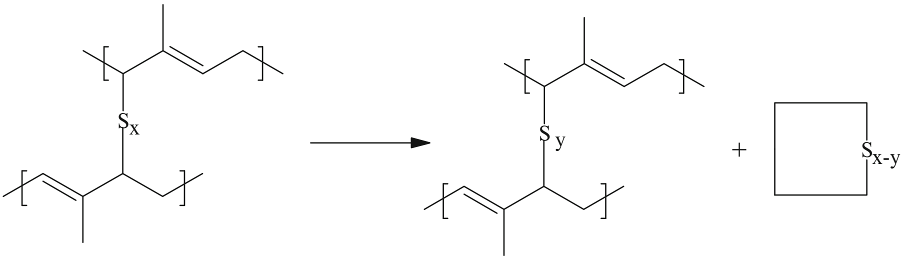
Once the cross-links are formed, further transformations take place. Some of them consist of reactions that shorten the polysulfide links:



Also, some cross-links are lost through elimination reactions:

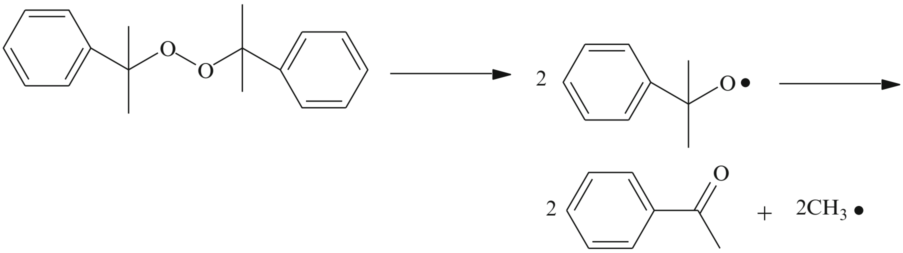


In addition, some cyclic sulfur compounds form in the process [273]:

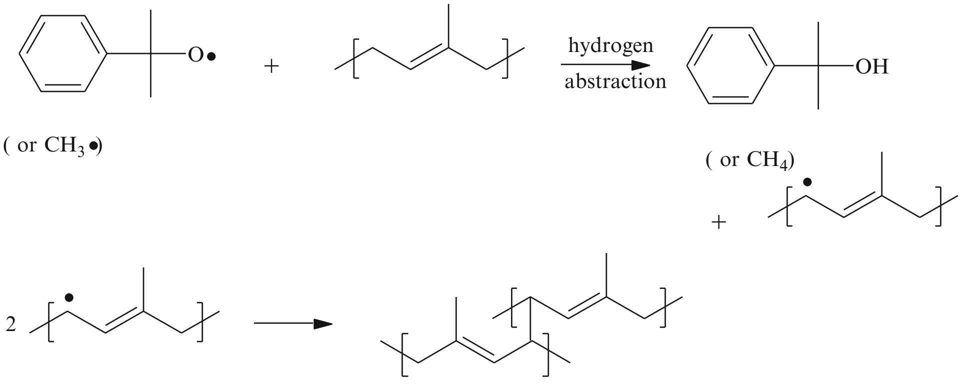


9.5.2 *Cross-linking of Polymers with the Aid of Peroxides*

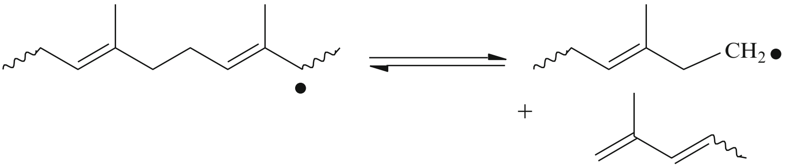
The reaction can be utilized with many polymers such as polyolefins, polymers of dienes, and others. The reactions with natural rubber can be illustrated as



follows [274]:



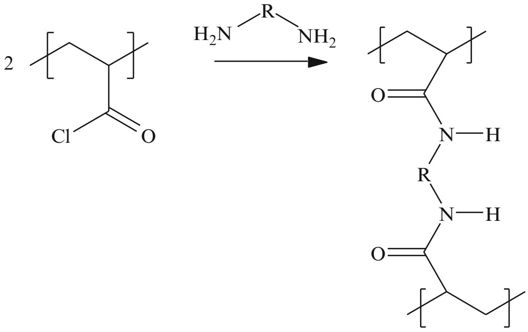
The extent of the cross-linking, as shown above, is not clear. It is known, however, that cleavage reactions that are followed by free-radical recombinations can take place [274]:



Polymeric chains bearing free radicals combine with each other to give branched structures. Additions of chains with freeradical to double bonds result in formations of cross-links [274].

9.5.3 Miscellaneous Cross-linking Reactions of Polymers

Many other miscellaneous cross-linkings of polymeric materials are reported in the literature. For instance, poly(acryloyl chloride) can be cross-linked with diamines [275]:



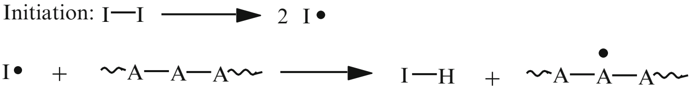
In a similar manner, polymers with pendant chlorosulfonate groups cross-link when reacted with diamines or with glycols [275].

9.6 Graft Copolymers

This is an important part of polymer syntheses that is used in many industrial processes. In 1967, Battaerd and Tregear [282] published a book on the subject that contains 1,000 references to journal publications and 1,200 references to patents. In addition, there are several monographs and many review papers [283]. The synthetic methods developed to date range from using free radical attacks on polymeric backbones to highly refined ionic reactions. There are examples where these ionic reactions attach the side-chains at well-designated locations.

9.6.1 Free-Radical Grafting by Chain-Transferring Process

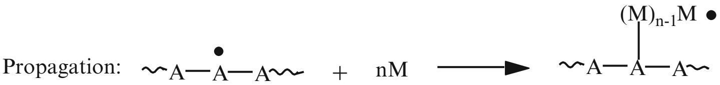
This technique is probably one of the simplest ways to form graft copolymers. It consists of carrying out free-radical polymerizations of monomers in the presence of polymers preformed from different monomers. A prerequisite for this synthesis is that the active sites must form on the polymeric backbones during the course of the reactions. Ideally, this occurs if the steps of initiations consist only of attacks by the initiating radicals on the backbones:



$$\text{Initiation: } I{-}I \longrightarrow 2\ I\bullet$$

$$I\bullet + \sim A{-}A{-}A\sim \longrightarrow I{-}H + \sim A{-}\overset{\bullet}{A}{-}A\sim$$

Propagations then precede from the backbone sites:



$$\text{Propagation: } \sim A{-}\overset{\bullet}{A}{-}A\sim + nM \longrightarrow \sim A{-}\overset{(M)_{n-1}M\bullet}{\overset{|}{A}}{-}A\sim$$

Terminations can take place in many ways. Of course, termination by combination will lead to cross-linked insoluble polymers and that is undesirable. An ideal termination takes place by chain transferring to another site on a polymer backbone to initiate another chain growth.

The above, however, is an ideal picture. In reality, the efficiency of grafting by this technique depends upon the following:

1. Competitions between the different materials present in the reaction mixture, such as monomer, solvent, and polymer backbone for the radical species. This includes competition between chains growth and chain transferring to any other species present.
2. Competition between the terminating processes, such as disproportionation and chain transferring.

The conditions can vary considerably and it is possible to carry out the reactions in bulk, solution, or in emulsion. When the reaction take place in emulsion, the success depends greatly on experimental techniques. The rate of diffusion is a factor and anything that affects this rate must be considered. Because grafting efficiency depends upon chain transferring to the backbone, knowledge of the chain-transferring constants can help predict the outcome of the reactions. Sometimes, the information on the chain-transferring constants is not available from the literature. It may, however, be possible to obtain the information from reactions of low molecular weight compounds with similar structures [284–286]. One assumes equal reactivity toward attacking radicals. The validity of such an assumption was demonstrated on oligomers [281–283].

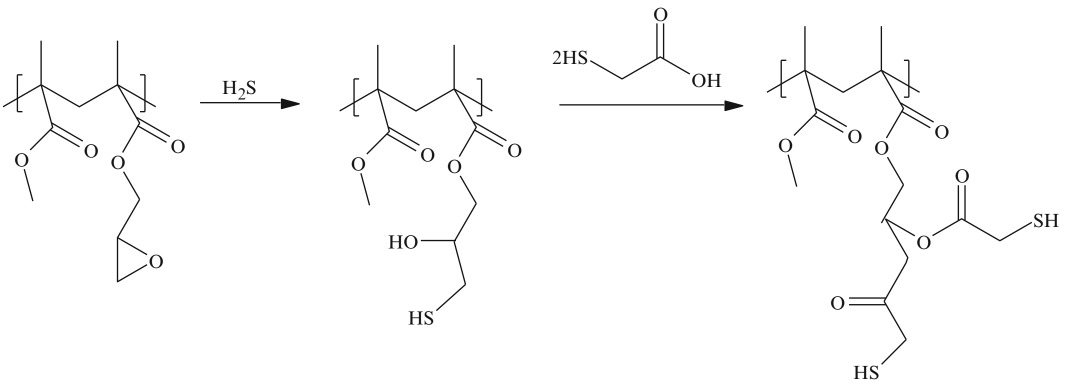
The reactivity of the initiating radicals toward the backbones can vary and this can also vary the efficiency of grafting. Benzoyl peroxide-initiated polymerizations of methyl methacrylate monomer, for instance, in the presence of polystyrene [284] yield appreciable quantities of graft copolymers. Very little graft copolymers, however, form when di-*t*-butyl peroxide initiates the same reactions. Azobisisobutyronitrile also fails to yield appreciable quantities of graft copolymers. This is due to very inefficient chain transferring to the polymer backbones by *t*-butoxy and isobutyronitrile radicals.

A better approach is work by Chung and coworkers [288] who grafted maleic anhydride to polypropylene with the use of Borane/O_2 initiator. This initiator is claimed to form in situ a monooxidized adduct (R–O* *O–BR_2). These adducts then carry out hydrogen abstractions from the polypropylene chains at ambient temperature. This results in formation of stable tertiary polymer radicals that react with maleic anhydride to form graft copolymers:

Not all chain transferring to the backbones results in formations of graft copolymers. An example is polymerization of vinyl acetate in the presence of poly(methyl methacrylate). No graft copolymers form and this is independent of the reactivity of the initiators [285]. In fact, grafts of poly(vinyl acetate) to poly(methyl methacrylate) and to polystyrene cannot be prepared by this technique [286].

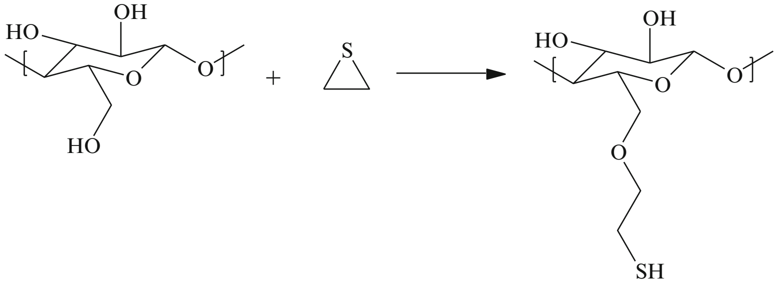
Grafting efficiency may increase with temperature [287]. This could be due to higher activation energy of the transfer reaction than that of the propagation reaction [288]. Meaningful effects of temperature, however, are not always observed. In grafting polystyrene to poly(butyl acrylate) in emulsion, for instance, there is no noticeable difference between 60 and 90°C by this technique [289].

The presence of sites with high transfer constants on the polymeric backbone enhances the efficiency of grafting. Such sites can be introduced deliberately. These can, for instance, be mercaptan groups [290] that can be formed by reacting H_2S with a polymer containing epoxy groups:



Free-radical polymerizations of acrylic and methacrylic esters in the presence of the above backbones result in high yield of graft copolymers [291, 292].

Another example is formation of mercaptan groups on cellulose in order to form graft copolymers [293]:



Pendant nitro groups are also effective in chain transfer grafting reactions. Thus, graft copolymers of polystyrene with cellulose acetate *p*-nitrobenzoate [294] and with poly(vinyl *p*-nitrobenzoate) [295] form readily. Nitro groups appear to be more effective in formations of graft copolymers by radical mechanism than are double bonds located as pendant groups [294].

9.6.2 Free-Radical Grafting Reactions to Polymers with Double Bonds

Carbon to carbon double bonds, either in the backbone or in the pendant groups, are potential sites for free-radical attacks. In addition to the double bonds, the hydrogen atoms on the neighboring carbons are allylic and potential sites for chain transferring. Because rubbers, natural and synthetic, possess such unsaturations, they are used extensively as backbones for various grafting reactions. Whether the reactivity of the initiating radical is important in determining grafting efficiency is not completely established. Graft copolymers of poly(methyl methacrylate) on gutta-percha, however, form in good yields when the initiator is benzoyl peroxide [296, 297]. Yet, when azobisisobutyronitrile is used, only a mixture of homopolymers forms. Work with ^{14}C-labeled initiators shows that the primary radicals react both by addition to the double bonds and by transfer to the methylene group [298].

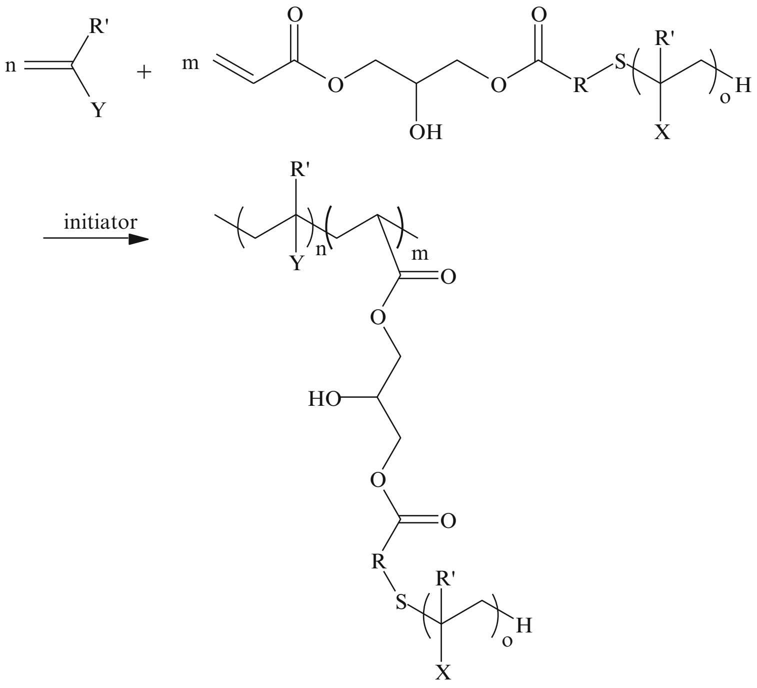
Grafting reactions to polybutadiene, however, proceed via chain transferring from the growing chain radical to the backbone [299]. Nevertheless, strong evidence also shows that the initiator radicals can interact directly with polymeric backbones [299, 300].

When graft copolymers of polystyrene to natural rubber form, the chain length of the attached branches equals to the chain lengths of the unattached polystyrene homopolymer that forms simultaneously [301]. This led to the following conclusions [303]:

1. As the concentration of rubber increases, the length of the grafted branches diminishes, while their number remains the same.
2. When the concentration of the initiator increases, the length of the branches diminishes, but the number of branches increases.
3. When the concentration of monomers increases, the length of the branches also increases, but their number diminishes.
4. When the polymerization time increases, the length of the branches remains the same, but their number increases.

9.6.3 Preparation of Graft Copolymers with the Aid of Macromonomers

The chain-transferring methods for preparing graft copolymers suffer from the disadvantages of low efficiency and contamination by homopolymers. The efficiency in forming graft copolymers, however, increases with the use of *macromonomers*. A macromonomer is a macromolecular monomer, an oligomer, or a polymer with a polymerizable end group. When macromonomers are copolymerized with other monomers, comb-shaped polymers form [302, 303]. The copolymerizations can be free radical or ionic in mechanism. Some examples of macromonomers are presented in Table 9.1. A preparation of graft copolymers with the aid of macromonomers can be illustrated as follows [304]:



Many variations on the above technique are possible.

Table 9.1 Some macromonomers reported in the literature

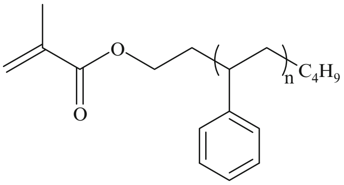
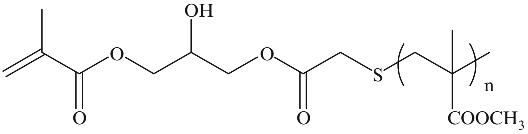
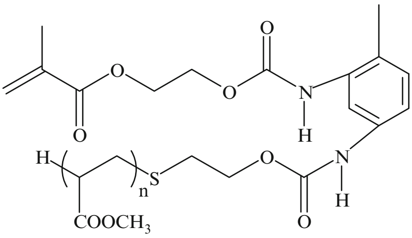
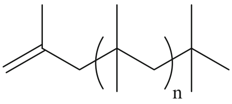
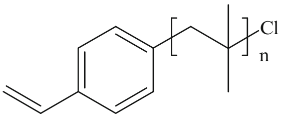
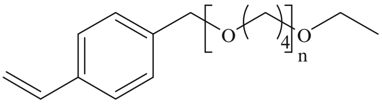
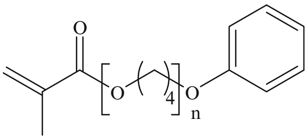
Macromonomer	References
	[320]
	[321]
	[322]
	[323]
	[324]
	[325]
	[326]

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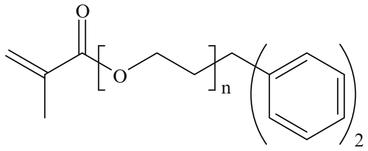
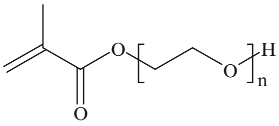
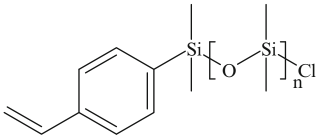
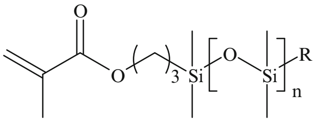
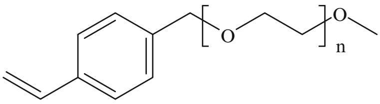
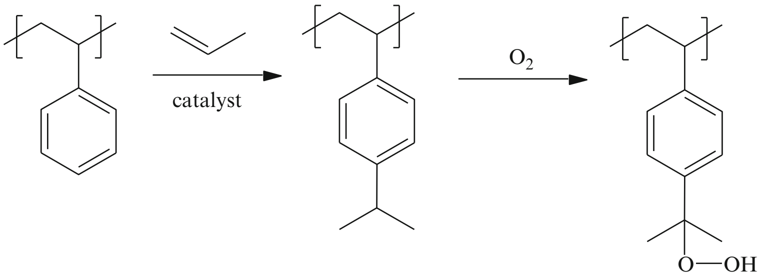
Table 9.1 (continued)

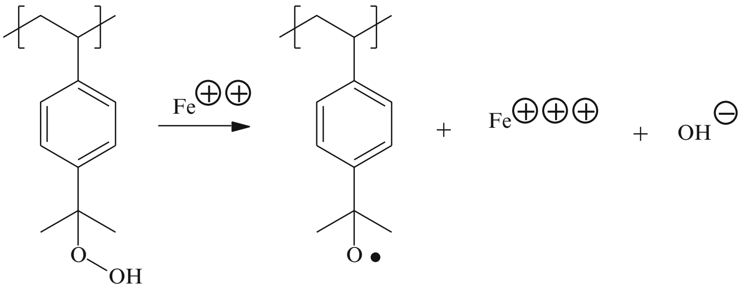
Macromonomer	References
	[327]
	[328]
	[329]
	[330]
	[331]

9.6.4 *Initiations of Polymerizations from the Backbone of Polymers*

High degrees of grafting by free-radical mechanism can be attained when polymerizations are initiated from the backbones of the polymer. One way this can be done is to form peroxides on the backbone structures. Decompositions of such peroxides can yield initiating radicals. Half of them will be attached to the backbones. An example is preparation of graft copolymers of polystyrene [305, 306]:



Thermal cleavage of the above peroxides leads to both macromolecules with free-radicals sites. Hydroxyl radicals also form and initiate formations of homopolymers. Decompositions of the peroxides by redox mechanisms, however, increase the yields of graft copolymers, but do not stop all formations of hydroxy radicals [303]:



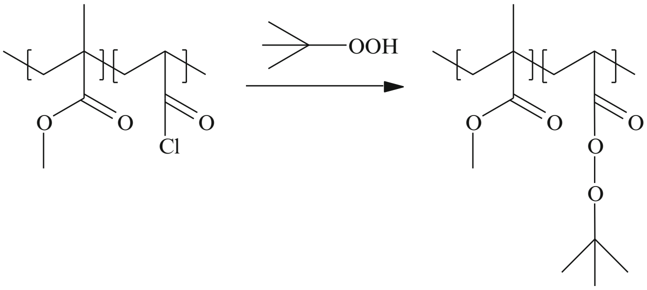
Some homopolymers still form [307].

Air oxidation of polypropylene can result in formation of hydroperoxide units at the sites of the tertiary hydrogens [383]. The polymer can also be oxidized when dissolved in cumene that contains some cumene hydroperoxide at 70–80°C. A product containing 0.8% oxygen by weight as a hydroperoxide [308] can be formed and can subsequently be reacted to form graft copolymers. Various monomers [309–311] can be used, such as vinyl acetate or 2-vinyl pyrrolidone.

Many other hydroperoxidations of polymers were reported in the literature. The materials are used in formations of graft copolymers. One example is hydroperoxidation of poly(ethylene terephthalate) and poly(ε-caproamide). The products yield graft copolymers with various acrylic and methacrylic esters and acrylic and methacrylic acids [312–314].

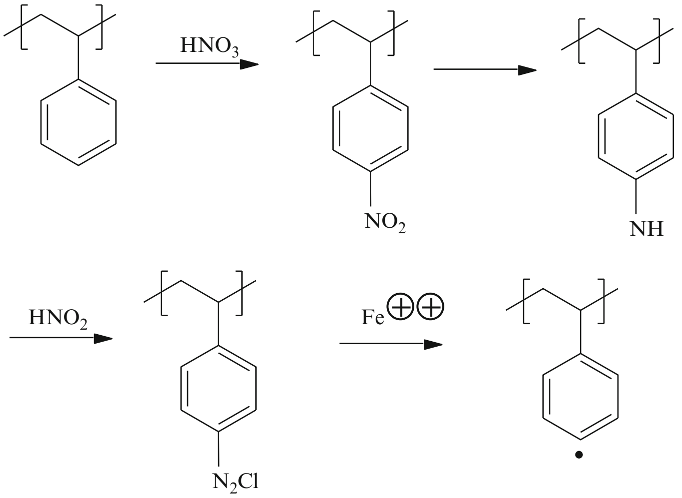
Ozone treatment of polymers can also cause hydroperoxidation of labile hydrogens. It can, however, also cause extensive degradation of the backbone polymers, because attacks by ozone on double bonds in the backbones convert them to unstable ozonides. Starch can be ozonized to form graft copolymers [315, 316]. The same is true of cellulose [317], poly(vinyl chloride) [318], and polyethylene [319]. Hydroperoxides form without noticeable degradation. This allows subsequent preparations of graft copolymers.

In a similar manner, it is possible to start with copolymers of acryloyl or methacryloyl chloride and react them with hydroperoxides [332]. This can be illustrated as follows:

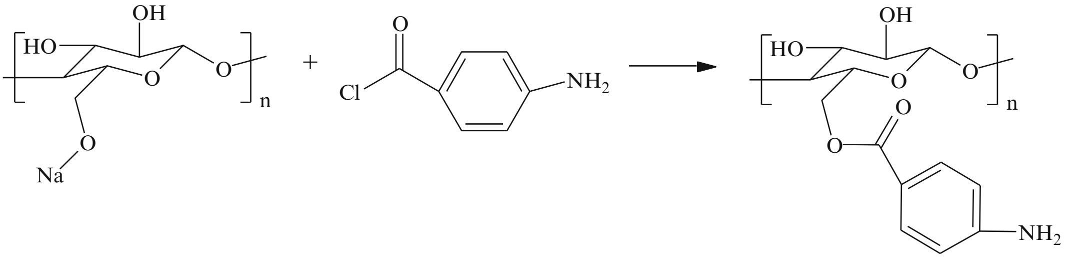


The decomposition of the pendant peroxide in the presence of vinyl monomers yields mixtures of graft copolymers and homopolymers.

Preparation and subsequent decomposition of polymers with diazonium salts can also be used to form graft-copolymers. An example is nitrated polystyrene, reduced to the amine derivative and then diazotized [333]. The decomposition of the diazonium salt results in formation of radicals:

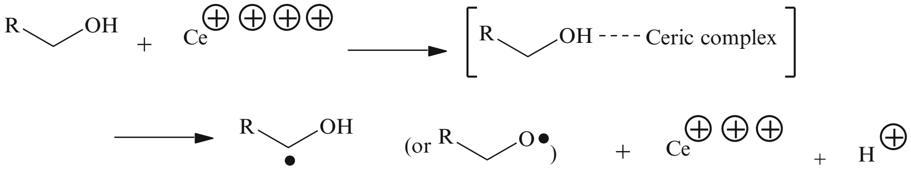


The radical sites are capable of initiating polymerizations of monomers. A similar approach can be taken with cellulose [334]. Mercerized cotton and sodium salt of carboxymethyl cellulose will react with *p*-aminophenacyl chloride:



The material can be converted to diazonium salts and then decomposed with ferrous ions in the presence of some vinyl monomers to form graft copolymers. Acrylonitrile forms graft copolymer readily without formation of any homopolymers. Styrene and vinyl acetate, however, do not. A modification of this technique is to conduct the diazotization reaction in the presence of emulsifiers [335]. The amounts of graft copolymers that form with acrylic and methacrylic monomers and *N*-vinylpyrrolidone depend upon the nature and pH of the emulsifiers, the reaction time, and the temperature.

Ceric ions form graft copolymers with various macromolecules by a redox mechanism. The reactions can be illustrated as follows:

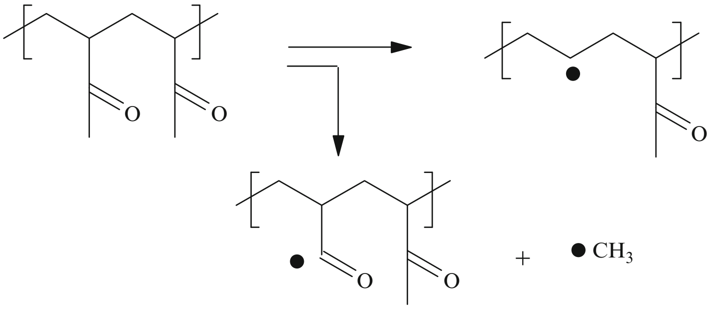


The almost exclusive formation of free radicals on the polymeric backbones results in formations of many products that are close to being free from homopolymers [346, 350]. The reactions are widely used in formations of graft copolymers of poly(vinyl alcohol) and particularly of cellulose and starch. The grafting reaction fails, however, when attempted on polysaccharides that lack free hydroxyl groups on the second and third carbons. This led to speculation [351] that the bond between these carbons cleaves. In the process, free radicals, presumably, form on the second carbons and aldehyde structures on the third carbons of the glucose units. This point of view, however, is not generally accepted. Instead, it was proposed that more likely positions for attacks by the ceric ions are at the C_1 carbons of the glucoses at the end of the polysaccharide chains [352]. This is supported by observation that oxidation of cellulose is an important prerequisite for the formation of graft copolymers [353].

Graft copolymerizations by redox mechanism can also take place with the aid of other ions. This includes grafting on cellulose backbones with ferrous ions and hydrogen peroxide [354]. Redox grafting reactions can also take place on nylon and on polyester. For instance, graft copolymers of methyl methacrylate on nylon 6 can be prepared with manganic, cobaltic, and ferric ions [355]. Another example is grafting poly(glycidyl methacrylate) on poly(ethylene terephthalate) fibers with the aid ferrous ion–hydrogen peroxide. The reaction depends on the concentration of the monomer, hydrogen peroxide, time, and temperature [356].

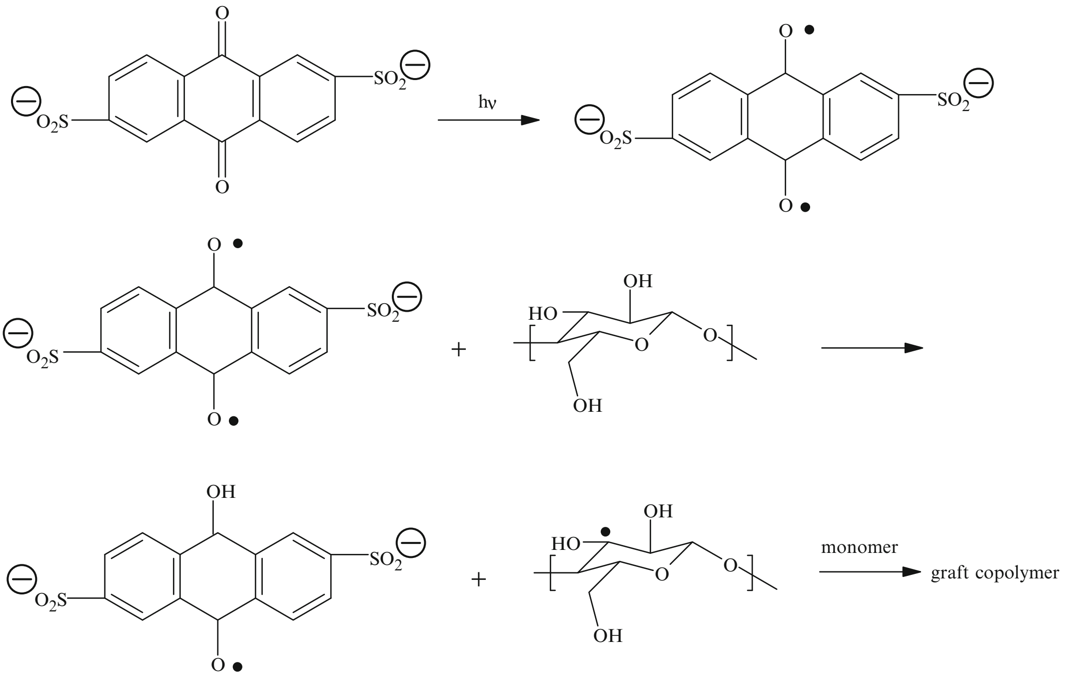
9.6.5 *Photochemical Syntheses of Graft Copolymers*

Photo labile groups on polymers can serve as sites for photoinitiated graft copolymerizations. For instance, when polymers and copolymers of vinyl ketone decompose in ultraviolet light in the presence of acrylonitrile, methyl methacrylate or vinyl acetate graft copolymers form [357]:



The free radicals that are unattached to the backbone polymers, like the methyl radical shown above, also initiate polymerizations and considerable amounts of homopolymers form as well.

In some instances, graft copolymers form as a result of chain transferring that takes place after photodecomposition of the photo labile materials. An example is formation of graft copolymers of polyacrylamide on natural rubber, poly(vinyl pyrrolidone), or dextrin with the aid of benzophenone and ultraviolet light [358]. The free radicals from photodecomposition of benzophenone react with the polymers by chain transferring. The growth of acrylamide is subsequently initiated from the polymer backbones. Photo tendering dyes can be used in this manner with cellulose [359]. Thus, anthraquinone dyes can be adsorbed to cellulose. Upon irradiation, proton abstractions take place, creating initiating radicals on the backbone polysaccharide:



It is believed that the above dye mono radicals disproportionate to hydroquinones and quinones. Transfer reactions to solvent lead to formations of homopolymers. This gives high yields of graft copolymers of methyl methacrylate with cellulose. The same is true of acrylonitrile [360]. On the other hand, only small quantities of graft copolymers form with styrene or vinyl acetate monomers [360].

It is also possible to form graft copolymers on the surface of fibers by coating them with photoinitiators, like benzophenone together with a monomer and then irradiating them with ultraviolet light [414]. Similar to the action of the anthraquinone dyes shown above, benzophenone in the excited triplet state mainly abstracts hydrogens and forms radicals on the surface [415].

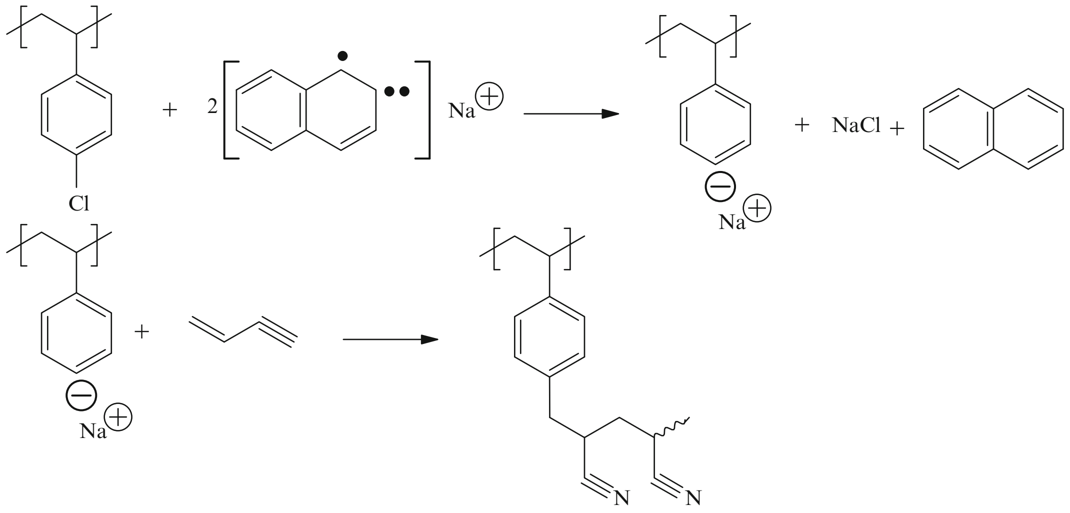
9.6.6 Graft Copolymer Formation with the Aid of High-Energy Radiation

High-energy radiation sources include gamma rays from radioactive elements, electron beams from accelerators, and gamma rays from nuclear reactors. The energy radiated by these sources is sufficiently high to rupturing covalent bonds. This results in formations of free radicals. Several different methods are used to form graft copolymers. One of them is ***irradiation in open air***. The free radicals that form scavenge oxygen and form peroxides and hydroperoxides on the polymeric chains. These are subsequently decomposed in the presence of monomers to form graft copolymers. When they are decomposed thermally [361], the hydroperoxides yield much greater quantities of homopolymers then do the peroxides. When, however, the decompositions are done at room temperature by redox mechanisms, formations of homopolymers are reduced [361, 362]. Another method is ***irradiation in vacuum***. This results in formations of trapped radicals on the polymer backbones. After irradiation, the polymers are heated in the absence of oxygen and in the presence of vinyl monomers. The best results are obtained when irradiations are done at low temperatures, below T_g of the polymers. High degree of crystallinity is also beneficial, because mobility of the chains results in loss of trapped radicals. When the monomers are added, however, heat must be applied, but this can result in loss of some of the radicals. The third method is ***mutual irradiation*** in an inert atmosphere of polymers and monomers together. The polymers are either swelled or dissolved by the monomers. The relative sensitivities of the two species, the monomer and the polymer to radiation, can be important factors in this third procedure. Efficiency of grafting depends upon formations of free radicals on the polymer backbones. If only a small number of free radicals form, the irradiations produce mainly homopolymers. Also, if the polymers tend to degrade from the irradiation, block copolymers form instead. Presence of solvents and chain-transferring agents tends to lower the amount of the grafting [363].

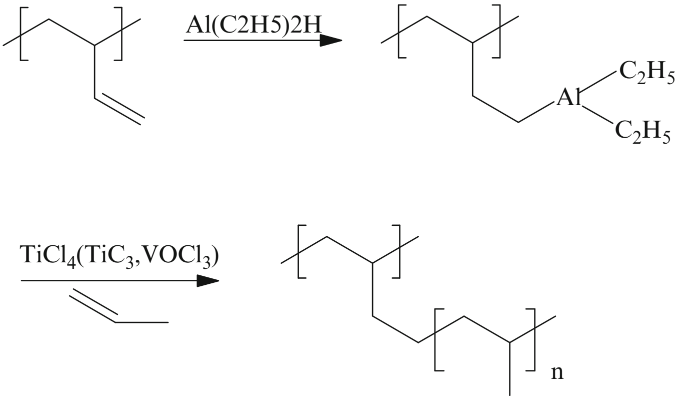
It was also shown [409] that energetic heavy ions can also produce graft copolymers. The results appear similar to those obtained by electron beams. Also, many papers reported use of plasma for surface modification of films. The process can result in formation of graft copolymers when it is accompanied by an introduction of a monomer or monomers. One such example is a use of argon plasma to graft polyacrylamide to polyaniline films [410]. The near ultraviolet light plasma induces the reaction. Other monomers that can be grafted by this reaction are 4-styrenesulfonic acid and acrylic acid [410].

9.6.7 Preparation of Graft Copolymers with Ionic Chain-Growth and Step-Growth Polymerization Reactions

Both anionic and cationic mechanisms can be used to form graft copolymers. A typical example of graft copolymer formation by anionic mechanism is grafting polyacrylonitrile to polystyrene [364]:

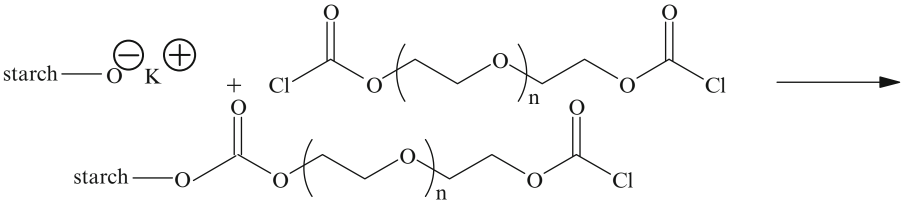


Another example of ionic graft copolymerization in a reaction carried out on pendant olefinic groups using Ziegler-Natta catalysts in a coordinated anionic type polymerization [365]. The procedure consists of two steps. In the first one, diethylaluminum hydride is added across the double bonds. The product is subsequently treated with a transition metal halide. This yields an active catalyst for polymerizations of α-olefins. By this method, polyethylene and polypropylene can be grafted to butadiene styrene copolymers. Propylene monomer polymerization results in formations of isotactic polymeric branches:



Another example is formation of graft copolymers of formaldehyde with starch, dextrin, and poly (vinyl alcohol) [366, 367]. This procedure is also carried out in two steps. Potassium naphthalene is first reacted with the backbone polymer in dimethylsulfoxide. The formaldehyde is then introduced in gaseous form to the alkoxide solution.

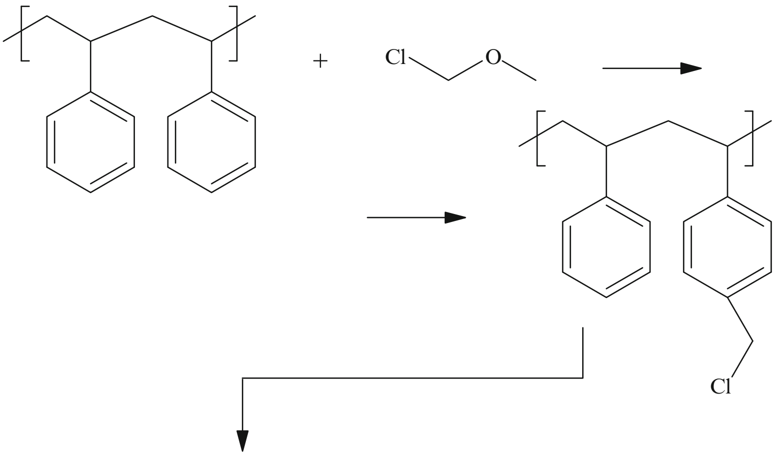
A similar reaction can be used to form graft copolymers of poly(ethylene oxide) on cellulose acetate [391]. Poly(ethylene oxide) can also be grafted to starch. For instance, a preformed polymer [392] terminated by chloroformate end groups can be used with potassium starch alkoxide:

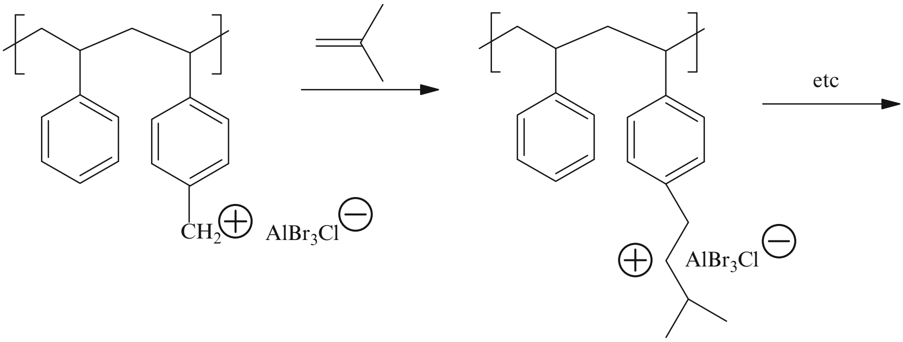


The products are water-soluble. The efficiency of the coupling process, however, decreases with an increase in the DP of poly(ethylene oxide).

Lithiated polystyrene reacts readily with halogen-bearing polymers like polychlorotrifluoroethylene [411]. This can be utilized in formation of graft copolymers. The reactions can be conducted in solutions as well as in preparations of surface grafts on films [411].

An example of a cationic grafting reaction is formation of graft copolymers of polyisobutylene on polystyrene backbones [393]. Polystyrene is chloromethylated and then reacted with aluminum bromide in carbon disulfide solution. This is followed by introduction of isobutylene:





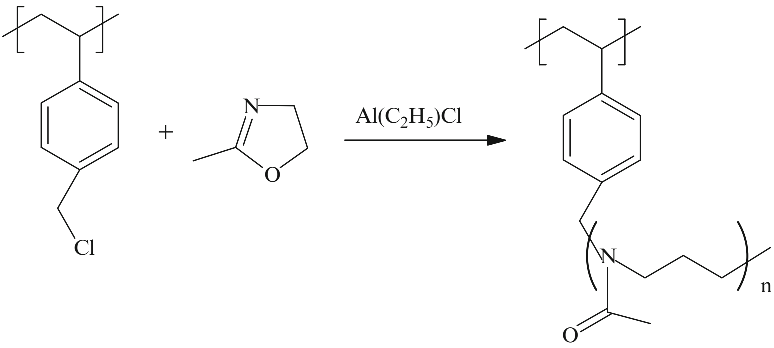
The above, however, yields only 5–18% of a graft copolymer, even at −60°C. It is possible that considerable amounts of cross-linking occur at the reaction conditions and may, perhaps, be the reason for the low yield [393].

Another example is grafting to cellulose. BF_3 can be adsorbed to the surface of the polymer. It then reacts with hydroxy groups and yields reactive sites for cationic polymerization of α-methyl styrene and isobutylene [402]. These reactions are carried out at −80°C.

Cationic graft copolymerizations of trioxane can be carried out with the help of reactive C–O–C links in a number of polymers, like poly(vinyl acetate), poly(ethylene terephthalate), and poly(vinyl butyral) [403]. Many graft copolymers can also be formed by ring opening polymerizations [404]. The reactions with active hydrogens on the pendant groups, like hydroxyl, carboxyl, amine, amide, thiol, and others, can initiate some ring opening polymerizations. An example is preparation of graft copolymers of ethylene oxide with styrene [405]. Copolymers of styrene with 1–2% of hydrolyzed vinyl acetate (vinyl alcohol after hydrolysis) can initiate polymerizations of ethylene oxide and graft copolymers form.

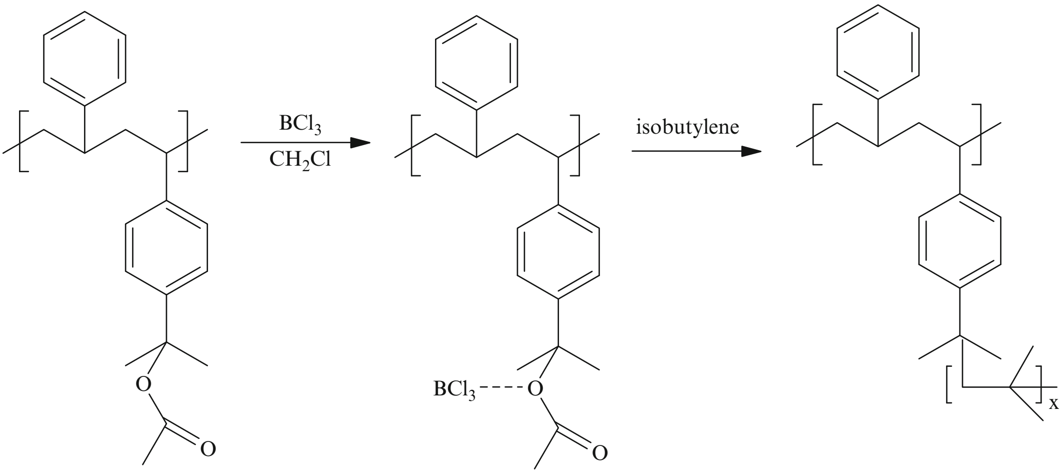
Recently, solutions of polysilanes were treated with controlled amounts of triflic acid (CF_3SO_2OH) in CH_2Cl_2 and afterwards with tetrahydrofuran. This yielded a graft copolymer of poly(tetramethylene oxide) on polysilane backbones [412].

An interesting series of papers were published by Kennedy and coworkers on use of alkylaluminum compounds as initiators of graft copolymerizations [366, 367]. Allylic chlorines form very active carbon cations in the presence of this initiator. This is also true of macromolecular carbon cation sources [402]. As a result, very high grafting efficiency is achieved in many different polymerizations using macromolecular cationogens and alkylaluminum compounds. In some instances, formation of graft copolymers is greater than 90%. The grafting reaction can be illustrated as follows [367].



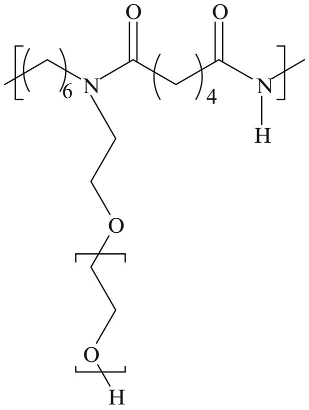
The temperatures of the reactions and the nature of the aluminum compounds are the most important synthetic variables [367].

On the other hand, many other graft copolymerizations by cationic mechanism suffer from low grafting efficiencies. They are also often accompanied by large formations of homopolymers. Use, however, of living cationic processes appears to overcome this drawback. An illustration of this can be another preparation of a graft copolymer of polyisobutylene on a polystyrene backbone [413]:



9.6.8 Miscellaneous Graft Copolymerizations

In a rather interesting reaction, ethylene oxide can be graft-copolymerized with nylon 6,6 [406]. Formation of the graft copolymer greatly enhances flexibility of the material, while the high melting point of the nylon is still maintained. Thus, nylon 6,6 that contains as much as 50% by weight of grafted poly(ethylene oxide) still melts at 221°C and has an apparent T_g below −40°C. It also maintains flexibility and other useful properties over a wide range of temperatures [406]:



An entirely different procedure can be used to form graft copolymers by a step-growth polymerization [347]. Formaldehyde is condensed with either phenol, *p*-cresol, or *p*-nonyl phenol and the resin is attached to either nylon 6, nylon 6,6, nylon 6,10, or nylon 11 backbones. Initially, the formaldehyde is prereacted with an excess of phenol in the presence of the nylon, but without any catalyst, at temperatures high enough to cause condensation. This is followed by addition of toluenesulfonic acid at lower temperatures. At that point, when free formaldehyde is no longer present in the reaction mixture to cause gelation, the novolac molecules attach themselves to the nylon backbones. The excess phenol is washed away, leaving pure graft copolymers [347].

Yagci and coworkers reported a special preparation of perfectly alternating poly(*p*-phenylene) amphilitic graft copolymers by combination of controlled free-radical polymerization and Suzuki coupling process [345].

9.7 Block Copolymers

These polymers consist of two or more strands of different polymers attached to each other. There does not appear to be any general stipulation to the minimum size of each block. There does appear to be, however, a general agreement that each sequence should be larger than just a few units. In describing a block copolymer, it is helpful if the following structural parameters are available to characterize the material:

1. Copolymer sequence distribution as well as the length and the number of blocks.
2. The chemical nature of the blocks.
3. The average molecular weight and the molecular weight distribution of the blocks and of the copolymer.

Block copolymers, particularly of the A—B—A type, can exhibit properties that are quite different from those of random copolymers and even from mixtures of homopolymers. The physical behavior of block copolymers is related to their solid state morphology. Phase separation occurs often in such copolymers. This can result in dispersed phases consisting of one block dispersed in a continuous matrix from a second block. Such dispersed phases can be hard domains, either crystalline or glassy, while the matrices are soft and rubber-like.

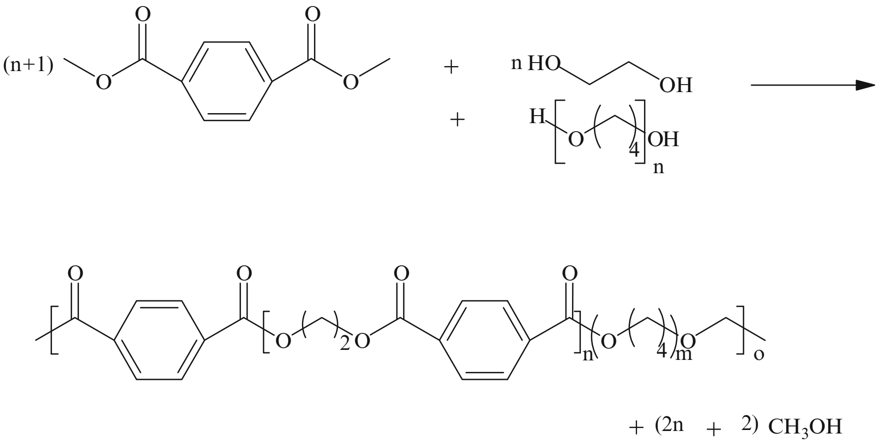
An interesting example of block copolymers is work by de Ruijter et al. [348], who prepared a series of block copolymers that contain rigid liquid crystal forming blocks of poly(*p*-phenylene terephthalamide) and flexible blocks of hexamethylene adipamide. The polymers have been prepared in a one-pot procedure by a low-temperature polycondensation reaction in *N*-methyl-2-pyrrolidone.

9.7.1 Block Copolyesters

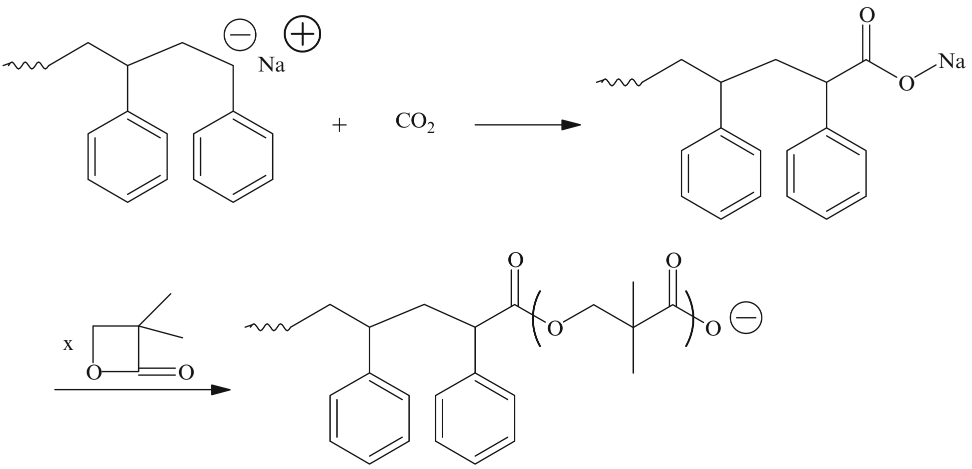
Two polyester homopolymers can react and form block copolymers in a molten state at temperatures high enough for ester interchange [414]. As the reaction mixtures are stirred and heated, the interchanges initially involve large segments. With time, however, smaller and smaller segments form as the transesterifications continue. To prevent eventual formation of random copolymers, the reactions should be limited in time.

Ester interchange can be retarded, particularly when esterification catalysts like zinc or calcium acetate are present by addition of phosphorous acid or triphenyl phosphite [415]. This improves the chances of forming block copolymers. The procedure can be applied to preparation of block copolymers of poly(ethylene terephthalate) with poly(ethylene maleate), poly(ethylene citraconate), and poly(ethylene itaconate) [416]. With ester interchange catalysts, like titanium alkoxides or their complexes, melt randomization may be inhibited by adding arsenic pentoxide that deactivates them [417].

Block copolyesters also form in reactions between hydroxy and acid chloride-terminated prepolymers [419]. This can take place in the melt or in solution in such solvents as chlorobenzene or *o*-dichlorobenzene [418]. For relatively inactive acid chlorides, like terephthaloyl chloride, high reaction temperatures are required. Phosgene also reacts with hydroxy-terminated polyesters to form block copolymers. The reactions must be carried out in inert solvents. Block copolyethers also form readily by ester interchange reactions with low molecular weight diesters [348]:



Acetates of tin, lead, manganese, antimony, and zinc as well as esters of orthotitanates catalyze the reactions [421]. Optimum temperatures for these reactions are between 230 and 260°C at 0.03–1 mm Hg pressure [421]. Block copolymers can also form by ring opening polymerizations of lactones, when carboxyl-terminated macromolecular initiators are used [422]:



9.7.2 Block Copolyamides

Simple melt blending reactions can also be applied to preparations of block copolyamides, similarly to the process for polyesters. With time, total equilibrium conditions also are gradually achieved in the melt [423]. Interfacial polycondensation is also useful in preparation of block copolymers. When mixed diacid chlorides and/or mixed diamines are reacted, the more active diacid chlorides and/or diamines react preferentially and blocks form. In addition, it is possible to carry out the growth of one of the segments first, to a fairly large size and follow it by addition of the other comonomers [424].

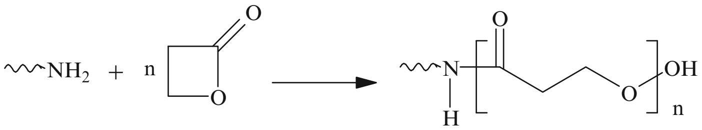
9.7.3 Polyurethane-Polyamide Block Copolymers

These block copolymers can be formed in many ways. One technique is to prereact a diamine with a diacid chloride. The polyamide that forms is then treated with bischloroformate to attach to polyurethane blocks [425]. The process can be reversed and the polyurethane can be formed first and then attached to polyamide blocks [425].

9.7.4 Polyamide-Polyester Block Copolymers

Block copolymers consisting of polyamide and polyester blocks can form through melt blending [426]. The reactions probably involve aminolyses of the terminal ester groups of the polyesters by the terminal amine groups of the polyamides. Ester interchange catalysts accelerate the reaction [427].

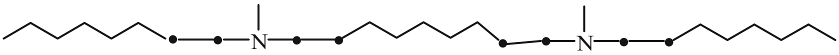
Block polyester-polyamides also form through initiation of ring opening polymerizations of lactones by the terminal amine groups of the polyamides [428]:



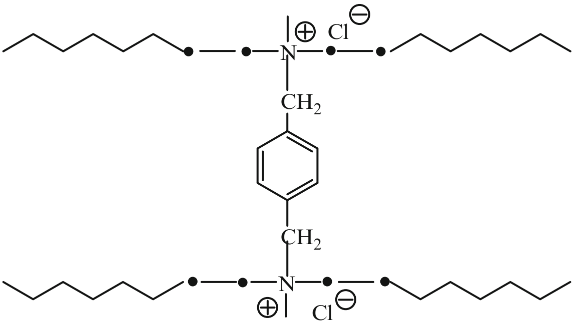
If the polyamide has terminal amine groups at both ends, then triblock copolymers form.

9.7.5 Polyurethane Ionomers

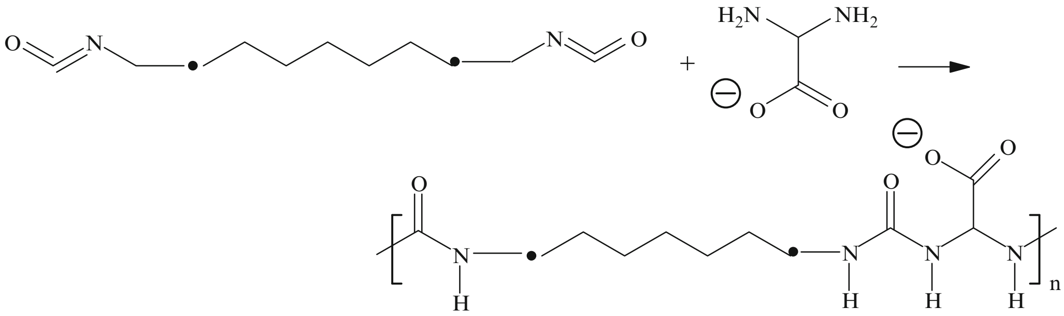
These materials were reviewed as a special class of block copolymers [433]. They are linear polyaddition products of diisocyanates containing nonrandom distributions of ionic centers. The preparations are similar to those of polyurethane elastomers that are described in Chap. 6. One example is a material prepared from high molecular weight polyester that is free from ionic centers and that is terminated by isocyanate groups at each end. The prepolymer is coupled with *N*-methylamino-2,2′-diethanol to form a segmented polymer:



Similar products form from isocyanate-terminated polyethers. This material can be cross-linked with difunctional quaternizing agents, such as 1,4-bis(chloromethyl) benzene [434]:



The products are cationic ionomers. Anionic ionomers form very similarly through coupling of chains with bifunctional anionic "chain lengtheners" [435]:



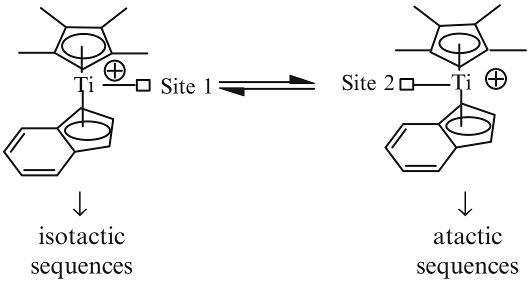
Because of interactions between the chains, the polyurethane ionomers are similar in properties to cross-linked elastomers. In solution, they are strongly associated.

9.7.6 Block Copolymers of Poly(α-Olefin)s

These block copolymers form readily when appropriate Ziegler-Natta catalysts are used [436]. This is discussed in Chaps. 4 and 6. In addition, there is a special technique for preparations of such block copolymers. At the outset of the reaction, only one monomer is used in the feed. A typical catalyst might be α-$TiCl_3/(C_2H_5)_3Al$. After the first monomer has been bubbled in for a short period, perhaps 5 min, the addition is stopped and the unreacted monomer removed by evacuation or by flushing. The second monomer is then introduced and may also be bubbled in for the same period. The addition of the second monomer may then be stopped, the second monomer evacuated, and the whole thing might be repeated. If equal length of each block is desired, the addition times of each monomer may be varied to adjust for different rates of polymerization [436].

Kuhlman and Klosin [436] reported forming multiblock copolymers of polyethylene and tuning block composition by catalyst selection. Chain shuttling, the fast exchange of growing polymer chains among catalyst centers mediated by a chain shuttling agent (CSA), has enabled the production of ethylene-based olefin block copolymers. Diethyl zinc was used as a chain shuffling agent. Thus, copolymerization of ethylene and α-olefin by certain catalyst pairs in the pretense of a CSA produces blocks that are alternately highly or lightly branched. Chain shutling polymerizations are bet conducted in continuous reactors.

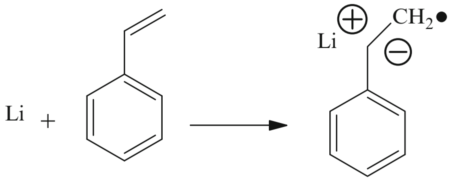
A catalyst system derived from titanocene complex and methyl-aluminoxane (see Chap. 5) has been used to polymerize propylene and, depending on polymerization conditions, produce a block copolymer of crystalline and amorphous, elastomeric polypropylene [440]:



In the above process, the formation of crystalline domains involves consecutive insertions from one of the lateral coordination sites of the catalyst so as to give rise to isotactic sequences, whereas consecutive insertions at the other site (2) give rise to atactic amorphous sequences. Interconversion between these two states must occur within the lifetime of a given polymer chain in order to generate a physically cross-linked network and is believed to occur via occasional isomerizations of the polymer chains (i.e., interconversion at the metal center). Preparation of an oscillating catalyst that yields an elastomeric polypropylene was also reported by others [441].

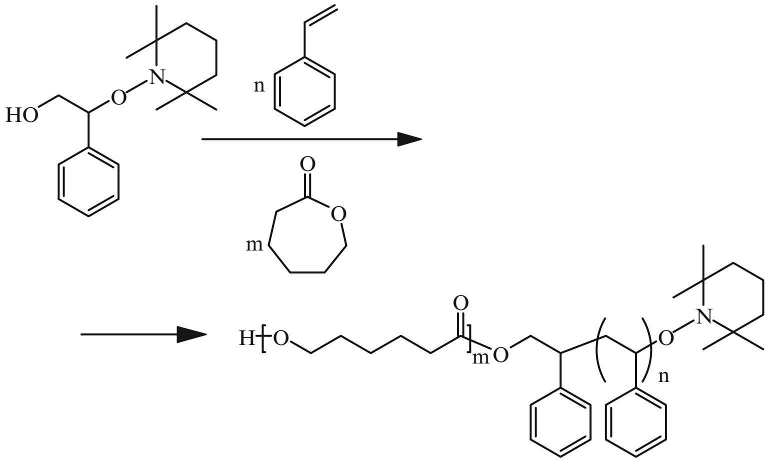
9.7.7 Simultaneous Use of Free Radical and Ionic Chain-Growth Polymerizations

This technique allows formation of many different types of block copolymers [437]. Lithium metal can be used to initiate polymerizations in solvents of varying polarity. Monomers, like styrene, α-methylstyrene, methyl methacrylate, butyl methacrylate, 2-vinylpyridine, 4-vinyl pyridine, acrylonitrile, and methyl acrylate, can be used. The mechanism of initiation depends upon formation of ion-radicals through reactions of lithium with the double bonds:



Propagation reactions proceed from both active sites, the radical and the carbanion. When two different monomers are present, free-radical propagation favors formation of copolymers, while propagation at the other end favors formation of homopolymers. There is a tendency, therefore, to form AB—B type block copolymers.

Several publications appeared recently that describe use of controlled/"living" radical polymerizations to form block copolymers. Thus, Jerome et al. [435] described formation of block copolymers by using an initiator capable of initiating simultaneously dual living polymerizations:



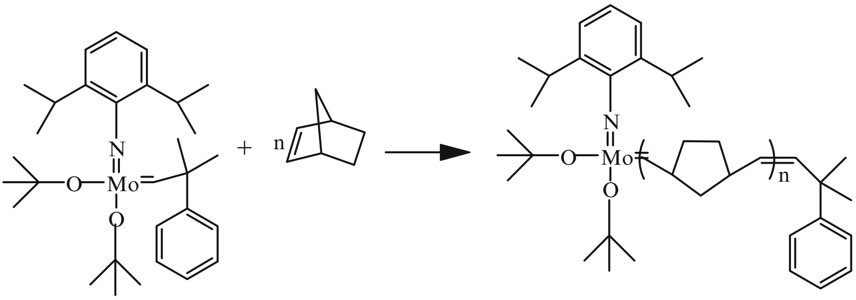
In a similar manner, Yoshida and Osagawa [436] synthesized poly(ε-caprolactone) with 2,2,6,6-tetramethylpiperdine-1-oxyl (TEMPO) at one end by anionic polymerization of caprolactone using an aluminum tri(4-oxy-TEMPO) initiator. The TEMPO-supported polycaprolactone behaved as a polymeric counter radical for a controlled/"living" radical polymerization of styrene to form block copolymers [436].

Also, Kotani et al. [437] reported using controlled/"living" atom transfer radical polymerization (ATRP) to form block copolymers of ethyl and *n*-butyl methacrylates. A ternary initiating system that consists of carbon tetrachloride, tris(triphenyl-phosphine)ruthenium dichloride [$RuCl_2(PPh_3)_3$], and aluminum compounds produced ABA triblock copolymers [437].

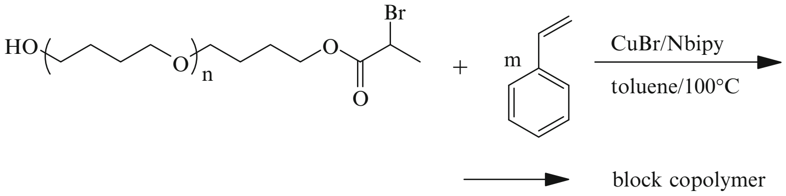
Huang and coworkers [437] reported preparation of a series of well-defined amphiphilic block copolymers containing conjugated poly(fluorene) (PF) block and coil like poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA). The block copolymers were synthesized through ATRP. The reactions were initiated by a 2-bromoisobutyrate end-capped macroinitiator using CuCl/ 1,1,4,7,10,10-hexamethyltriethylenetetramine as the catalyst.

Matron and Grubbs formed block copolymers by combining ring opening metathesis polymerization with ATRP [437]. Use was made of fast initiating ruthenium metathesis catalyst to form three different monotelechelic poly(oxa)norbornenes. The ends were functionized and ATRP polymerizations of styrene and *tert*-butyl acrylate followed.

Coca et al. [438] showed a general method of transforming living ring opening metathesis polymerization into controlled/"living" atom transfer polymerizations to form block copolymers. Ring opening polymerizations of norbornene or dicyclopentadiene were followed by Witting-like reactions with *p*-(bromomethyl)benzaldehyde to form efficient (ATP) macroninitiators for formation of block copolymers with styrene [478]:



Other cationic ring opening polymerizations can also be transformed to ATRP to yield block copolymers [439]. Thus, formation of block copolymers was initiated by poly(tetramethylene glycol) containing one bromopropionyl end group. These were used to form block copolymers by ATP polymerization of styrene, methyl methacrylate, and methyl acrylate.



9.7.8 Preparation of Block Copolymers by Homogeneous Ionic Copolymerization

Formation of block copolymers by this method depends upon the ability to form “living” chain ends. Among the anionic systems, the following polymerizations fit this requirement:

1. Polymerizations of nonpolar monomers with alkali metal-aromatic electron transfer initiators in ethers [398].
2. Polymerizations of nonpolar monomers with organolithium compounds in hydrocarbon solvents [399].
3. Acrylonitrile polymerizations in dimethyl formamide initiated by sodium triethylthioisopropoxyaluminate at −78°C [340].
4. Copolymerizations of hexafluoroacetone and cyclic oxides initiated by CsF [341].
5. Polymerization of alkyl isocyanates initiated by organoalkali species in hydrocarbons at −78°C [342].

Among the cationic “living” polymerizations that can be used for block copolymer formation are:

1. Polymerizations of isobutylene [361] and/or vinyl ethers [363] with appropriate catalysts. This includes formation of block copolymers from the two types of monomers [365].
2. Polymerizations of tetrahydrofuran with the aid of chlorobenzene diazonium hexafluorophosphate [343], triphenylmethyl hexachloroantimonate [344], or phosphorus pentafluoride [445].
3. Polymerization of *p*-methyl styrene, *N*-vinylcarbazole, and indene with appropriate catalysts.

The preparations by anionic mechanism of A—B—A type block copolymers of styrene and butadiene can be carried out with the styrene being polymerized first. Use of alkyl lithium initiators in hydrocarbon solvents is usually a good choice, if one seeks to form the greatest amount of *cis*-1,4 microstructure [346]. This is discussed in Chap. 4. It is more difficult, however, to form block copolymers from methyl methacrylate and styrene, because “living” methyl methacrylate polymers fail to initiate polymerizations of styrene [347]. The poly(methyl methacrylate) anions may not be sufficiently basic to initiate styrene polymerizations [345].

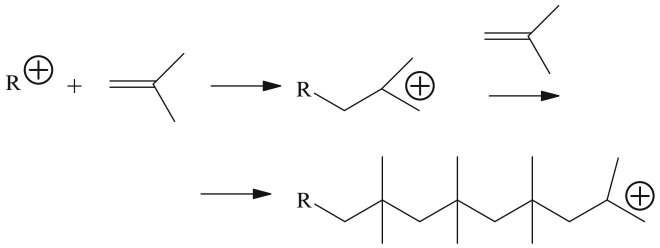
A “living” cationic polymerization of tetrahydrofuran, using BH_3 as the initiator in the presence of epichlorohydrin and 3,3-bis(chloromethyl)oxacyclo-butane [348], results in formation of block copolymers. Two types form. One is an A—B type. It consists of polytetrahydrofuran blocks attached to blocks of poly(3,3-bis(chloromethyl)oxacyclo-butane). The other one is an A—AB—B type [348].

The preparation of well-defined sequential copolymers by anionic mechanism has been explored and utilized commercially for some time now. Initially, the cationic methods received less attention until it was demonstrated by Kennedy [424] that a large variety of block copolymers can be formed. The key to Kennedy’s early work is tight control over the polymerization reaction. The initiation and propagation events must be fundamentally similar, although not identical [424]:

Ion generation:

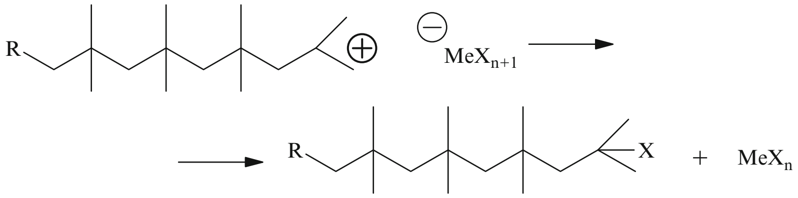
$$RX + MeX_n \rightleftharpoons R^{\oplus}MeX_{n+1}^{\ominus}$$

Cationization and propagation:



In this scheme, chain transfer to monomer must be absent and the termination is well defined.

Termination:



where X is a halogen, Me is a metal.

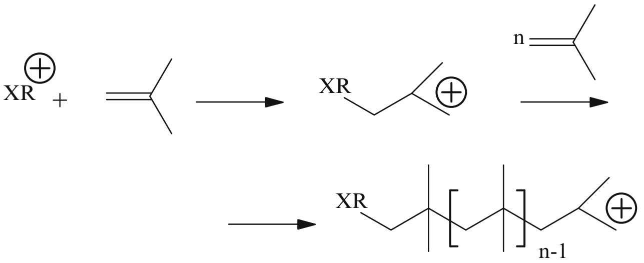
This allows formation of macromolecules with terminal halogens. They can be used to initiate new and different polymerizations.

Three methods were developed to overcome transfer to monomer [424]. These are: (1) use of *inifers*; (2) use of proton traps; and (3) establishing conditions under which the rate of termination is much faster than the rate of transfer to monomer. The first one, the inifer method, is particularly useful in formation of block copolymers. It allows preparation of *head* and *end* (α and ω) functionalized telechelic polymers. Bifunctional initiators and transfer agents (*inifers*) are used. The following illustrates the concept [424]:

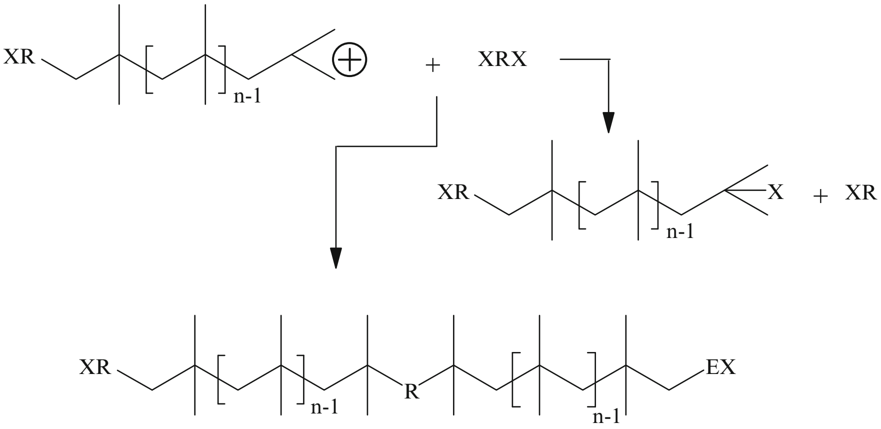
Ion generation:

$$XRX + MeX_n \rightleftharpoons XR^{\oplus} + MeX^{\ominus}_{n+1}$$

Cationization and propagation:



Chain transfer with inifers:



In the above scheme, the inifer, XRX, is usually an organic dihalide. If chain transferring to the inifer is faster than chain transferring to the monomer, the polymer end groups become exclusively terminated with halogens.

It is also possible to carry out "living" cationic polymerization of isobutylene, initiated by a difunctional initiator [435]. This results in a formation of bifunctional "living," segments of polyisobutylene that are soft and rubbery. Upon completions of the polymerization, another monomer, one that yields stiff segments and has a high T_g, like indene, is introduced into the living charge. Polymerization of the second monomer is initiated from both ends of the formed polyisobutylene. When the reaction is complete, the polymerization is quenched. Preparations of a variety of such triblock and star block polymers have been described [435].

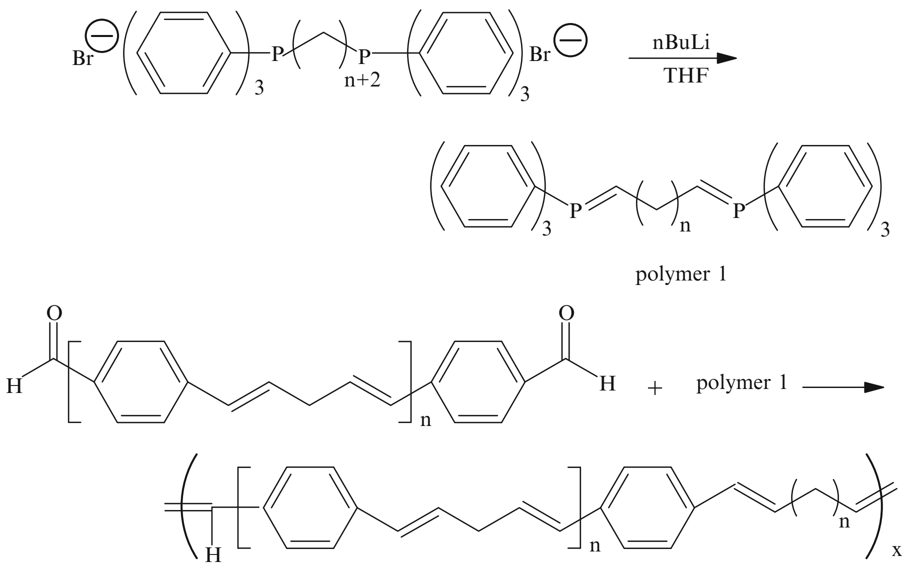
A technique was developed, by introducing cationic to anionic transformation [438]. A "living" carbocationic polymerization of isobutylene is carried out first. After it is complete, the ends of the chains are quantitatively transformed to polymerization-active anions. The additional blocks are then built by an anionic polymerization. A triblock polymer of poly(methyl methacrylate)-polyisobutylene-poly(methyl methacrylate) can thus be formed. The transformation takes several steps. In the first one, a compound like toluene is Friedel-Craft alkylated by α,ω-di-*tert*-chloropolyisobutylene. The ditolylpolyisobutylene, which forms, is lithiated in step two to form α,ω-dibenzyllithium polyisobutylene. It is then reacted with 1,1-diphenylethylene to give the corresponding dianion. After cooling to −78°C and dilution, methyl methacrylate monomer is introduced for the second polymerization [438] in step 3.

Formation of block copolymers from polymers with functional end groups has been used in many ways. In anionic polymerization, various technique were developed for terminating chain growth with reactive end groups. These end groups allow subsequent formations of many different block copolymers. One such active terminal group can be toluene diisocyanate [439]. The isocyanate group located ortho to the methyl group is considerably less reactive toward the lithium species due to steric hindrance [438]. The unreacted isocyanate group can be used for attachment of various polymers that are terminated by hydroxy, carboxy, or amine groups. Other functional compounds that can be used in such reactions are alkyl or aryl halides, succinic anhydride, *n*-bromophthalimide [448], and chlorosilanes [449].

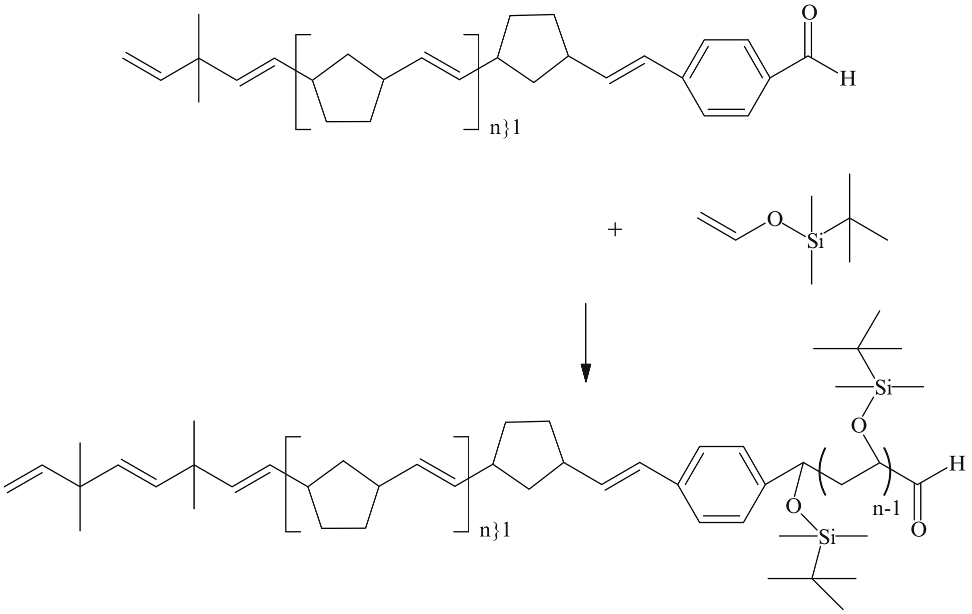
Because block copolymers can often offer properties that are unattainable with simple blends or random copolymers [364], many efforts were made to combine dissimilar materials, like hydrophilic with hydrophobic, or hard with soft segments, as was shown earlier. One paper [432] describes formation of block copolymers containing helical polyisocyanide and an elastomeric polybutadiene. Compound $[(\eta^3\text{-}C_3H_5)\text{-}Ni(OC(O)CF_3)]_2$ was used to carry out "living" polymerization of butadiene and then followed by polymerization of *tert*-butyl isocyanide to a helical polymer.

9.7.9 Special Reactions for Preparation of Block Copolymers

A special case is the use of the *Witting* reaction. Poly(*p*-phenylene pentadienylene) [415] is prepared by this reaction first. This is utilized in a preparation of a block copolymer [456] according to the following scheme:

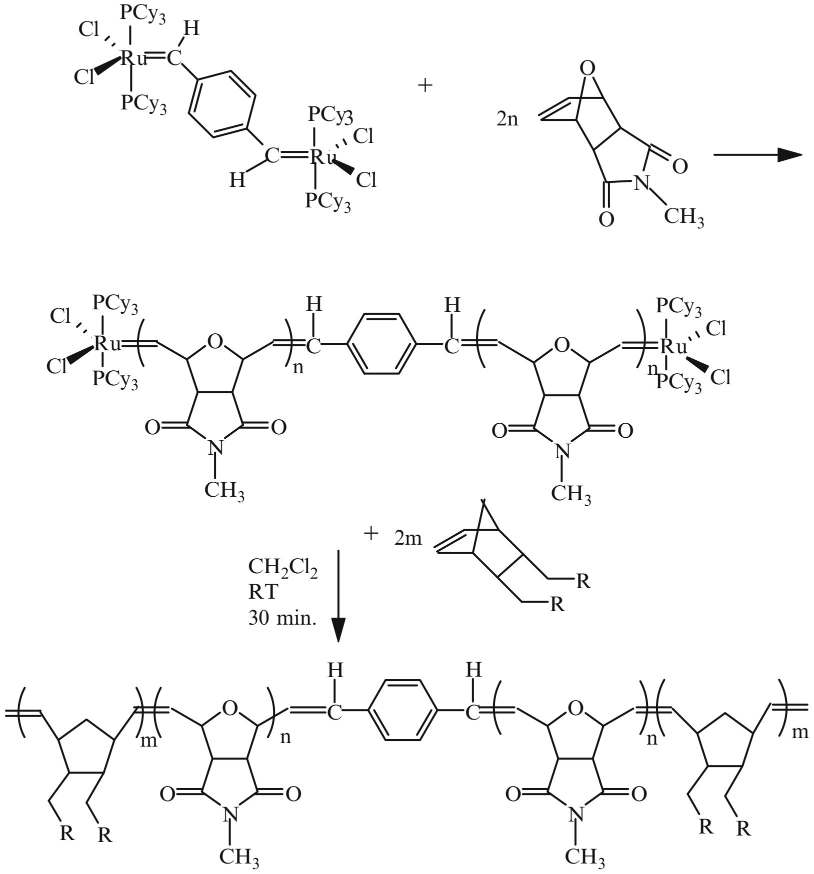


A preparation of block copolymers by “living” ring-opening olefin metathesis polymerization was reported [417]. Initially, norbornene or *exo*-dicyclopentadiene are polymerized by bis(η^5-cyclopentadienyl)titanacyl butane. The resulting living polymers are then reacted with terephthaldehyde to form polymers with terminal aldehyde groups. The aldehyde groups in turn initiate polymerizations of *t*-butyldimethylsilyl vinyl ether by aldol-group transfer polymerizations [418]. Following is an illustration of the process:

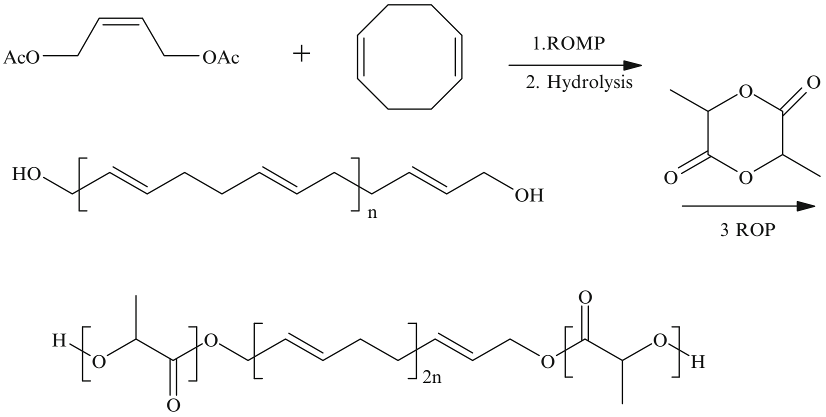


Subsequently, the terminal aldehyde group is reduced with $NaBH_4$ and the silyl groups cleaved off by treatment with tetrabutylammonium fluoride to produce a hydrophobic-hydrophilic A—B diblock copolymers.

Living metathesis type polymerization was also employed to form block copolymers from norbornene and its derivative with bimetallic ruthenium catalysts, $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4CH=)RuCl_2(PR_3)_2$ [434]. This can be illustrated as follows [434]:



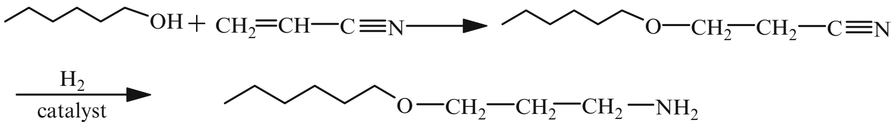
Pitet and Hillmyer [436] formed triblock copolymers from 1,5-cycloocatadiene and DL-Lactide by combining ring opening metathesis polymerization with cyclic ester ring opening polymerization.



Proto et al. [434] living isoselective coordination polymerization of styrene to form isoselective block copolymers. This was accomplished by sequential monomer addition.

9.7.10 *Miscellaneous Block Copolymers*

Polyamide-polyether block copolymers can be formed by a variety of techniques. One of them consists of initial preparation of amine-terminated polyethers. This can be done by reacting hydroxy-terminated polyethers with acrylonitrile and then reducing the nitrile groups to amines [429]:

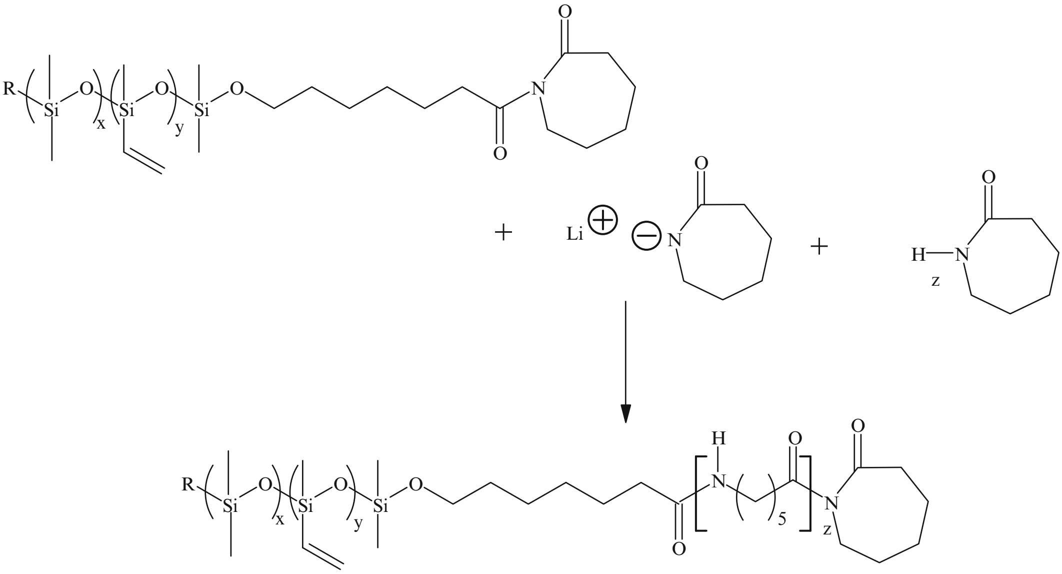


The products of the reduction condense with carboxylic acid-terminated polyamides to form block copolymers.

Another one is to form the polyethers with terminal chloride groups [430]. Hydroxy-group-terminated polyethers, for instance, can be converted to halogen-terminated polyethers. The products will react with ammonia and the amine-terminated polymer will react with carboxylic acid-terminated polyamides [430].

A British patent describes preparations of block copolymers in two steps. In the first one, two different salts of hexamethylene diamine are formed; one with carboxylic acid-terminated polyoxyethylene and the other one with adipic acid (nylon 6,6 salt). In the second step, the two salts are reacted in the melt. Caprolactam can be used in place of the second salt [431]. Also, a Japanese paper describes formations of block copolymers by reacting polyoxyethylene in melt condensation reactions with caprolactam in the presence of dicarboxylic acids [432].

Polyamide-6 (nylon 6) can form block copolymers with rubber [419] and with poly(dimethylsiloxane) [420]. In the latter case, the polysiloxane forms first by "living" polymerization and is terminated by an acylated caprolactam. The caprolactam portion of the molecule is then polymerized with the aid of lithium caprolactamate:



This diblock copolymer can be melt annealed at ca. 250°C. It exhibits superior mechanical properties to nylon 6 homopolymer [420].

9.7.11 Mechanochemical Techniques for Formation of Block Copolymers

These techniques rely upon high shear to cause bond scissions. Ruptured bonds result in formations of free radical and ionic species [413]. When this application of shear is done in the presence of monomers, block copolymers can form. This approach is exploited fairly extensively. Such cleavages of macromolecules can take place during cold mastication, milling, and extrusion of the polymers in the visco-elastic state. Both homolytic and heterolytic scissions are possible. The first one yields free radical and the second one ionic species. Heterolytic scissions require more energy, but should not be written off as completely unlikely [413]. Early work was done with natural rubber [413]. It swells when exposed to many monomers and forms a visco-elastic mass. When this swollen mass is subjected to shear and mechanical scission, the resultant radicals initiate polymerizations. The mastication reaction was shown to be accompanied by formation of homopolymers [413]. Later the technique was applied to many different polymers with many different monomers [414].

9.8 Processes in Polymer Degradation

There are many causes of degradation of polymers. The chief ones among them are heat, oxidation, light, ionic radiation, hydrolysis, and mechanical shear. The effect can be discoloration, loss of molecular weight, cross-linking, or cyclization. The loss of molecular weight can be so severe that the polymer is degraded to a mixture of monomers and oligomers. The other effects can be blackening or charring and loss of useful properties. On the other hand, mechanical shearing is often applied to some polymers like rubbers to deliberately reduce molecular weight for commercial processing. In the environment, synthetic polymers generally degrade due to man-made environmental pollutants in the atmosphere, like carbon monoxide, sulfur dioxide, nitrogen oxide, and oxidizing smog rich in ozone.

Molecular weight loss occurs through the breaking of primary valence bonds. Such chain scissions may occur at random points along the polymer backbone or they may take place at the terminal ends of the polymer where monomer units are released successively. This last effect can be compared to *unzipping*. The response of any particular polymeric material to specific causes of degradation depends upon the chemical structure.

This chapter presents the degradation processes in some typical commercial polymers. The materials selected were those that received major attention in the literature.

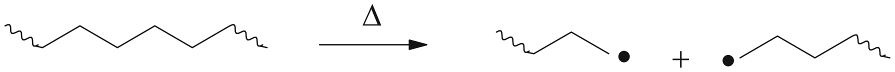
9.8.1 Thermal Degradation of Common Chain-Growth Polymers

Thermal degradation of polymers is conveniently studied by pyrolytic methods. The polymer literature contains many reports on such studies conducted at various temperatures in inert atmospheres, in air, or in vacuum. The volatile products are usually monitored with accompanying measurements of the weight loss per unit time. The reaction rates are thus measured by:

1. Loss of molecular weight as a function of temperature and the extent of degradation
2. The quantity and the composition of the volatile and nonvolatile products of degradation
3. The activation energy of the degradation process

A general scheme for thermal degradations of chain-growth polymers by free-radical reactions can be written as follows:

Random type chain scission:



Chain-end type scission:

In a thermal chain depolymerization, the degradation can also be random. Rupture occurs at various points along the chain. The products are various size fragments of the polymer, usually larger than individual monomers. Both reactions shown above can take place simultaneously in the same polymer chain or only one of them might take place exclusively. Also, chain depropagation may not necessarily be initiated from the terminal ends of the macromolecules, though such depolymerizations are more common. They may instead start from some points of imperfection in the chain structures. These imperfections might consist of incorporated initiator fragments, or peroxides, or ether links. They might have formed as a result of oxygen molecules being present during chain growths. Weak points in polymer backbones can also be at locations of some tertiary hydrogens. Each individual polymer will depolymerize at its own specific rate and the degradation products will be peculiar to the particular chemical structure of the polymer [446–452]. For instance, poly(methyl methacrylate) can be converted almost quantitatively back to the monomers. The depolymerization occurs from the terminal end in an unzipping fashion with the overall molecular weight decreasing slowly in proportion to the amount volatilized. Polyethylene, on the other hand, undergoes scission into longer olefin fragments. Very little monomer is released. At the same time, the molecular weight tends to decrease rapidly and only a small amount of volatilization takes place. The two polymers are good examples of extreme behavior of chain-growth polymers. Most of the chain-growth polymers, however, fall between the two. The depolymerization reaction of chain-growth polymers generally occurs by a free-radical mechanism and the reactions are similar. If depropagation is the major portion of the degradation process, then the molecular weight reduction is proportional to the quantity of the monomer that forms. If, on the other hand, chain transferring is the major portion of the degradation process, then there is rapid loss of molecular weight with little accompanying monomer accumulation and the reaction products are large segments of the chains. The rate of depolymerization exhibits a maximum.

When depropagation takes place at an elevated temperature, at a rate that is equal to the propagation in a free-radical polymerization, then the temperature of the reaction is a ceiling temperature (see Chap. 3). Termination can take place by disproportionation. Secondary reactions, however, may occur in the degradation process depending upon the chemical structure of the polymer. Such side reactions can, for instance, be successive eliminations of hydrochloric acid, as in poly(vinyl chrolide), or acetic acid as in poly(vinyl acetate).

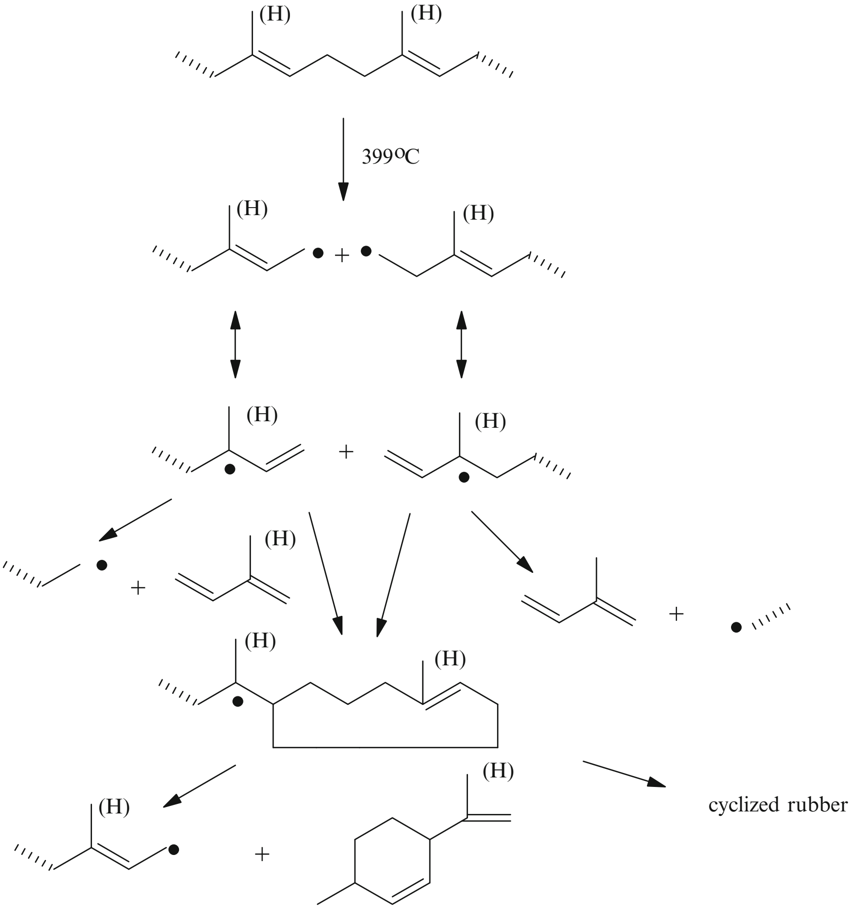
9.8.2 Thermal Degradation of Polyolefins and of Polymers from Conjugated Dienes

One early study of *thermal degradation of polyethylene* was carried out on low molecular weight polymers [453]. Later the work was repeated with high-density polyethylene [454]. The volatile products were identified by gas chromatography. The biggest portion of the volatiles was found to be propylene.

The remaining materials were methane, ethane, propane, and a number of unsaturated and saturated higher hydrocarbons. The quantity of ethylene increased slightly with an increase in the temperature of pyrolysis. Formation of propylene can occur in two ways. The first one is through intramolecular radical transfer to the second carbon, followed by a decomposition reaction. This, however, is not believed to contribute significantly to the quantity of propylene obtained, based on theoretical consideration [454]. The second one can occur as a result of scissions of C–C bonds located in the positions β to the terminal double bonds. Such double bonds probably form in large quantities during decomposition and this process is thought to be the main source of propylene [454]:

It was observed that *isotactic polypropylene decomposes* thermally by a mechanism that varies at different temperatures and conditions [455]. Thus, at 340°C the major volatile product is propane, while at 380°C it is *n*-pentane, and at 420°C it is propylene. The propane is believed to originate from some weak spot in the polymeric chain. Formation of *n*-pentane involves a radical abstraction and a six-membered ring formation in a backbiting process. Propylene may come from a free-radical depolymerization process or a cyclic six-membered ring formation involving a terminal double bond [455].

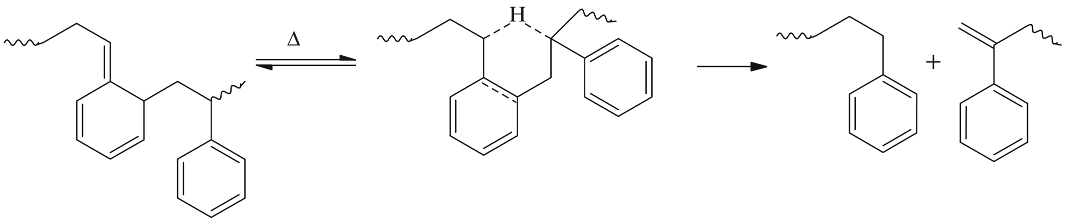
The thermal *degradation of diene polymers* was the subject of several studies [456, 457]. The scheme for polyisoprene and polybutadiene degradation was postulated in part by Golub and Garguila [458, 460]. It is based on infra-red spectra and NMR studies of the products:

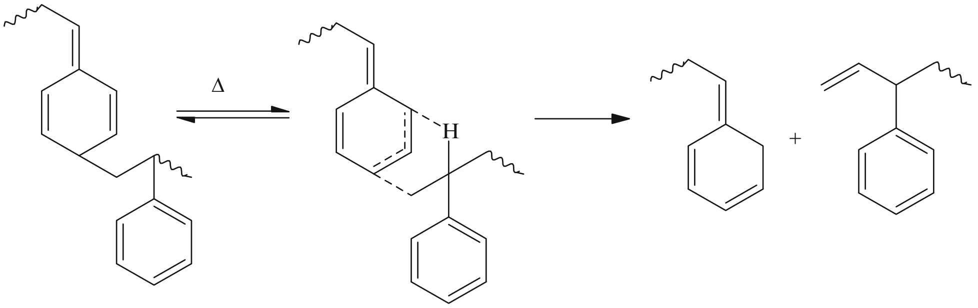


In addition, spectroscopic evidence shows that *cis–trans* isomerizations as well as cyclizations occur in the process of thermal degradation of 1,4-polyisoprene. It is interesting that the *cis–trans* isomerizations were observed at temperatures as low as 200°C [460].

9.8.3 Thermal Degradation of Polystyrene and Polystyrene-Like Polymers

Thermal *degradation of atactic polystyrene* results in formation of volatile products that contain as much as 42% of the monomer and small quantities of toluene, ethylbenzene, and methylstyrene. The rest of the volatile material is made up of dimers, trimers, and tetramers. No large fractions were isolated. This suggests that the main mechanism of decomposition is depropagation. The rate, however, exhibits a maximum and there is a rapid decline in molecular weight. This indicates scission of the chains. Some evidence was presented that rapid decrease in molecular weight is a result of scission of weak points in the polymer and is independent of the free-radical depropagation reaction [461–465]. Some of the weak spots are believed to be occasional "head-to-head" placement of monomers [19]. It was suggested that some weak spots may also be structures that form as a result of monomer additions to the aromatic ring during the chain growth (see Chap. 6) [466]. The following scheme of chain scission was, therefore, proposed [466]:





The identity of the weak spots, however, has not been established with certainty [467]. The evidence does indicate that the "weak points" are head-to-head bonds, branch points, or unsaturated structure [467].

The rate of conversion of polystyrene into volatiles was measured in numerous studies.

In contrast to polystyrene, poly(α-methyl styrene) yields in vacuum pyrolyses at temperatures between 200 and 500°C 95–100% monomer. By comparison, polystyrene only yields about 40.6% [457]. The difference can be attributed to the fact that hydrogen transfer is completely blocked from the sites of chain scission by the methyl groups in the α-positions [457]. As a result, the terminal free-radicals unzip into monomers and dimers.

Polystyrenes that are substituted on the benzene ring, like poly(vinyl toluene), behave similarly to polystyrene when pyrolyzed [457]. Also, poly(*m*-methylstyrene) at 350°C yields 44.4% monomer as compared to polystyrene that yields 40.6% monomer at these conditions. The rate, however, for polystyrene at this temperature is 0.24 mol.%/min, while for poly(*m*-methylstyrene) it is 0.9 [457].

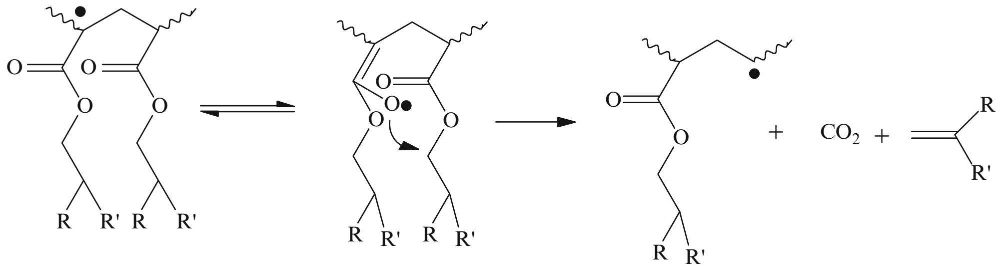
9.8.4 Thermal Degradation of Methacrylic and Acrylic Polymers

The thermal degradation of *polymers of acrylic* and *methacrylic alkyl esters* is a process of depolymerization to monomers at temperatures up to 250°C, provided that the alkyl group is small, less than butyl [468]. Poly(*t*-butyl methacrylate) yields quantitatively isobutene instead. It was shown that thermal depolymerization to monomers is probably common to all poly(methacrylate ester)s. As the size of the alkyl group increases, however, particularly within secondary or tertiary structures, there is increased tendency for the alkyl group to also decompose. This decomposition interferes with the depolymerization process

Thermal stability of poly(methyl methacrylate) appears to vary with the molecular weight. For instance, a sample of the polymer of molecular weight of 150,000 when heated in vacuum for 30 min at 318°C yields 74.3% volatiles. By comparison, a sample of this polymer of molecular weight of 5,100,000 when heated for 30 min at 319°C yielded only 35.2% volatiles [456].

The thermal stability of copolymers of long-chained diol dimethacrylates was investigated [583]. These copolymers included 1,4-butane-, 1,5-pentane-, 1,6-hexane-, 1,8-octane-, 1,10-decane-, or 1,12-dodecanediol dimethacrylates, respectively, as well as 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]propane and triethylene glycol dimethacrylate. The polymers were found to be thermally stable up to ≈250°C, as shown by the initial decomposition temperature and their degradation profiles.

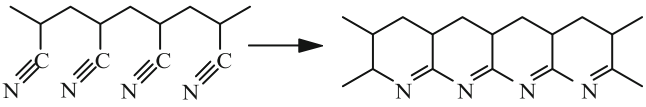
A quantitative investigation of the thermal degradation of poly(ethyl acrylate), poly(*n*-propyl acrylate), poly(isopropyl acrylate), poly(*n*-butyl acrylate), and poly(2-ethylhexyl acrylate) demonstrated that the principle volatile products are carbon dioxide, olefin, and alcohol corresponding to the alkyl group [469, 470]. The following mechanism of degradation was proposed [469, 470]:



More recently, another study was carried out on the thermal decomposition of homopolymers of ethyl methacrylate, *n*-butyl methacrylate, and 2-hydroxyethyl methacrylate as well as their copolymers [471]. The copolymers of hydroxyethyl methacrylate with ethyl methacrylate and butyl methacrylate were found to degrade by unzipping to yield the monomers similarly to poly(methyl methacrylate). In addition, there is competition between unzipping and cross-linking in binary copolymers of hydroxyethyl methacrylate with ethyl methacrylate and in *n*-butyl methacrylate.

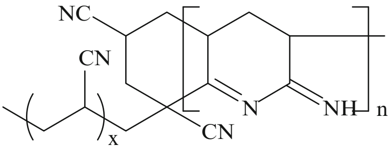
Thermal degradation of *nitrile polymers*, particularly acrylonitrile, was studied in detail [472–478]. It was shown that there can be two paths of degradation, depending upon the temperature (see also Chap. 8). One reaction takes place at a low temperature, between 100 and 200°C, and the other one occurs above 240°C. At the low temperature, the polymers develop dark color. There is, however, very little evolution of volatiles. At the high temperature, on the other hand, there are evolutions of volatiles and thermally stable residues develop.

The low temperature darkening process of polyacrylonitrile was shown to be intramolecular cyclization and polymerization of the cyanide groups [475, 476]. The overall reaction can be illustrated as follows:



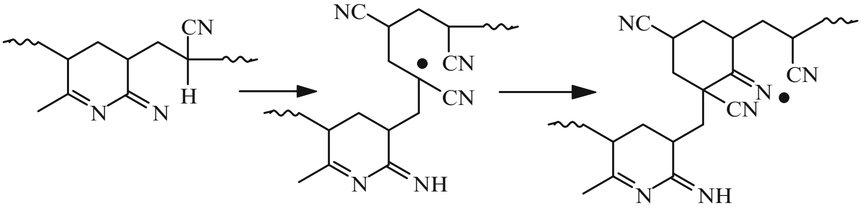
The above shown ladder structure is actually a vary idealized picture. Nevertheless, the formation of fused tetrahydropyridine rings was demonstrated by IR data [475, 476]. At the same time, there are many irregularities in the above shown structure. Also, it was demonstrated that the longer are the isotactic sequences in the polymeric structures, the longer are the sequences of ladder structures that form [479].

High temperature degradation of polyacrylonitrile leads to formation of oligomers. The general form of the oligomerized material can be shown as follows [480]:



where, $x = 0$–2 and $n = 0$–5.

The above structure occurs as a result of an initiation and termination process of cyclization at frequent intervals along the chain. The growth of the ladder structure, however, terminates due to hydrogen transfer. This process is associated with the atactic sequences in the polymer chain:



Polymethacrylonitirle develops color upon heating as a result of linking up of adjacent carbons and nitrogen atoms in intramolecular cyclization reactions similar to acrylonitrile.

This reaction is initiated primarily by impurities that are often present in the polymer both at the end of the chains and at various locations at the backbones. Due to this ring formation, the amount of monomer that can be obtained from the polymer at 200°C is approximately 50%. If, however, the polymer is prepared from highly purified monomer, the yield of monomer upon thermal degradation at 300°C is 100%. Also, a yellow color does not develop from such a polymer at temperatures of 120–220°C [457].

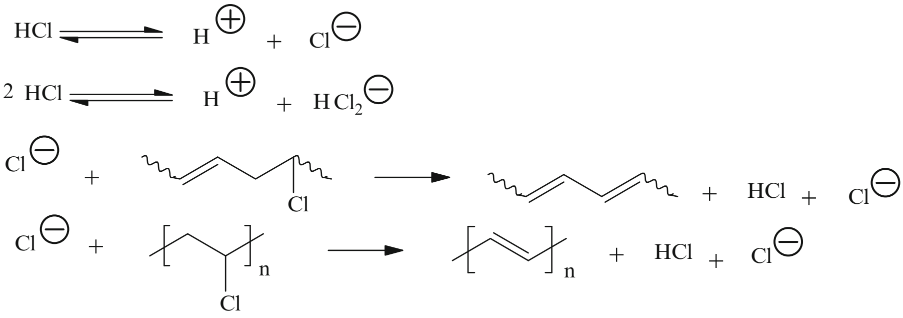
Poly(vinylidine cyanide) has the structure that would suggest formation of a double ladder polymer upon pyrolysis. It was shown, however, in an early study that this does not happen. Instead, the polymer mostly depolymerizes [481, 482].

9.8.5 Thermal Degradation of Chlorocarbon and Fluorocarbon Polymers

The thermal instability of *poly(vinyl chloride)* is a cause for concern commercially and has, therefore, stimulated extensive investigations. The overall process of degradation is complex and still not completely resolved. Some of the questions that remain are:

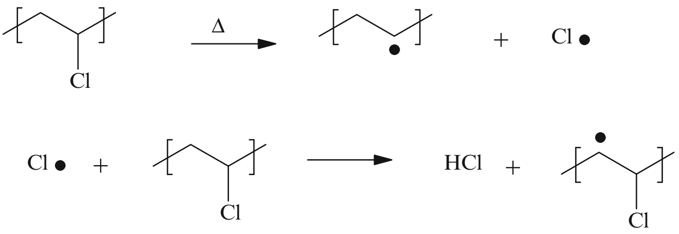
1. Is the overall process of degradation ionic or free radical in nature?
2. What is the exact mechanism of initiation?

It is easily observable that the degradation is accompanied by evolution of HCl and blackening of the polymer. Also, at elevated temperatures, poly(vinyl chloride) not only gives off hydrogen chloride, but this dehydrochlorination is also accompanied by rapid depolymerization [483]. The rate of decomposition decreases with increasing molecular weight and is highest in oxygen and lowest in helium atmosphere. It was claimed that HCl exerts no catalytic effect upon the rate of decomposition [483]. This contrasts with evidence that was presented earlier that HCl does accelerate thermal degradation [484]. The earlier evidence was obtained from autocatalytic decmposition of films. Based on that eveidence, it was hypothesized that the chloride ion acts as a base (supporting an ionic mechanism of decomposition) [484]:

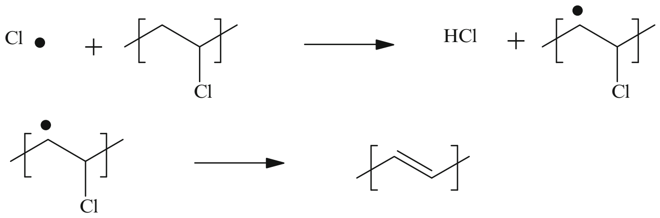


In a more recent study, HCl was also found to be essential for the initiation of the unzipping process, but may or may not be essential to the depolymerization reaction itself, once the process has been started [485]. The above shown ionic mechanism was disputed in a study where ESR signals were recorded during thermal decomposition of the polymer at elevated temperatures [486]. This strongly supports a free-radical mechanism. A free-radical mechanism was proposed earlier by Bamford and Feuton [487]. This mechanism illustrates the formation of hydrochloric acid and is based on rupture of carbon–chlorine bonds:

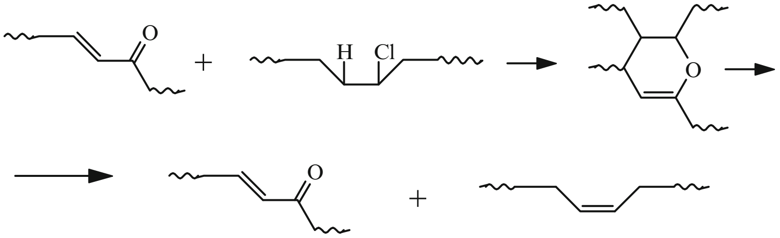
Initiation:



Propagation:

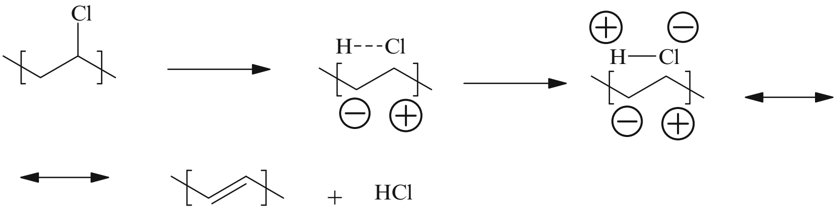


Subsequent interaction of macromolecular radicals leads to cross-linking. Many additional investigations demonstrated that thermal decompositions of vinyl polymers with pendant electronegative groups that we can designate as X, result, after elimination of HX and formation of macromolecular residues, with polyene structures [488]. In addition to that, at higher temperatures the polyene sequences that form rearrange into a large numbers of aromatic hydrocarbons [489–492]. Formation of polyenes is common to poly(vinyl chloride), poly(vinyl bromide), poly(vinyl alcohol), and poly (vinyl acetate) [493]. The polyene structures partly decompose at formation due to bond stress and molecular reorganization processes. The stresses result from formation of conjugated structures along the polymeric chains. When the chains fracture, the remaining portions of polyene sequences form aromatic compounds [47]. It was postulated that the process initially involves reactions of enone groups, which are present in poly(vinyl chloride) as anomalies, with chlorine units of a neighboring polymeric chains [494, 495]:



The first step is formation of a dihydropyran ring. This is followed by a retro-Diels-Alder splitting and leads to regeneration of the α,β-unsaturated ketone and to formation of a double bond in the poly (vinyl chloride) molecule. The double bond initiates a subsequent elimination of hydrogen chloride from that molecule [495].

An intramolecular initiation process that explains constant rate of dehydrochlorination was also proposed [496]:



It was pointed out that poly(vinyl chloride) is, in a sense, its own worst enemy, in that all the structural defects that are known to contribute appreciably to its thermal instability. They are formed in the polymer molecules during the process of polymerization by routes involving hydrogen abstraction from the polymer backbone [584].

Gupper et al. used micro Raman spectroscopy to study thermal degradation of poly(vinyl chloride) containing various additives [586]. They observed a linear increase in conjugated sequences in the process of dehydrochlorination.

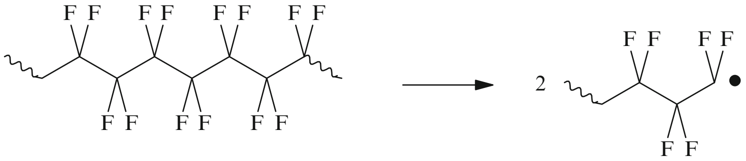
Carty and coworkers investigated thermal decomposition of chlorinated poly(vinyl chloride) [496]. The thermal decomposition of pure chlorinated poly(vinyl chloride) (without stabilizer or lubricant) was studied by dynamic thermogravimetric analysis at heating rates from 5 to 100°C/min in atmospheres of nitrogen, air, and oxygen. In each case, a two-step decomposition was observed, similar to that for poly(vinyl chloride) where dehydrochlorination is followed by pyrolysis/oxidation of the carbonaceous residue. The rate of dehydrochlorination was dependent on atmosphere, occurring slightly slower in nitrogen than in air, and slightly more quickly in oxygen than in air. The decomposition of the residual char was clearly dependent on the conditions that it formed in. Under dynamic conditions, chars formed at high heating rates appeared more resistant to oxidative degradation than those formed more slowly. However, when chars were formed by heating at different rates and then held at 500°C, the char formed at the slowest heating rate was the slowest to be oxidized. The uptake of oxygen by the char appears to be rate limiting. At low heating rates, char oxide is similar in both air and oxygen. As the heating rate is raised, the rate of mass loss of char in air becomes progressively closer to that in nitrogen until at 100°C/mm they are almost identical.

The rates of thermal decompositions of *poly(vinylidine chloride)s* were shown to depend upon the method by which the polymers were prepared [497]. Those that were formed from very pure monomers by mass polymerization are most stable. Polymers prepared by emulsion polymerization, on the other hand, degrade fastest. The mechanism of degradation of poly(vinylidine chloride) was proposed to be as follows [498–500]:

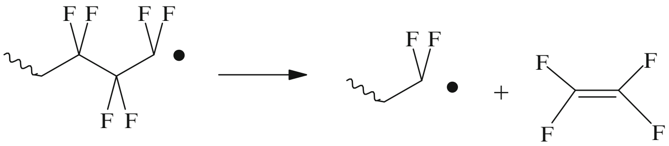
1. Hydrochloric acid is eliminated in a chain reaction.
2. Conjugated sequences condense to form cross-linked structures.

Some support for the above mechanism came from stepwise heating studies of poly(vinylidine chloride) [501].

Although *polytetrafluoroethylene* has the reputation for being quite stable thermally, it does degrade at elevated temperatures. The polymer upon pyrolysis yields almost 100% of monomer. The mechanism is believed to be free-radical unzipping of the chains until the entire chain is consumed. This can be illustrated as follows [457]. Initially, the chain ruptures:



this is followed by formation of monomers:

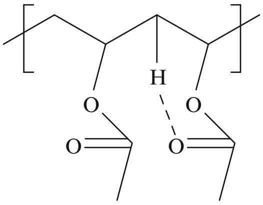


Polychlorotrifluoroethylene is less stable thermally than polytetrafluoro-ethylene. It yields as much as 86.0% volatiles in 30 h at 331.8°C [11]. These volatiles contain large amounts of monomer. A mechanism that resembles the postulated degradation mechanism of polytetrafluoroethylene was proposed [457].

Unlike polytetrafluoroethylene, *polyvinyl fluoride, poly(vinylidine fluoride),* and *polytrifluoroethylene* yield primarily on heating HF [457]. Among these three, poly(vinylidine fluoride) yields larger amounts of HF than do the other two polymers with an accompanying formation of double bonds.

9.8.6 Thermal Degradation of Poly(Vinyl Acetate)

Thermal decomposition of poly(vinyl acetate) results in a loss of acetic acid. The reaction is typical of thermal cleavages of esters. It is facilitated by formation of pseudo six-membered rings as a result of interactions between the β-hydrogens of the alcohol residues and the carboxylic groups:



When double bonds form, adjacent methylene groups become activated. The loss of acetic acid is the main product at temperatures up to 200–250°C. Beyond these temperatures, aromatic pyrolytic compounds form.

Studies of thermal degradation of copolymers of vinyl chloride with vinyl acetate showed that the copolymers are thermally less stable than the homopolymers [502, 503]. The ratio of hydrochloric acid to that of acetic acid that volatilize remains constant during the degradation. This indicates that neither is evolved preferentially, once the reaction begins [502, 503]. It is interesting to note that degradation studies of a copolymer of vinyl chloride and styrene also demonstrated that the copolymer is less stable than each of the homopolymers [504].

9.9 Thermal Degradation of Common Step-Growth Polymers

The thermal decomposition of step-growth polymers cannot take place by a chain reaction like that of chain-growth polymers. As a result, these materials degrade in a random fashion, rupturing at the weakest bonds first.

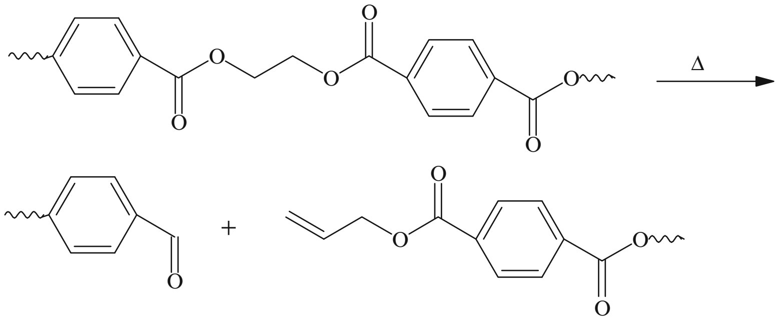
9.9.1 Thermal Degradation of Polyoxides

Polyoxymethylene depolymerizes into formaldehyde at 220°C. This was found to be a first-order reaction with the rate varying from 0.42 to 5.8%/min, depending upon conditions of polymer preparation and the molecular weight of the polymer [457].

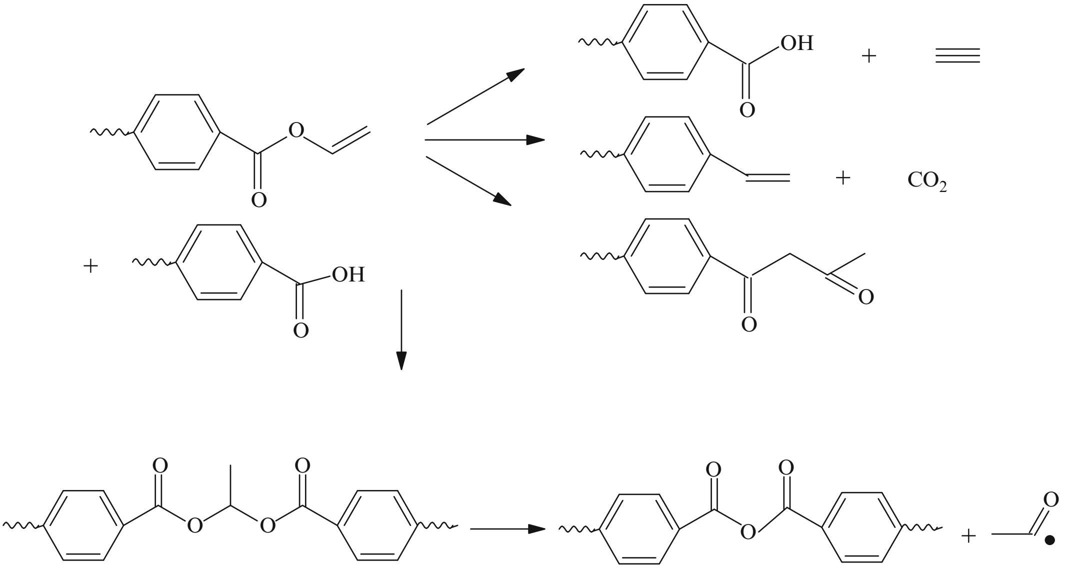
Poly(ethylene oxide) decomposes upon heating at lower temperatures than does polyethylene. Among the volatile products are found formaldehyde, ethanol, ethylene oxide, carbon dioxide, and water. *Poly(propylene oxide)* is also less heat stable than polypropylene. Isotactic poly(propylene oxide) is somewhat more stable than the atactic one.

9.9.2 Thermal Degradation of Polyesters

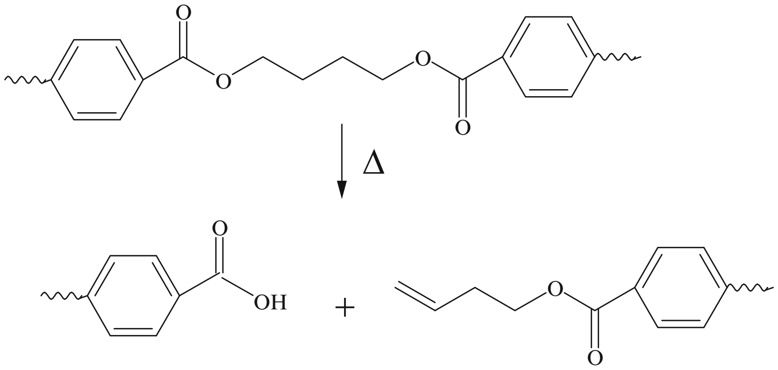
Poly(ethylene terephthalate) decomposes upon heating through a series of different reactions. These run either concurrently or consecutively. The result is a complex mixture of volatile and nonvolatile products. It was found that when poly(ethylene terephthalate) is maintained in molten condition under an inert atmosphere at 282–323°C, it slowly converts to a mixture of gaseous low molecular weight fragments [581]. The major products from pyrolysis of poly(ethylene terephthalate) are carbon dioxide, acetaldehyde and terephthalic acid. In addition, there can be detected trace amounts of anhydrides, benzoic acid, *p*-acetylbenzoic acid, acetophenone, vinyl benzoate, water, methane, ethylene, acetylene, and some ketones [505]. The following mechanism of degradation was postulated [505]:



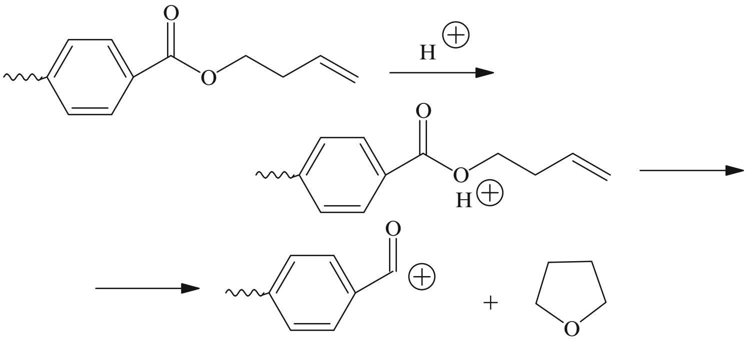
The vinyl end groups that form from cleavage of the ester groups decompose further in a number of ways:



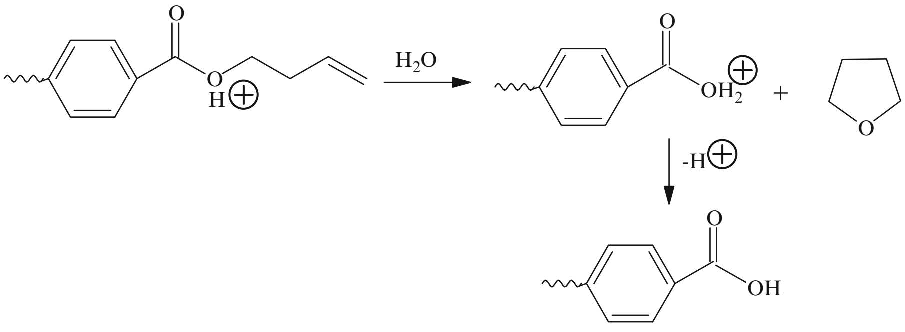
The thermal degradation of *poly(butylene terephthalate)* was examined with the aid of a laser microprobe and mass spectrometry [506]. A complex multistage decomposition mechanism was observed that involves two reaction paths. The initial degradation takes place by an ionic mechanism. This results in an evolution of tetrahydrofuran. This is followed by concerted ester pyrolyses reactions that involve intermediate cyclic transition states and result in formation of 1,3-butadiene. Simultaneous decarboxylations occur in both decomposition paths. The latter stages of decomposition are characterized by evolutions of carbon monoxide and various aromatic compounds, like toluene, benzoic acid, and terephthalic acid. The first step can be shown as follows [506]:



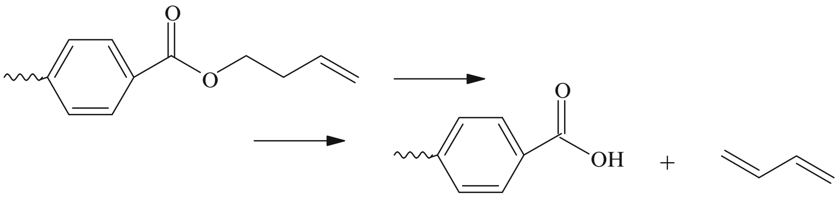
The subsequent decomposition, shown below, can actually take place at lower temperatures:



There are indications that there is moisture among the decomposition products. This may imply that acid hydrolysis plays a part in tetrahydrofuran formation:



At higher temperatures, the reaction path involves elimination of 1,3-butadiene [506, 507];



In oxidations of hydrocarbons, oxygen is believed to act as a diradical in the ground state. This would explain radical combination reactions:

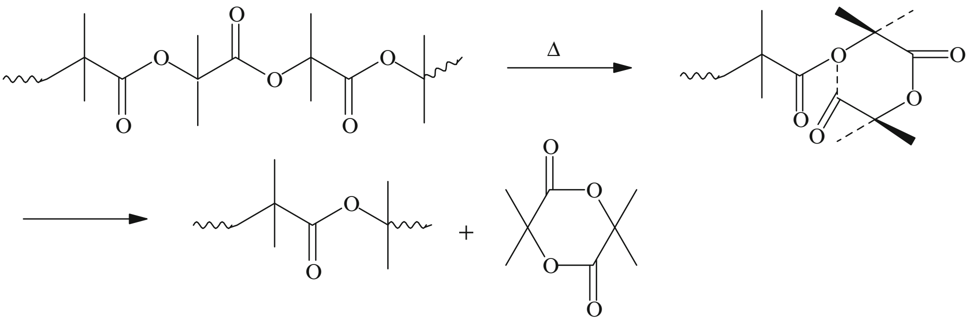
$$\mathrm{R{\bullet}+{\bullet}O{-}O{\bullet}} \rightarrow \mathrm{R{-}O{-}O{\bullet}}$$

and the subsequent hydrogen abstraction reaction:

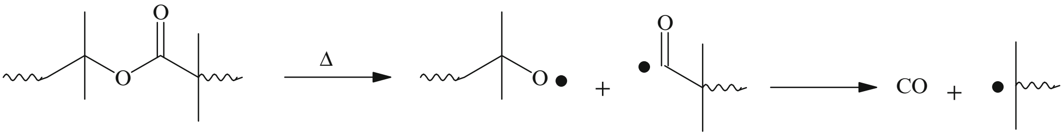
$$\mathrm{R-O{-}O{\bullet}} + \mathrm{R'}H \rightarrow \mathrm{RO-OH} + \mathrm{R'{\bullet}}$$

The rate of formation of the peroxy radical is much higher than is the rate of hydrogen abstraction [521]. The overall rate of oxidation of polymeric materials by atmospheric oxygen is strongly affected by light, heat, oxygen concentration, moisture, and the presence of traces of impurities. The impurities, however, can act as either catalysts or as inhibitors of oxidation.

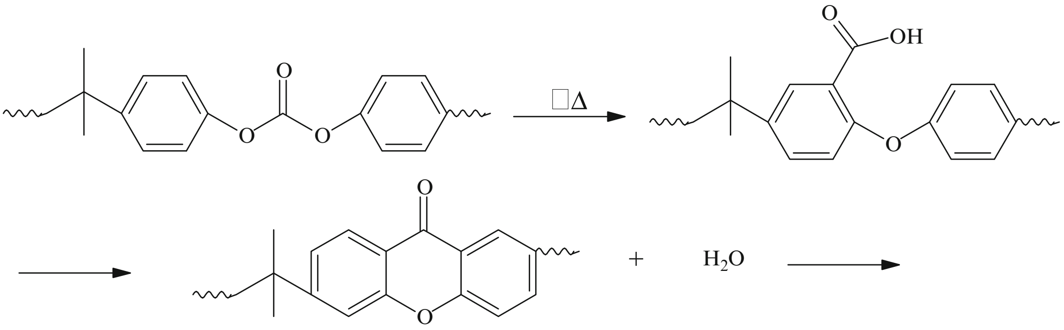
The degradation of *poly-α-esters* was studied on poly(isopropylidine carboxylate) [518] over a range of temperatures, from 200 to 800°C. Among the decomposition products were found tetramethyl glacolide, acetone carbon monoxide, and to a lesser extent methacrylic acid. The primary decomposition product appears to be tetramethylene glacolide that becomes an intermediate upon further pyrolysis:

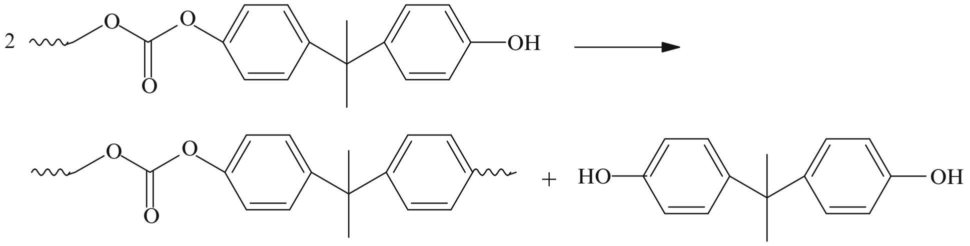


also:



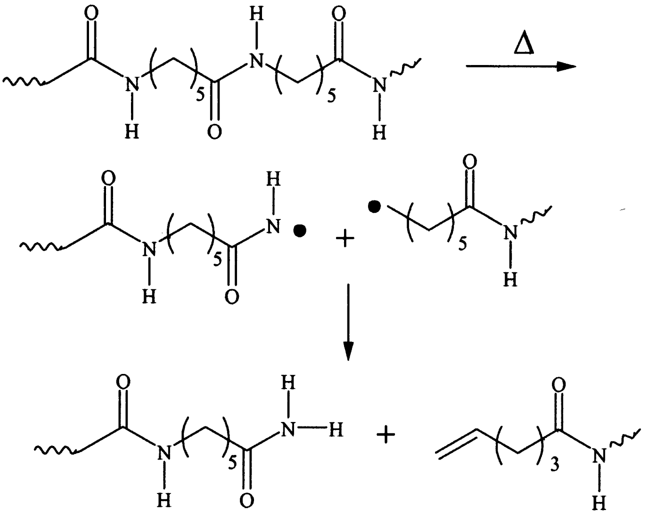
Decomposition of polycarbonates was studied on poly[2,2′-propane-bis-(4-phenyl) carbonate] [519]. It was concluded that a rearrangement mechanism is the main intermediate material in subsequent formation of carbon dioxide and volatile phenolic compounds [519]:



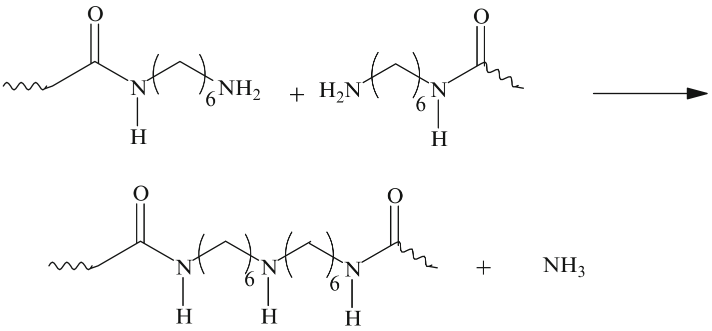


9.9.3 Thermal Degradation of Polyamides

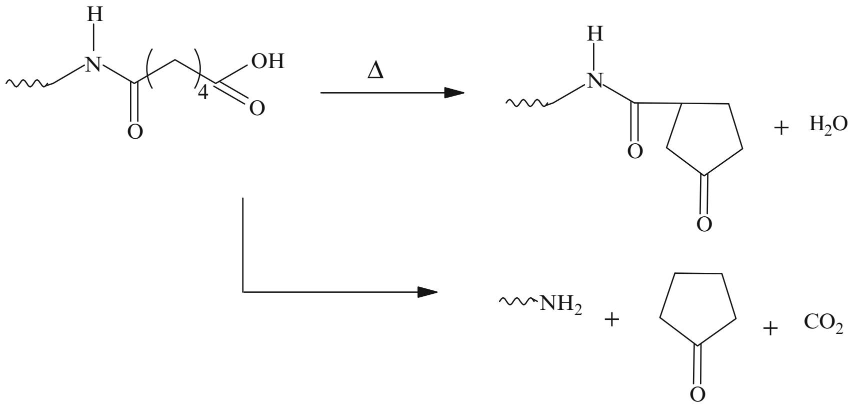
The thermal degradation of polyamides starts with free-radical cleavage of nitrogen–carbon bonds [520]. Degradation of *nylon 6* can be illustrated as follows:



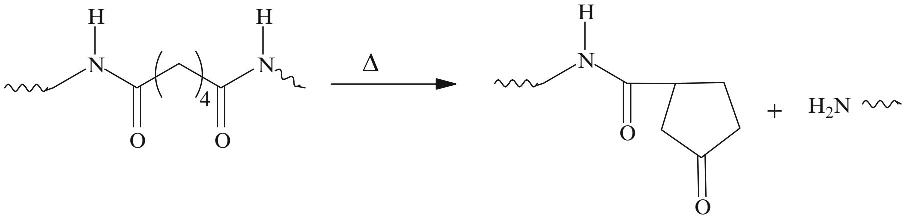
When nylon 6 is heated for 100 h at 305°C, half of the nitrogen escapes from the polymer and a small amount of carbon dioxide forms [457]. This was postulated by Kamerbeek et al. as being the result of reactions of two terminal amine groups [579]:



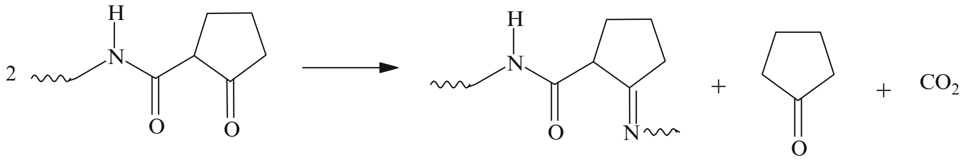
In decomposition of *nylon 6,6,* there is the additional tendency for ring closure by adipic acid [509]:



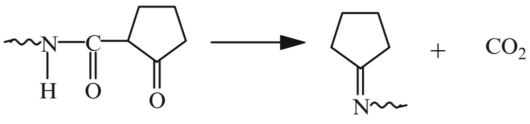
The cyclization reaction can also occur as follows [509]



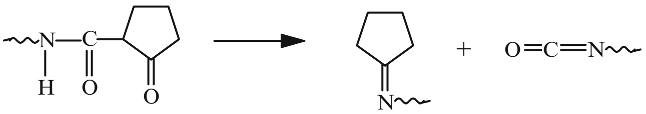
or, perhaps, as a bimolecular reaction [509]:



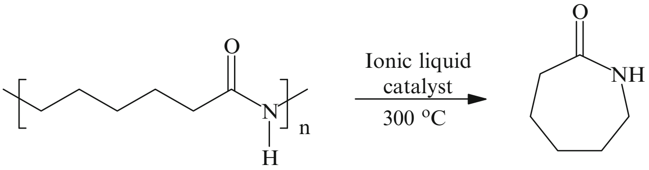
At higher temperatures, the carbamoyl ketone might convert to the Schiff base by a monomolecular process [509]:



The route to the Schiff base may also be through elimination of an isocyanate [509]:



Rather than thermal degradation of nylon 6, it is possible to depolymerize this polyamide. Kamimura and Yamamoto reported that it is possible to depolymerize this nylon back to caprolactam [510]:

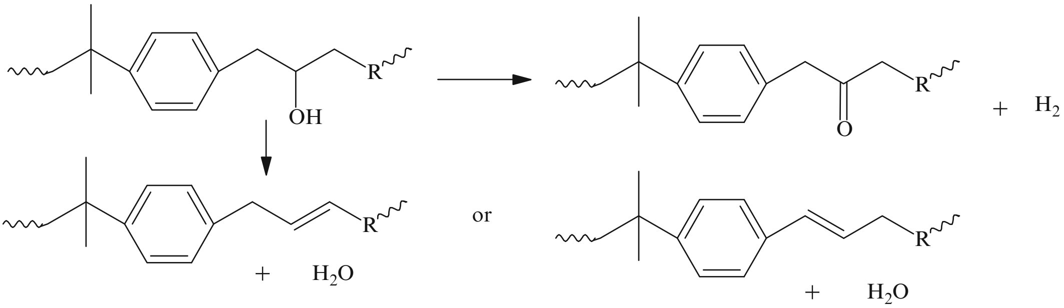


The best yield of caprolactam was 86% obtained with *N*-methyl, *N*-propyl piperidinium bis (trifluoromethyl-sufonyl)imide as the solvent and *N*,*N*-dimethylpyridine as the catalyst.

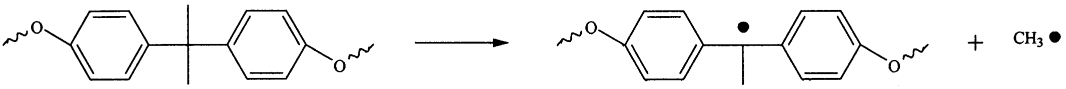
In the past, it was believed that at high temperatures nylons degrade at a faster rate at elevated humidity. This assumption, however, was shown to be erroneous by Bernstein et al. [457].

9.9.4 Thermal Degradation of Epoxy Resins

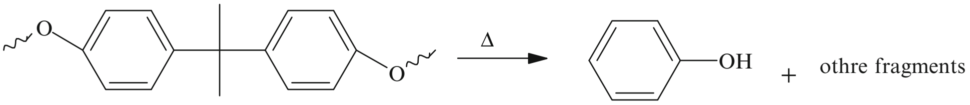
The thermal degradations of *Bisphenol A-based epoxy resins* cross-linked with diaminodiphenylmethane or with phthalic anhydride were studied with the aid of pyrolysis and radiochemical gas chromatography technique [511]. The products of degradation depend upon the temperature. At 400°C, the amine cross-linked resins yield hydrogen, methane, and water. The resins cross-linked with phthalic anhydride yield hydrogen, methane, carbon dioxide, and water. The number of degradation products increases with temperature. It was concluded that the most important nonscission reactions in these resins are competing with dehydration and dehydrogenation reactions [511]:



A nonscission reaction that yields methane is:

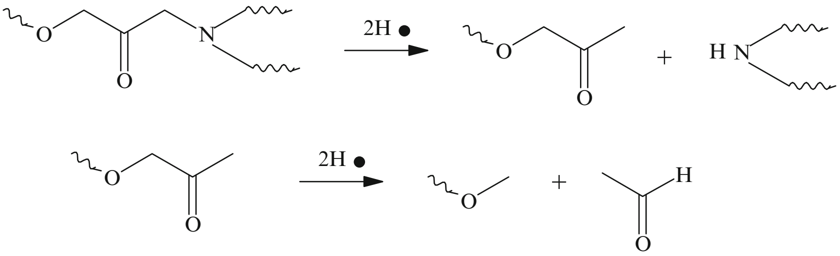


The scission reactions can take place at various weak spots. The breakdown of bisphenol A segments produces phenol [511]:

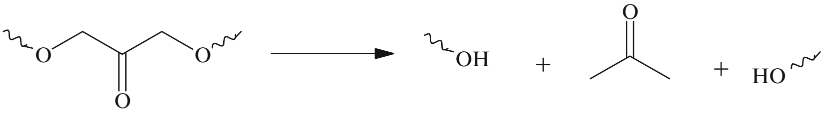


The main differences that were observed between amine-cured and anhydride-cured resins are [511]:

1. The amine cross-linked resin generated more water and hydrogen, because they contained more $–CH_2–CHOH–CH_2–$ groups.
2. Scissions of anhydride-reacted resins tend to regenerate the anhydride and release CO and CO_2 in large quantities
3. The aliphatic segments of the amine cross-linked resins yield more acetaldehyde than acetone. The reverse is true of the anhydride-cured resins. This is thought to be due to preferential rupture of carbon–nitrogen bonds [511]:

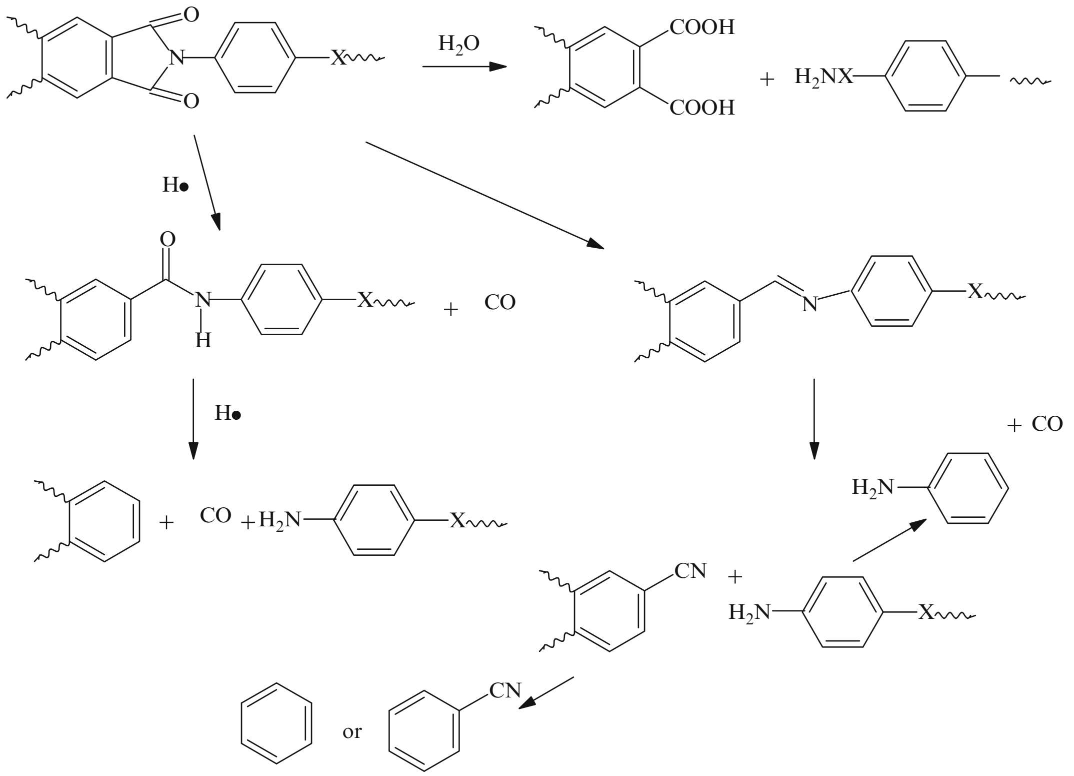


The anhydride-cured compositions may tend to break up symmetrically instead:



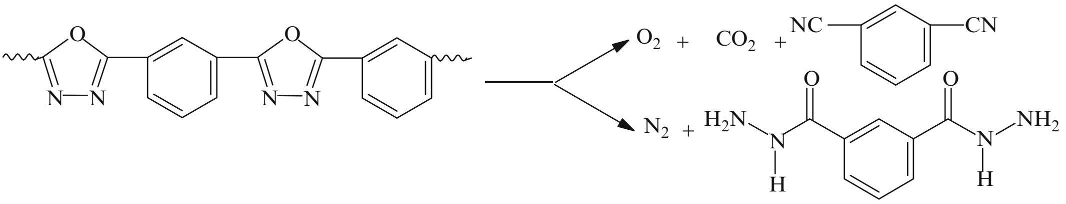
9.9.5 Thermal Degradation of Polyimides, Polyoxidiazoles, and Polyquinoxalines

The technique mentioned in the previous section of pyrolysis and radiochemical gas chromatography was also applied in a study to thermal degradation of *aromatic polyimides* [512]. Aromatic polyimides are more stable thermally than previously discussed polymers and require higher temperature for decomposition. Based on the experimental results, the following mechanism was proposed [512]. Initially, hydrogen radicals form. They come from various places of the polymer backbone during the pyrolytic decomposition. Also, decomposition of amic acid may yield water (see Chap. 6).

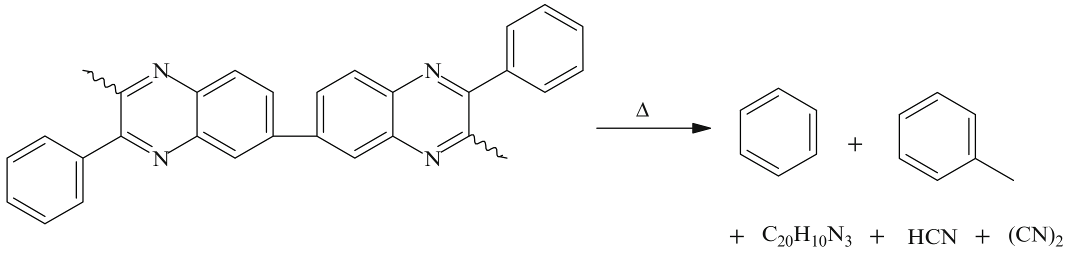


Another study of thermal degradation of aromatic polyimides led to similar conclusions [513]. At lower temperatures, the degradation of polyimides proceeds by a hydrolytic mechanism that is greatly influenced by presence of uncyclized units. At higher temperatures, the degradation is mainly by decarbonylation of the imide ring and breaking down of the polymer chain through "weak" bonds.

The thermal *degradation of polyoxidiazoles* was shown to proceed mainly through the heterocyclic rings that are apparently the weak spots [514, 515]:



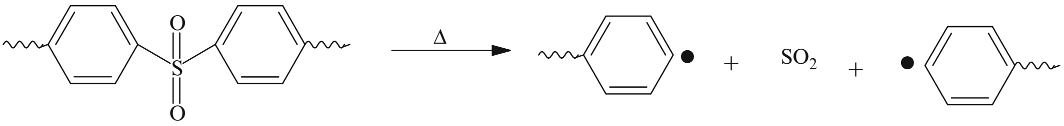
The process by which aromatic polyquinoxalines decompose is random. At 500–600°C, it involves the opening of the heterocyclic ring with loss of fragment [516]:



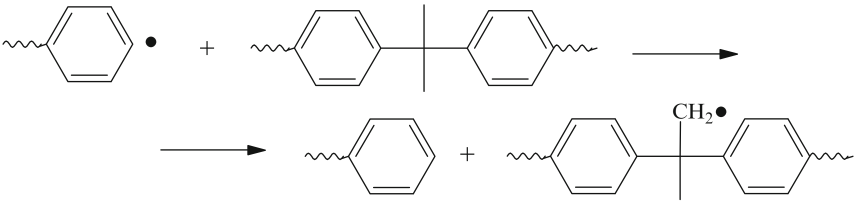
At still higher temperatures, between 640 and 690°C dehydrogenation of nitrogen residues takes place.

9.9.6 Thermal Degradation of Aromatic Polysulfones

In *aromatic polysulfones,* the weakest link was found to be the carbon–sulfur bond [517]. These polymers are processed at about 300°C. At that temperature, the thermodegradative processes as well as thermo-oxidative ones can occur. The rupture of the C–S bonds produces molecules of SO_2 and fragments of the polymer molecules with terminal phenyl radicals [517]:



The phenyl radicals then abstract hydrogens from the methyl groups that are present when the polysulfone is prepared from bisphenol A:



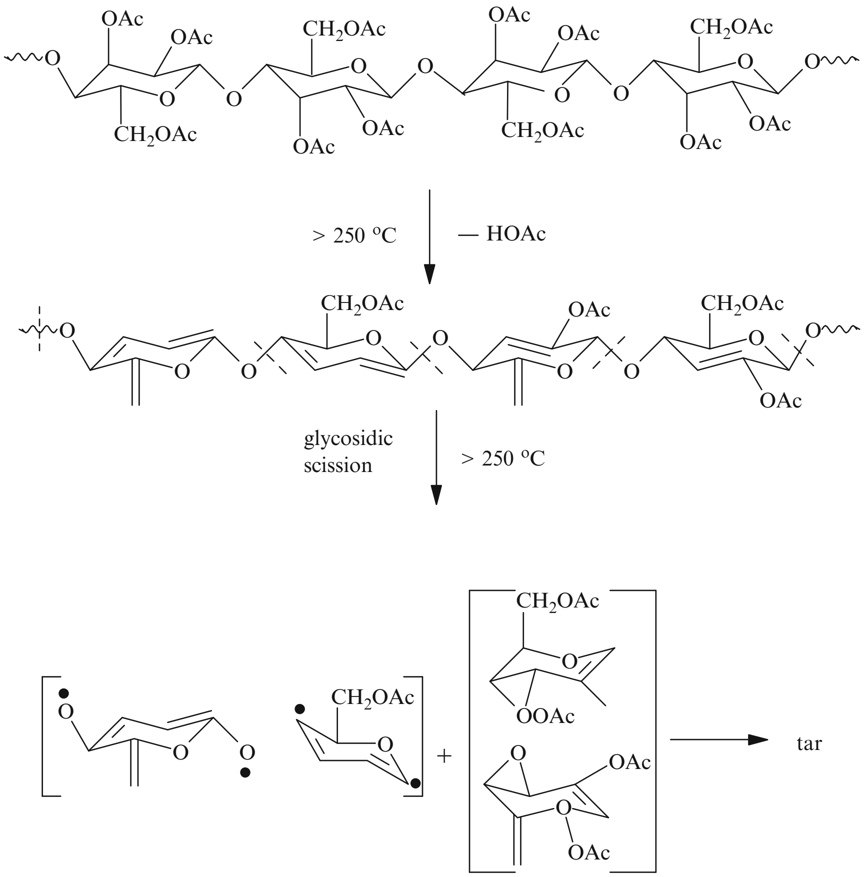
9.9.7 Thermal Degradation of Polyethers

The *aromatic polyethers* are subject to rupture at the ether link at around 300°C [518]. Products from such ruptures are somewhat similar to those obtainable from decomposition of the polysulfones, shown above.

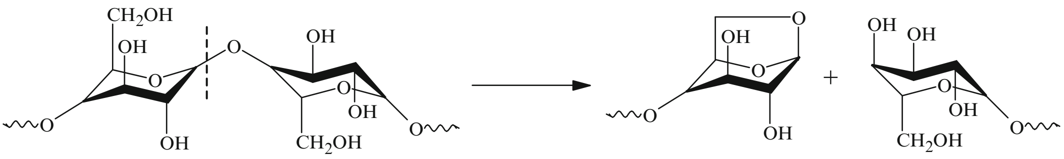
The thermal degradation of *polyoxymethylene* was found to be initiated at the chain ends. There appear to be three possible sites for initiation of homolytic bond cleavages [519]:

9.9.8 Thermal Degradation of Cellulosic Materials

The degradation of cellulose triacetate in vacuum was analyzed with the aid of chromatography, mass spectrometry, infra-red, and NMR spectroscopy [517]. The mechanism of degradation was proposed by Scotney to consist primarily of deacetylation in the polymer chain and scission of the chain at the 1,4 glycosidic linkage between the pyranose rings [517]. The type of products that are formed depends upon the degradation temperature. At temperatures above 250°C but below 350°C, unstable intermediates form. Continued heating results in loss of carbon monoxide, carbon dioxide, and acetic acid, and eventually end in formation of tar. Heating above 350°C causes condensation of radical intermediates, cross-linked aromatic, and hydroaromatic ring systems. This can be illustrated as follows:



The mechanism of thermal degradation of cellulose appears to include two reactions. The first reaction consists of dehydration and the second one of scission of C–O bonds in the chains between the rings or within the rings [457]. This can give rise to levoglucosan [457]:



9.9.9 *Hydrolytic Degradation of Polymers at Elevated Temperatures*

Hydrolytic degradation is only significant in polymers with chain links that can react with water, such as polyesters. A recent study reports on depolymerization of poly(ethylene terephthalate) during processing, if the material is not dried thoroughly, prior to melting [530]. The hydrolytic depolymerization of poly(ethylene terephthalate) was carried out in a stirred batch reactor at 235, 250, and 265°C above the polymer melting point and under autogenous pressure. The solid products were mainly composed of terephthalic acid. The liquid products were mainly composed of ethylene glycol and a small amount of its dimer. Moreover, an autocatalytic mechanism was detected. That indicates that some of the hydrolytic depolymerization of PET is catalyzed by the carboxylic acid groups produced during the reaction. The dependence of the rate constant on the reaction temperature was correlated by the Arrhenius equation [530].

9.9.10 Oxidative Degradation of Polymers

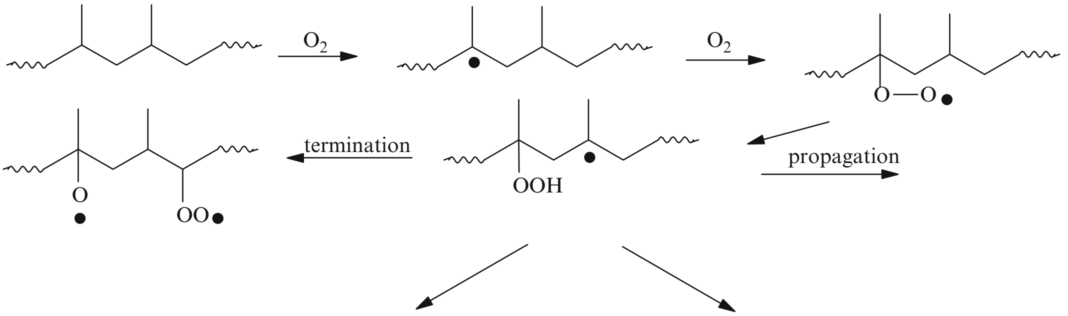
This section deals not only with oxidative reactions of polymers at room temperature, but also with thermo-oxidative degradation at elevated temperatures. Although this type of degradation resembles photo-oxidative degradation, for the purpose of maintaining clarity, the latter is discussed separately in the next section.

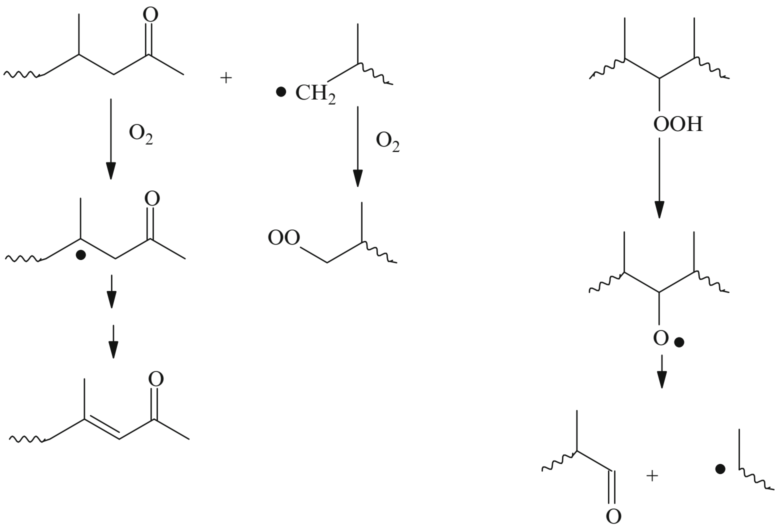
The simplest oxidative reactions occur in hydrocarbon polymers. This free-radical process generally follows the same path as the oxidation of low molecular weight compounds. The difference, however, is in the propagation of the reaction. In oxidation of low-molecular weight hydrocarbons, each step of chain propagation results in transfer of active center from on molecule to another. In polymers, however, the probability of such a transfer is low. Instead, the oxidation propagates along the polymer backbone [520].

9.9.11 Oxidation of Chain-Growth Polymers

Polymers that lack double bonds, like polyethylene, can be considered high molecular weight paraffin. They are slow to oxidize in the absence of UV light, much like the low molecular weight hydrocarbons. On the other hand, polymeric materials with double bonds oxidize rapidly. Nevertheless, polymers like polyethylene may oxidize rapidly as well when contaminated with metallic ions because such ions catalyze the decomposition of peroxides.

The chemical structure of the polyolefins determines their susceptibility to oxidative degradation. Linear polyethylene, in the absence of additives, is more resistant to oxidation that polypropylene that oxidizes rather readily due to the presence of labile tertiary hydrogens. It was demonstrated, for instance, that the molecular weigh of polypropylene sheets in a 138°C oven can drop from 250,000 to approximately 10,000 in 3 h [522]. The process of oxidation was shown to take place according to the following scheme [522]:



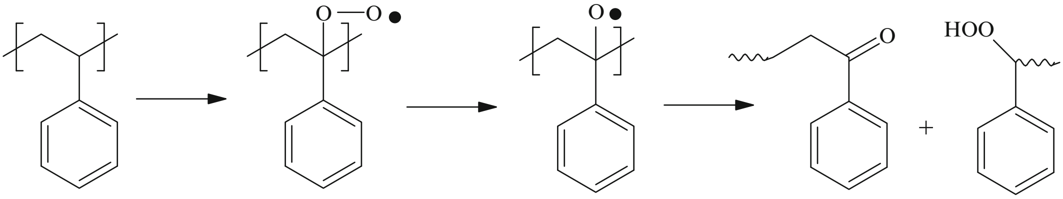


Further oxidative degradation of fragments leads to formation of a carboxylic acid, an ester, and a γ-lactone [522]. It was also found that the main oxidation products of polyethylene are an acid and a ketone. On the other hand, polypropylene yields upon oxidation approximately equal quantities of an acid, a ketone, an aldehyde, an ester, and a γ-lactone [522].

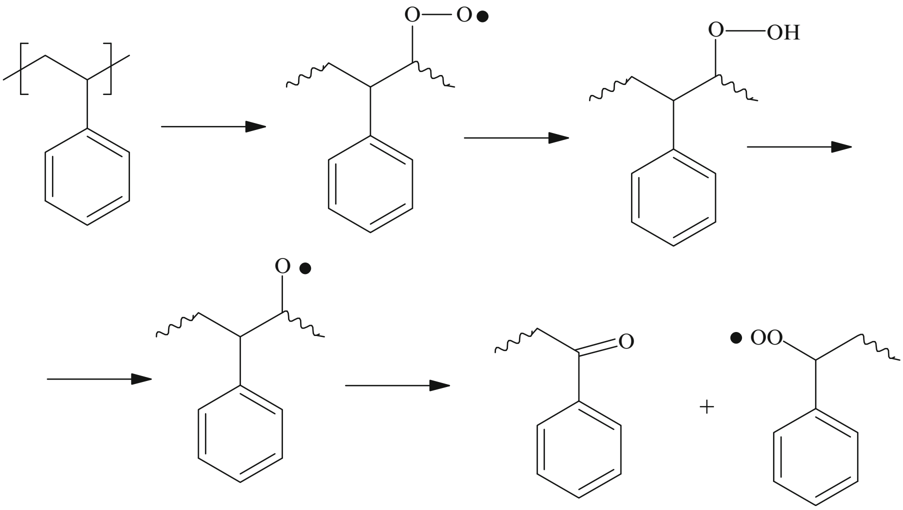
In order for a polymer molecule to be attacked by oxygen, it must come in contact with it. This means that oxygen must be able to permeate into the material. Otherwise, all the oxidation will occur only at the surface. It was shown that oxidation occurs more readily in amorphous regions of the polymers where permeation of oxygen is not hindered by the chains being packed tightly together in the crystallites. That is only true, of course, at temperatures below T_m of the polymer.

Among the chain-growth polymer, oxidation of *polystyrene* was investigated thoroughly. It was found that the rate of oxygen absorption and the number of chain scissions remain constant up to a high degree of reaction. There is no evidence of cross-linking under these circumstances [523]. During the degradation process, carbonyl groups accumulate in the polymer [524]. Among the degradation products were identified benzaldehyde [525] and a number of ketones [526].

The primary oxidation and chain scission process in polystyrene at room temperature is as follows [527]:

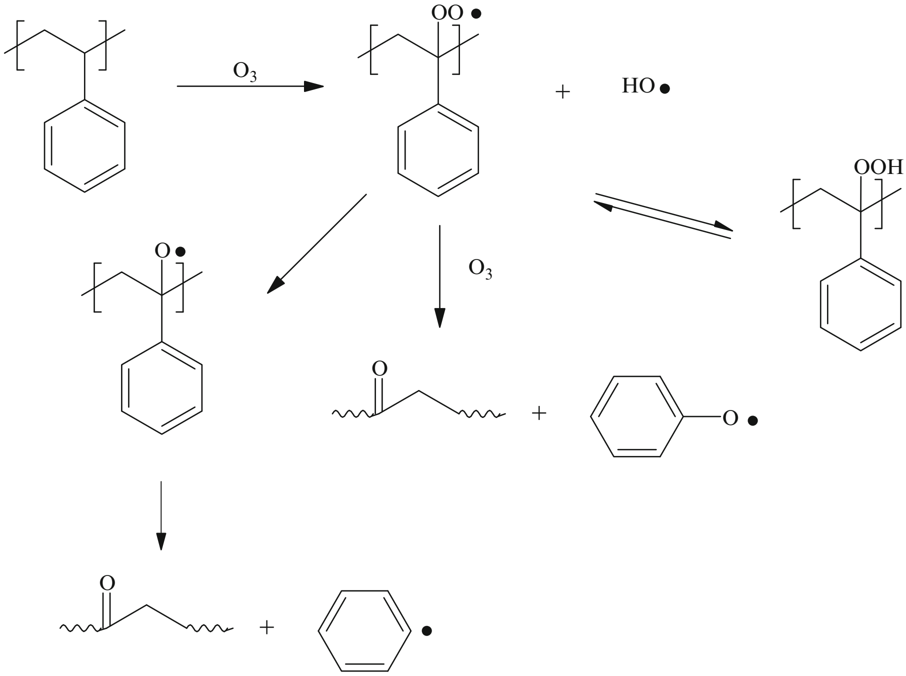


the reaction can also proceed in this manner:



Continuation of the process reduces the polymer to small fragments that include benzaldehyde and methyl phenyl ketone [527].

When solid polystyrene is subjected to an *ozone attack*, carbonyl, peroxide, and carboxylic acid groups form on the surface of the polymer [528]. The reaction rate is proportional to the concentration of the ozone and the surface of the sample. As a result of the ozone action, intramolecular cross-linking takes place. The reaction mechanism of the ozone attack on polystyrene can be shown as follows [528]:

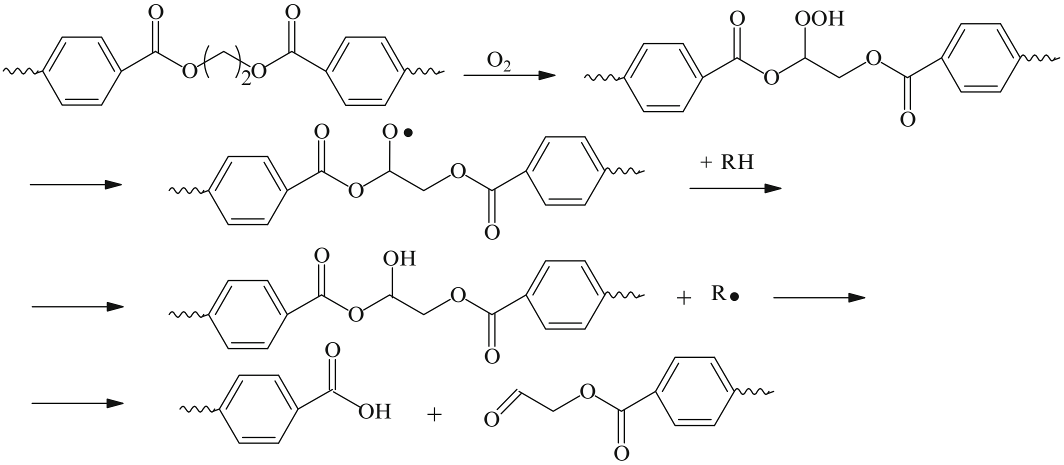


In *poly(vinyl toluene),* the initial oxidation steps consist of formations of radicals at the tertiary carbon atoms as they do in polystyrene. The radicals subsequently form peroxides that decompose into ketones and aldehydes.

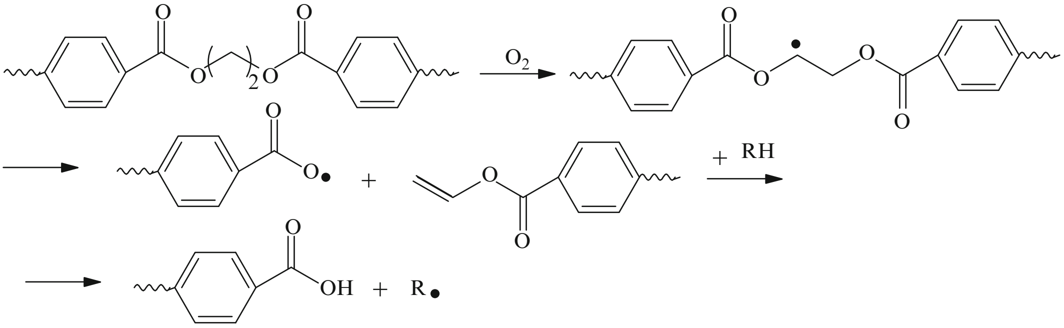
9.9.12 Oxidation of Step-Growth Polymers

Oxidation of step-growth polymers follows the paths that are similar to oxidation reactions of organic molecules. Thus, oxidation of poly(ethylene terephthalate) was shown to proceed as follows [529]:

Path1

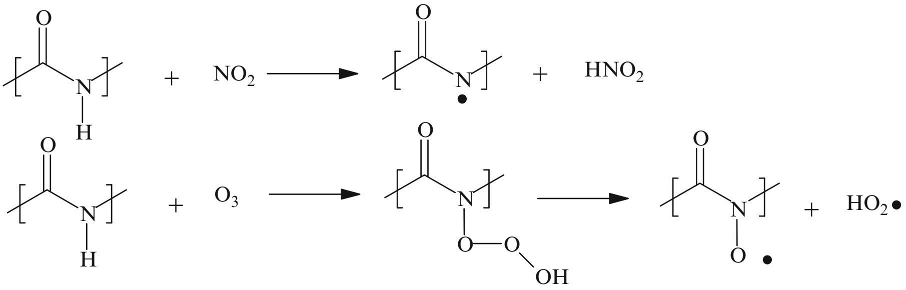


Path2



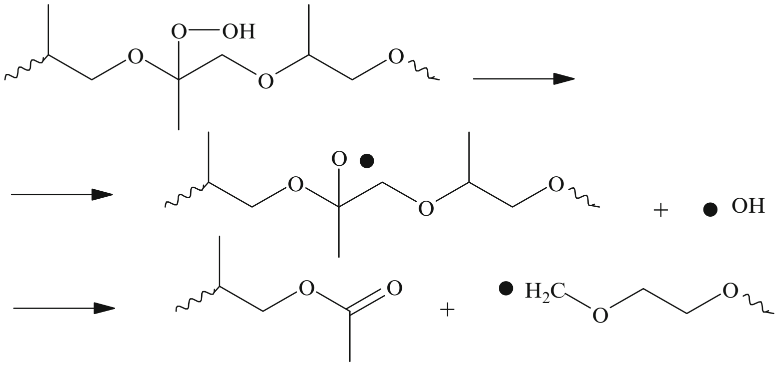
During thermal oxidation of *polyamides,* the *N*-vicinal methylene group is the preferred side of attack [531]. The reactivity depends, apparently, on the conformation of the amide group because an interaction takes place between the π-electronic system of the carbonamide group and its C–H bonds. In polycaprolactam, there exists a statistical distribution of both gauche and *trans*-conformations. The *N*-vicinal methylene groups in the *trans*-conformations to the amide groups are much more reactive than gauche [531].

When the oxidation of a polyamide occurs through an attack by NO_2 or ozone, then the amide groups themselves are subject to the attack [532]:

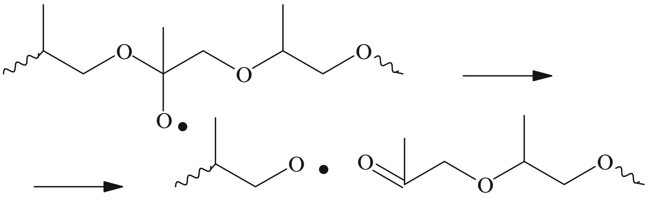


This appears to take place with hydrogen-bonded amide groups as well. The reaction, however, is inhibited by benzaldehyde or by benzoic acid. When the degradation does take place, it occurs at random [532].

Thermo-oxidative degradation of *polyoxyglycols* is reported to occur typically by a free-radical mechanism with the formation of hydroperoxides. The decomposition of the peroxides leads to formation of acids and carbonyl compounds [533]. A study of thermal oxidation of oligomers (molecular weight approximately 1,900) of polyoxypropylene glycols showed that at 70–120°C the end hydroxyl groups are not responsible for degradation and that chain ruptures occur through decomposition of the hydroperoxides [534]: Two types of cleavage are possible. One can take place through the carbon to carbon single bonds as follows:

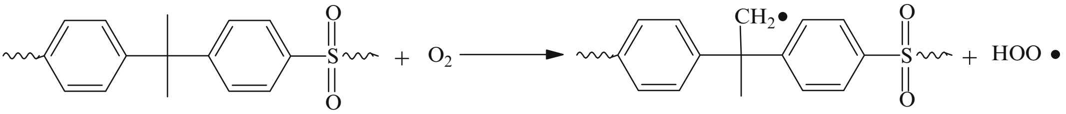


The other type of cleavage can occur through the oxygen–carbon bonds:



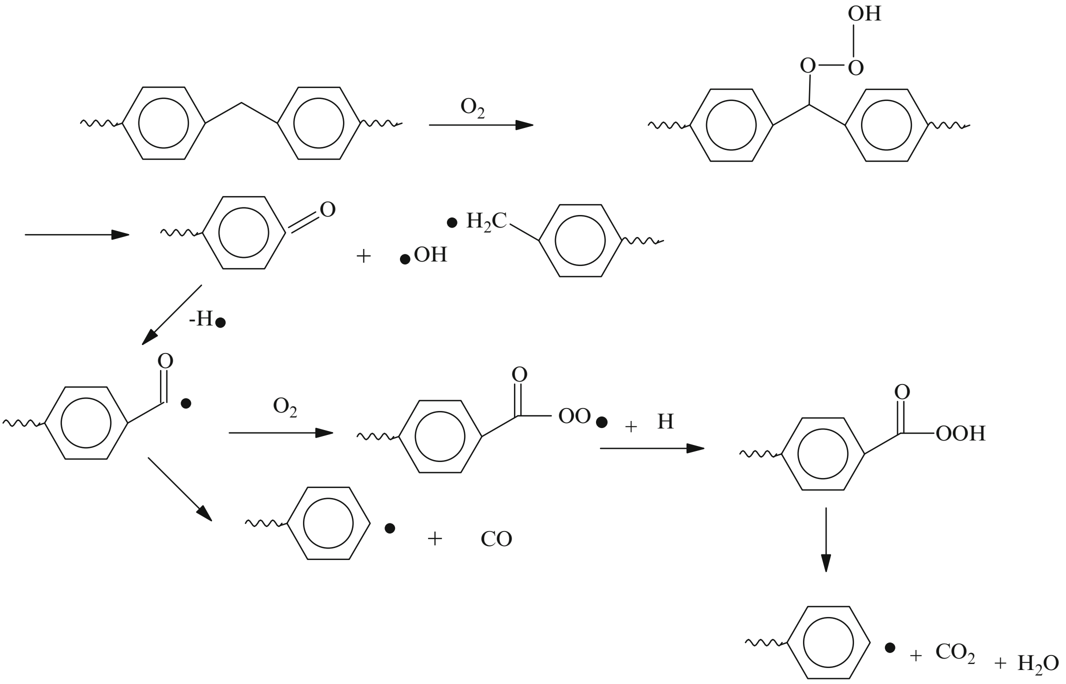
Both long and short molecular chains undergo degradation in an identical manner. The secondary radicals that form as a result of the decomposition of the alkoxy radical accelerate the oxidation process. It transforms into a chain process with an accompanying formation of various compounds. The products are alcohols, aldehydes, and ketones. The aldehydes are easily oxidized into peracids that degrade further into radicals.

Thermal–oxidative degradation of *polysulfones* was studied at 280°C [535]. The oxidation is a radical chain reaction with the initiation consisting of hydrogen abstraction from a methyl group:



The process then continues with formation of alkyl peroxide radicals, isomerization, breakdown, and formation of oxygen-containing compounds like aldehydes, and ketones.

In the oxidative pyrolysis of *poly-p-xylene,* the oxygen attacks methylene groups first to form hydroperoxides [536]. This is followed by chain cleavage:



9.9.13 Photo-Degradation of Macromolecules

The quantum energies associated with sunlight in the violet and near ultraviolet portions of the spectrum are of the magnitude sufficient to rupture chemical bonds present in most polymers [537]. The mechanism of photo-degradation, however, is more complex than would be visualized by the simple bond rupture, because photo-absorptions are complicated by various factors, including crystallinity that causes scattering of light. In addition, it was demonstrated that little light is absorbed above the wavelength of 2,800 Å. Yet, this wavelength represents the lower limit of sunlight reaching the earth. On the other hand, presence of impurities that can act as photosensitizes can markedly accelerate the degradation process.

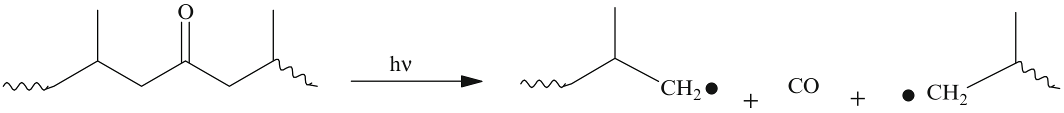
Polymers that are in current commercial use on a large scale fall roughly into three categories, depending upon their ability to withstand photo-degradation [538]:

1. Polymers that are resistant to sunlight attacks outdoors, like polyethylene and poly(methyl methacrylate).
2. Moderately stable polymers, like poly(ethylene terephthalate) and polycarbonate.
3. Polymers that are unstable in sunlight and require ultraviolet light stabilizer, like poly(vinyl chloride), polypropylene, nylons, rubbers, and cellulose.

In addition to structural instability of some polymer molecules in the ultraviolet light, degradation may also be accelerated by chromophores that can form from oxidation during preparation or processing. These compounds can act as excited donors and transfer the energy to the polymers that may act as acceptors. An intramolecular energy transfer may, actually, occur within the same polymer molecule. This can take place between an excited chromophore that is present in one segment of the chain and an acceptor at another segment. Also, chromophores, like carbonyl groups, can undergo Norrish Type I or a Norrish Type II reaction.

Several studies were carried out on *photolysis of polyethylene* [539, 540]. The primary process of photo-degradation, however, is still being elucidated. Direct irradiation of pure low-density polyethylene with ultraviolet light from a mercury lamp results in formation of free-radicals that were identified by ESR. They are alkyl radicals of the type: $\sim CH_2{-}CH_2^{\bullet}$ and $\sim CH_2{-}CH^{\bullet}{-}CH_2\sim$ [539, 540]. The true absorption bands of polyethylene, however, are located at wavelengths shorter than 200 nm. It is difficult, therefore, to accept that the radiation from the lamp caused chain scissions, because the output of the lamp is much longer in wavelength. It is suspected, therefore, that the degradation is a result of photo-oxidation. This is discussed in the next section.

A similar photo-degradation process is believed to take place in polypropylene [541]. The formation of free-radicals is ascribed to presence of oxidized molecules that form during processing. The oxidation products are carbonyl compounds and hydroperoxides [542]. The photolysis of the carbonyl derivatives is as follows [541]:



And the photolysis of chains carrying hydroperoxide group can be shown in this manner [541]:

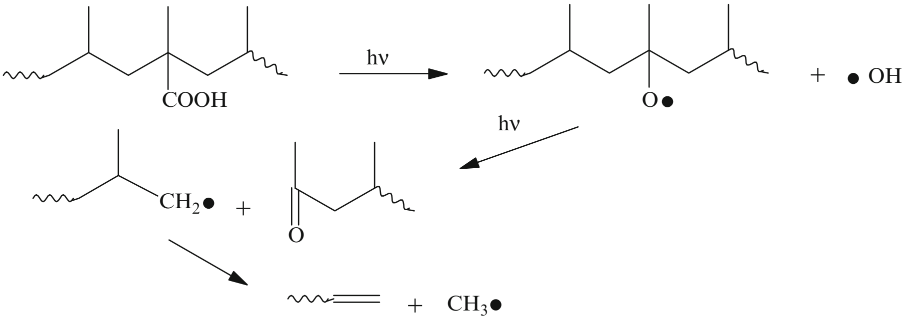
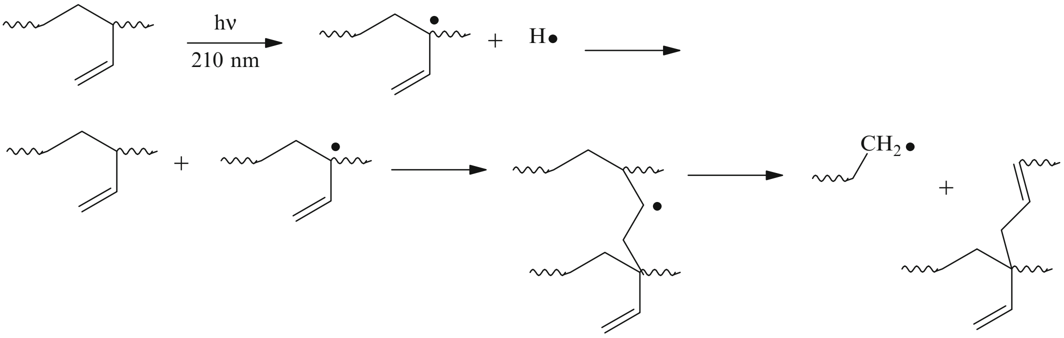
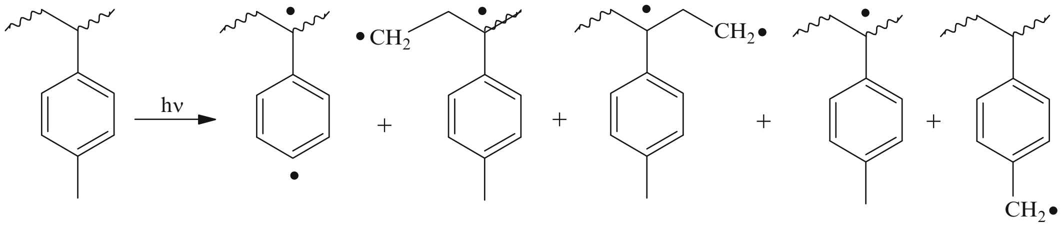


Photo-degradation of 1,2-polybutadiene was studied on a film [543]. Among the degradation products were found hydrogen, compounds with methyl groups, vinyl groups, and cross-linked material. The following mechanism of photo-initiation of the degradation reaction was proposed [543]:



The mechanism of photo-degradation of *poly(p-methylstyrene)* was studied by several investigators [544–547]. A gas evolution was observed during the irradiation with ultraviolet light. This gas contains hydrogen as its major portion and methane, ethane as the minor portions. There are also traces of styrene, *p*-methylstyrene, and toluene [101]. The gas evolution is accompanied by cross-linking. The start of the process is pictured as follows [547]:



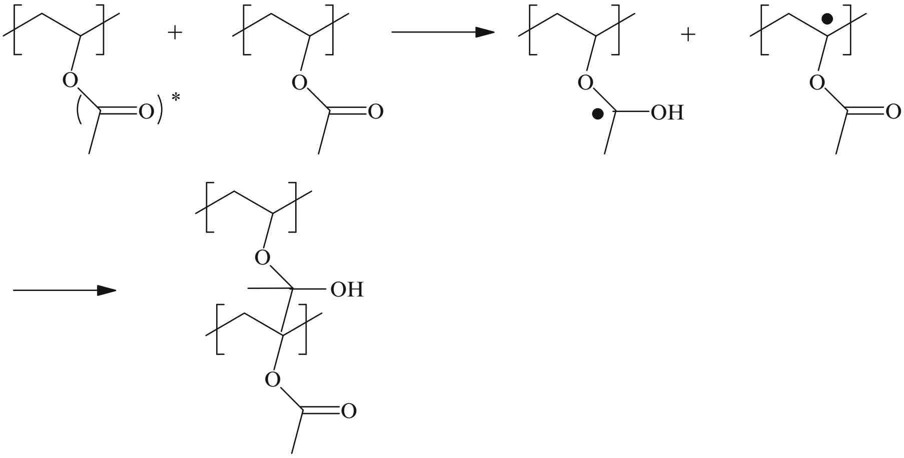
The products react to further yield hydrogen, cross-linked material, monomer, and cyclohexadiene.

Photolysis of *poly(p-isopropyl styrene)* with ultraviolet light of 254 nm in vacuum at 10^{-6} mbar and room temperature yields hydrogen as the main product and a small quantity of methane, ethane, and a trace of propane [548].

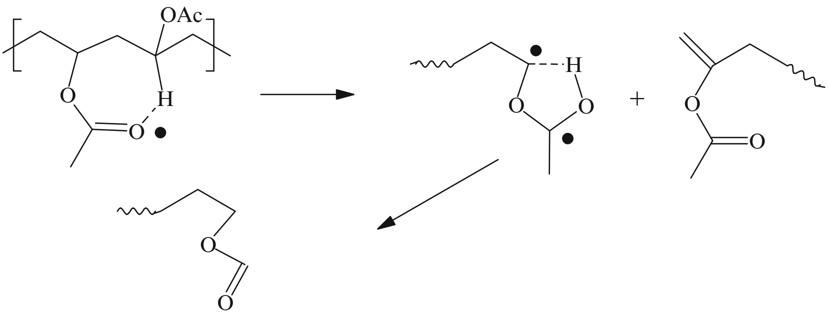
Poly(methyl methacrylate) depolymerizes at elevated temperature under the influence of ultraviolet light of 259.7 nm [549]. Irradiation of polyacrylonitrile, however, leads to chain scission at the acrylonitrile units. The difference between thermal and ultraviolet light degradation of polyacrylonitrile is principally in the different sites of initiation and the fact that the reaction occurs at 160°C in the presence of light and at 280°C in the darkness [550].

When a copolymer of methyl methacrylate and *n*-butyl acrylate is irradiated in vacuum at elevated temperature, like 165°C with light of 253.7 nm, the gaseous products are minor [551]. These are hydrogen, carbon monoxide, and methane. The liquid products are predominantly methyl methacrylate, *n*-butyl acrylate, *n*-butyl alcohol, and *n*-butyraldehyde. The degradation is explained by Grassie and coworkers [551] in terms of a radical process that is initiated by scission of pendant acrylate units. The propagation is actually a combination of depropagation of the chains and intra- and intermolecular chain transfer process. The relative importance of each phase of depropagation reaction depends upon the composition of the copolymer [551].

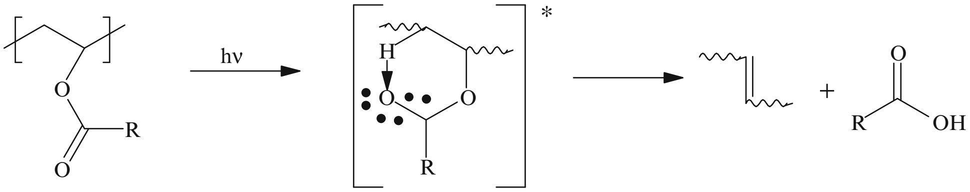
Poly(vinyl acetate) was shown to undergo simultaneous cross-linking and chain scission when irradiated in vacuum with ultraviolet light [552]. The following mechanism was proposed as the route to chain cleavage [552]:

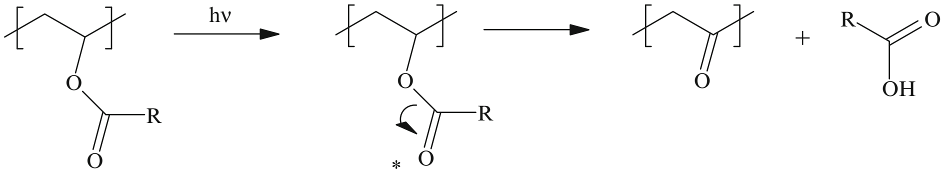


Also, intramolecular hydrogen abstraction is assumed to occur through a seven-membered ring transition state. This can provide a route to chain scission:

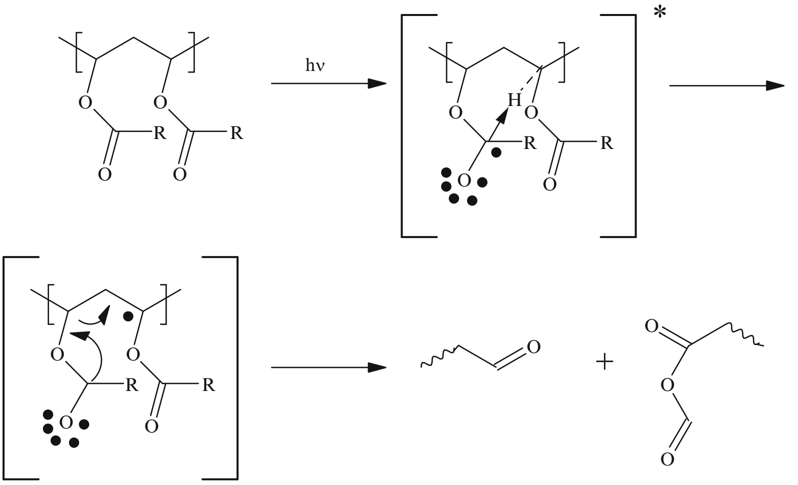


In subsequent studies of photo-degradation of poly(vinyl acetate) and poly(vinyl propionate) in vacuum, it was found that acids, aldehydes, and carbon dioxide were the principal products [553]. Two mechanisms, one involving hydrogen abstractions, were postulated. One of them takes place by abstraction by acyl radicals formed through Norrish Type I cleavages and the other by intramolecular hydrogen abstraction by excited carbonyl groups followed by fragmentation [553]:

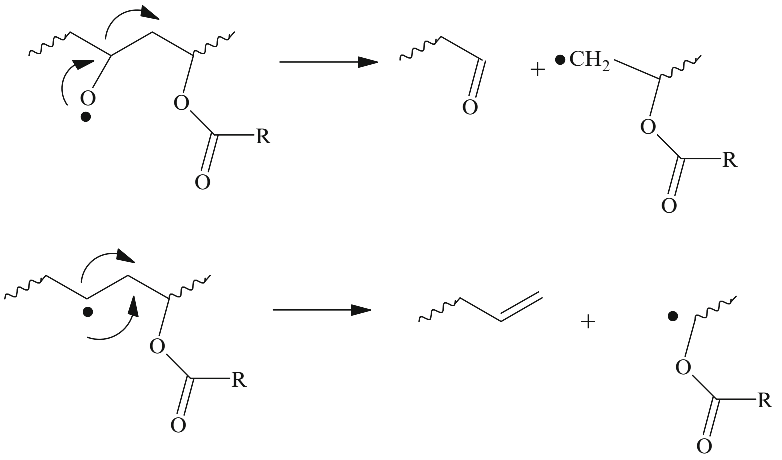




A second, perhaps more viable mechanism, was pictured for the production of aldehydes involving hydrogen abstraction as follows [553]:

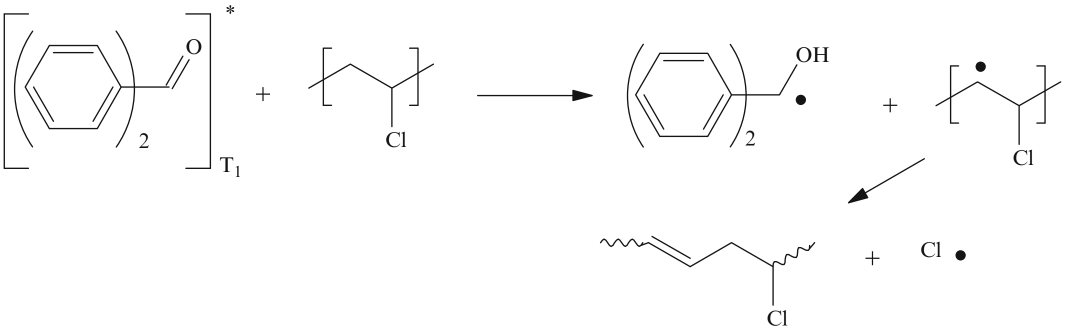


The main chain scissions are envisioned as involving fragmentation of the polymer alkoxy radicals that form [553]:



When cast *poly(vinyl chloride)* films are irradiated by ultraviolet light at various intensities and temperatures under a nitrogen atmosphere, dehydrochlorination reaction takes place [554]. This reaction occurs in two parts. During the first hour, the reaction is dependent on the intensity of light and the temperature, but after that it becomes independent of these two parameters.

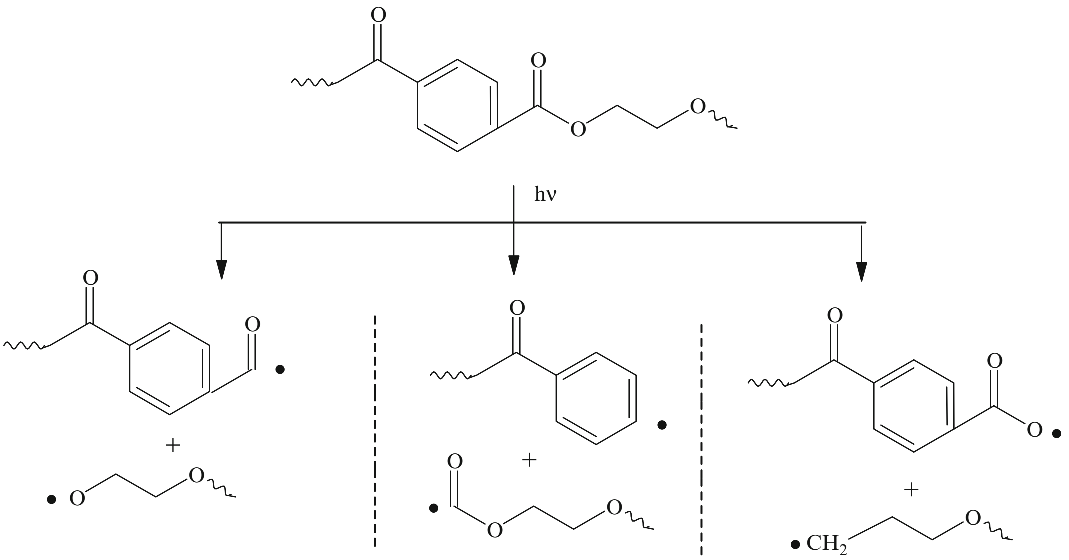
When poly(vinyl chloride) films are irradiated in the presence of benzophenone, the initiation is a result of hydrogen abstraction from the polymer by the excited triplet of the aromatic ketone [555]: This is followed by degradation that takes place by a chain mechanism:



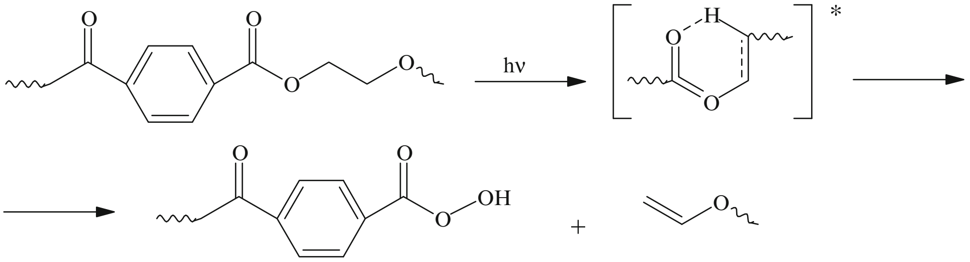
In the process, the chlorine radicals abstract hydrogens and form HCl. The quantum yield of hydrogen chloride from this reaction is $\Phi_{HCl} = 0.11$ [556]. This indicates that only 1 in every 100 photons that are absorbed causes the dehydrochlorination and is followed by formation of polyenes. It led to the conclusion that a photochemical process must take place between the polyene sequences and HCl [556, 557].

When *poly(phenyl vinyl ketone)* is irradiated by ultraviolet light of 365 nm, it degrades and exhibits a loss of molecular weight [558]. No benzaldehyde was found among the products. That excludes a Norrish Type I reaction and indicates that the polymer cleaves by a Norrish Type II mechanism [558].

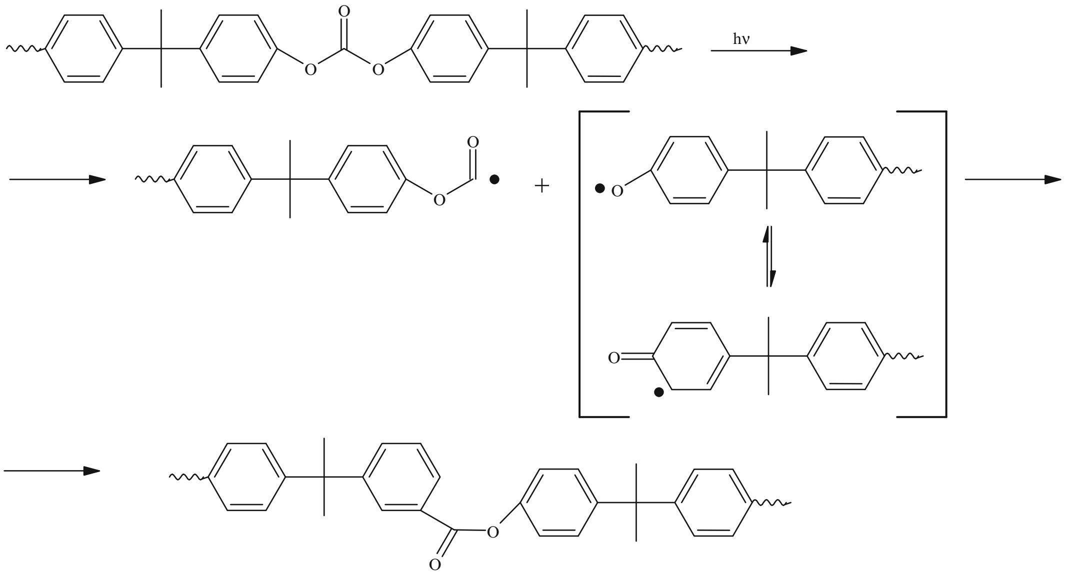
Day and Wiles have pictured the primary steps of photochemical decomposition of poly (ethylene terephthalate) as follows [559]:



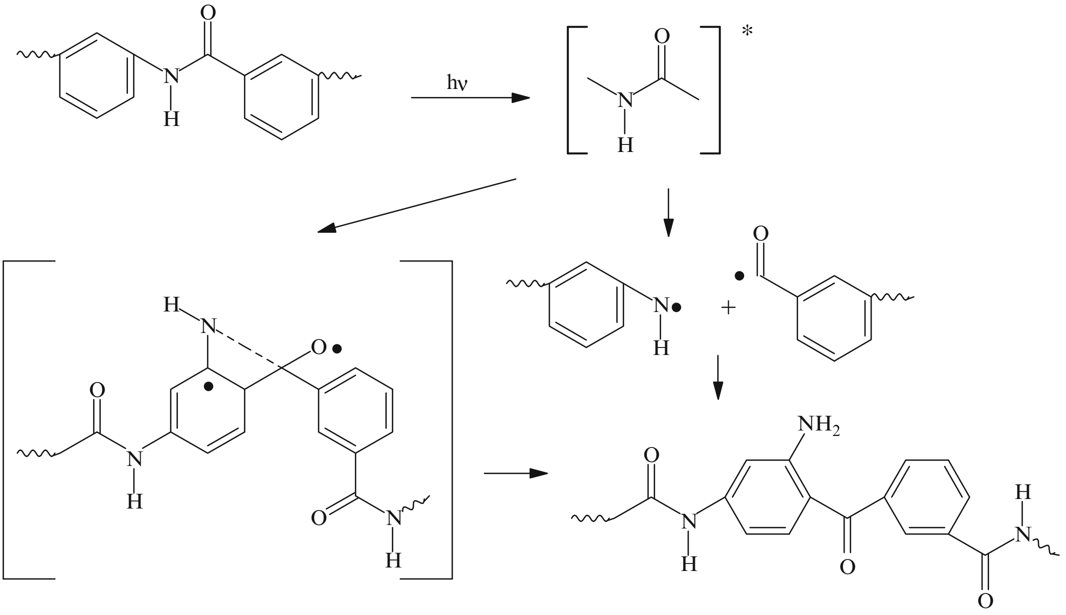
The mechanism of formation of carboxylic acid groups at the terminal ends of the degradation products was explained by a Norrish Type II reaction [559]:



In addition to the above, photo-Fries rearrangements occur in various aromatic polyester films upon ultraviolet light irradiation [560, 561]. Also, photo-Fries rearrangements are believed to occur in polycarbonate resins as well [562]. This can be illustrated as follows:



The same is true of aromatic polyamides where photo-Fries rearrangements are done according to the following mechanism [563]:



Photolytic decomposition of *polycarbonate* films was shown to produce products that are also consistent with the photo-Fries reaction. These are salicylic acid and bisphenol type species [580]. This is in agreement with earlier studies that showed that a variety of processes, including rearrangements (photo-Fries) and photo-oxidation, can occur when bisphenol A-based polycarbonate is photolyzed [581, 582].

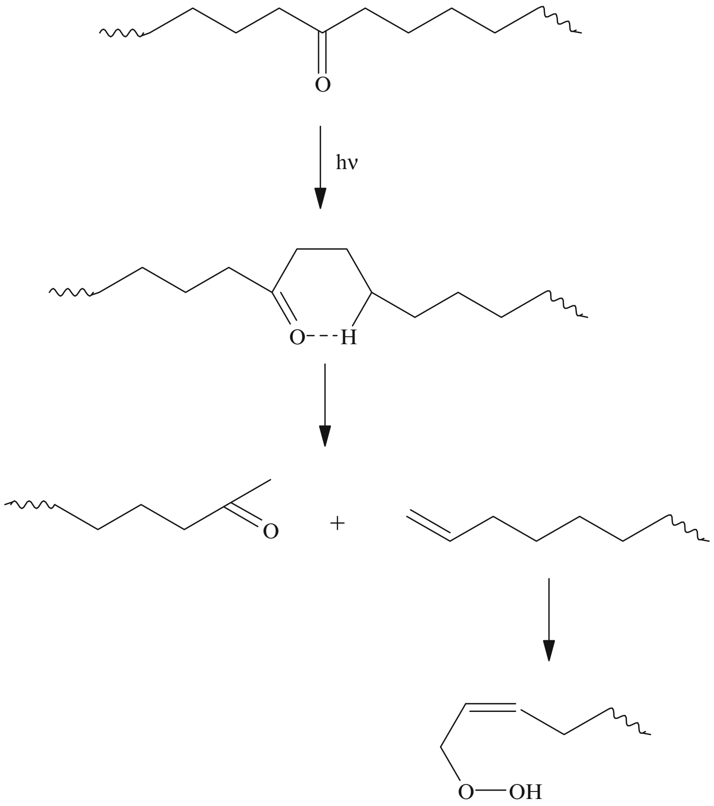
9.9.14 Photo-Oxidative Degradations of Polymers

Singlet oxygen, the lowest excited state of molecular oxygen, $^1\Delta_g\ O_2$, is known to cause rapid degradation of polymers. Singlet oxygen forms by several processes, including one of two mechanisms: (1) through photosensitization by some impurity; (2) through energy transfer from an excited triplet state of a chromophore.

Polyolefins that are unprotected from weathering react very readily with oxygen in the presence of sunlight even at room temperature. This leads to loss of molecular weight and often embrittlement. The mechanism of *photo-oxidation of polyethylene* was demonstrated to involve carbonyl groups that developed in the polymer via oxidation during processing [564, 565]. These carbonyl groups act as chromophores and their triplet states ($n \rightarrow \pi^*$) are quenched by molecular oxygen in the ground triplet state. Electronically excited singlet oxygen molecules form as a result [564].

$$>C = O^3(n \rightarrow \pi^*) + O_2(^3\Sigma_g{}^-) \rightarrow C = O(S_0) + {}^1O_2$$

The Norrish Type II reaction then takes place with a cleavage of carbon to carbon bonds, formation of olefins and, subsequently, formation of hydroperoxides:



The hydroperoxides apparently have no photo inductive effect on the overall oxidation of polyethylene [566]. Photolysis of hydroperoxides, however, initiates new vinylidine oxidation.

It was shown that the kinetics of photo-oxidation of polyethylene is characterized by the superposition of two phenomena. The first corresponds to an exponential increase in the concentration of the carbonyl groups with time and is observed when the kinetics are controlled by the diffusion of oxygen. The second one is not controlled by diffusion, but corresponds to a linear increase of the carbonyl concentration with time and takes place in degraded samples. This is explained in terms of chain rupture in the amorphous regions of the polymer, allowing free access of oxygen [567].

Commercial *polypropylene* can photo-degrade rapidly. This is due to a presence of chromophore groups that form during polymerization. In addition, chromophores may also form through oxidation by singlet oxygen during extrusion in air. At temperatures of 250–300°C, light of 300 nm will initiate oxidation by atmospheric oxygen [568]. The hydroperoxide groups that form are not stable and decompose to alkoxy radicals to form ketones on the backbones and at the ends of the chains. These ketones in turn undergo Norrish Type I and Type II reactions when irradiated with ultraviolet light [568]:

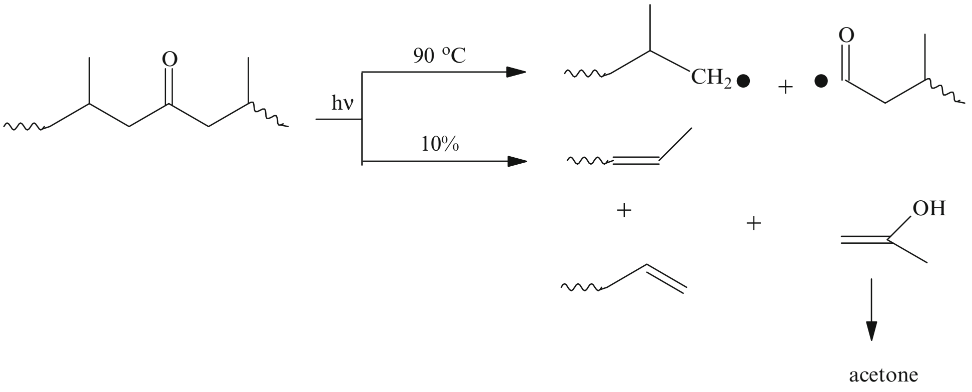


Photo-oxidation of *poly(vinyl chloride)* appears to be greatly enhanced by imperfections in the polymer structure that form during polymerization and processing. Formation of peroxide and carbonyl groups is very difficult to prevent. The initiation of photo-oxidation probably results from the free-radical that forms as these groups decompose upon irradiation [568]. In addition, double bonds that form from loss of HCl will sensitize formation of free radicals. These radicals are further oxidized and also promote cross-linking that results in gels.

Photo-oxidation of *cis-polybutadiene* was also shown to involve singlet oxygen [570]. Attacks by singlet oxygen on double bonds with formation of allylic hydroperoxides and shifts of these double bonds according to the *ene* reaction were confirmed by several other studies [571]. On the other hand, a study of model compounds for photo-oxidation of polyisoprene failed to show formation of endo peroxides by 1,4-cycloaddition [572].

Aromatic polyurethanes exhibit a strong tendency to yellow in sunlight. This may be accounted for by two mechanisms based on formation of different photoproducts. The first one was found to be a photo-Fries reaction caused by a short wave length light [572]. The second one, caused by longer wave length light, is formation of quinonoid structures [573]:

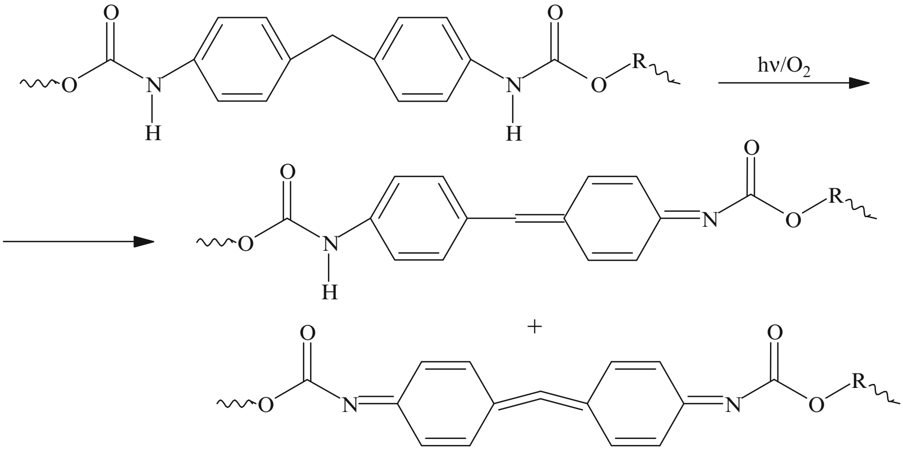
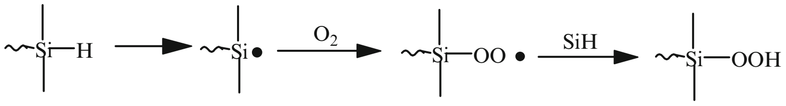


Photo-oxidation of Nylon 6 was also investigated [574]

The subject of *photo-oxidation of silicones* is seldom raised because these polymers are known for their stability to oxidation. Nevertheless, an investigation of photo-oxidative degradation of these materials showed that these materials can be affected by combined attacks of oxygen and ultraviolet irradiation [585]. The groups that are affected are the functional groups that are more fragile than the backbones. Thus, the silicon hydride group was found to be readily photo-oxidized, perhaps due to its low bond energy. The reaction can be illustrated as follows [585]:



The main process that occurs in silicones that contain vinyl groups is photo-scission. Also, the vinyl groups are photo-oxidized into silanols, carboxylic acids, and esters. Part of the silanols are condensed into high molecular weight silicones [585].

9.9.15 Degradation of Polymeric Materials by Ionizing Radiation

Ionizing radiation is not absorbed selectively like the ultraviolet. Instead, the absorption of gamma rays is a function of electron density in the path of the radiation. After a random ray strikes an atom, however, and energy transfer occurs, free-radicals may form and subsequent reactions, like oxidation and chain reactions, may proceed in the same manner as after UV light irradiation. In addition to creating free-radicals, ionizing radiation also gives rise to ions, electrons, and excited molecules in the medium. This is followed by reactions, like, chain scission, formation of unsaturation, and cross-linking that is accompanied by formation of volatile products.

Due to the high energy of ionizing radiation, if the irradiation dose is sufficiently high, all polymers will degrade to form low molecular weight fragments. The difference is in the rates of degradation and in the amounts of cross-linking.

Among vinyl polymers, those that tend to unzip and yield large quantities of monomers in thermal degradation are also likely to loose molecular weight rapidly upon irradiation. On the other hand, those vinyl polymers that yield low quantities of monomers during pyrolysis tend to cross-link instead. Also, it was observed that polymeric materials that exhibit high heats of polymerization during their formation tend to cross-link, while those that do not tend to degrade [575].

It was reported back in 1952 that *polyethylene* could be cross-linked by irradiation in a controlled manner [577]. The reaction is accompanied by evolution of considerable quantities of volatile gases that consist mainly of hydrogen. The portion of hydrogen that is released, however, is lower and the amount of volatile hydrocarbons is greater from polyethylene that is branched [578]. There appears to be an inverse relationship between the amount of branching and the quantity of hydrogen gas that is released [578].

Polypropylene was reported to cross-link under irradiation [579]. At the same time, there is a large evolution of gas. If the irradiation is carried out in air, there is marked degradation even at fairly low doses.

When polyisobutylene is irradiated, the molecular weight decreases rapidly until a viscous, low molecular weight liquid remains. At the same time, a mixture of hydrogen and methane (95% of total gas) is released [582].

Generally, aromatic structures are more stable to ionizing radiation than are the aliphatic ones. Accordingly, polystyrene is more resistant than polyethylene [575]. In addition, cross-linking predominates over chain scission.

The radiolysis of *poly(methyl methacrylate)* results in a rapid loss of molecular weight. This degradation increases with the intensity of the radiation [579]. The volatile products that form are hydrogen, carbon dioxide, carbon monoxide, methane, propane, and methyl methacrylate monomer. This varies with the temperature and the type of ionizing radiation that the polymer is exposed to.

Polytetrafluoroethylene is extremely sensitive to radiation and exhibits marked damage to its mechanical properties. It was shown that fluoride ions evolve from the polymer not only during irradiation, but also for long periods afterward [134]. The molecular weight of the polymer drops steadily with each dose. Many double bonds form in the polymer [580].

Review Questions

Section 9.1

1. What are the necessary conditions for a fair comparison of the reactivity of functional groups on macromolecules with those on small molecules.
2. When is unequal reactivity observed between large and small molecules?

3. Discuss the effect of diffusion-controlled reactions on reactivity of macromolecules.
4. Discuss how paired group and neighboring group effects influence random irreversible reactions.
5. Discuss reactions that favor large molecules.

Section 9.2

1. Explain, showing chemical equations, how hydrochlorination of natural rubber is often accompanied by cyclization.
2. Discuss chlorination of natural rubber. How can natural rubber and polybutadiene be brominated?
3. Discuss with the aid of chemical equations hydrogenation of 1,4-polybutadiene.
4. How can polyisoprene and polybutadiene be modified by additions of carbenes? Explain and discuss, showing the structures of the starting materials and the products.
5. Illustrate the Prins reactions of rubber with formaldehyde and with glyoxal. How can this reaction be carried out in the solid phase?
6. Discuss polar additions to unsaturated polymers. Give examples Include the *ene* reaction.
7. How can the Ritter reactions be carried out on isoprenes?
8. How can the Diels-Alder reactions are carried out with unsaturated polymers. Use chemical equations to illustrate.
9. Explain how polybutadiene and isoprene can be epoxidized, giving reagents and showing all by-products.

Section 9.3

1. Show how, and explain why, *cis*-polybutadiene rearranges to *trans* as a result of irradiation by gamma rays or ultraviolet light. Also, show what happens to polyisoprene when it is irradiated in the ultraviolet light.
2. Discuss with the aid of chemical equations the cyclization reactions of rubber.
3. How are polyacrylonitrile fibers converted to graphite-like fibers. Explain, showing all the steps in thermal cyclization of polyacrylonitrile.
4. Discuss migration of double bonds in polymers.
5. How does poly(4,4′-diphenylpropane isophthalate) rearrange upon irradiation with ultraviolet light?
6. Give examples of the Schmidt and Beckmann rearrangements.

Section 9.4

1. Discuss with the help of chemical equations the fluorination reactions of polyethylene.
2. Discuss chlorination of polyethylene and polypropylene.
3. How is chlorosulfonation of polyethylene carried out industrially. Explain and write the chemical equations for the reactions. How is the product used?

4. Discuss chlorination of poly(vinyl chloride).
5. Discuss chlorination of poly(vinylidine chloride) and poly(vinyl fluoride).
6. Describe the reactions of sodium azide with poly(vinyl chloride) and the subsequent reactions of the azide group. Use chemical equations.
7. Describe reactions of poly(vinyl chloride) with sulfur compounds.
8. What are the products of reactions of poly(vinyl chloride) with aniline? Show and explain.
9. Explain how carbanionic centers can be formed on the backbones of poly(vinyl chloride) molecules. Show what subsequent reactions can take place.
10. What happens when poly(vinyl chloride) is treated with organolithium compounds. Explain with the help of chemical equations.
11. Discuss photo chlorination of polystyrene.
12. Discuss chloromethylation reactions of polystyrene and its copolymers, showing all chemical reactions.
13. Discuss various reactions of chloromethylated polystyrene with the help of chemical equations.
14. Show examples of the Friedel-Craft reactions of polystyrene and chloromethylated polystyrene.
15. Discuss sulfonation of polystyrene.
16. Discuss nitration of polystyrene, reduction of nitropolystyrene, and the subsequent diazotization reaction.
17. Discuss matalation of polystyrene and subsequent reactions.
18. Discuss reduction reactions of the polymers of methacrylic and acrylic esters with metal hydrides. What solvents give optimum conditions?
19. Discuss nucleophilic substitution reactions of poly(methyl methacrylate); the Arndt-Eister reactions of poly(methacryloyl chloride) and the Curtius and Lossen rearrangements of poly (acryloyl chloride)
20. Show a Diels-Alder reaction of poly(furfuryl methacrylate) with maleic anhydride.
21. What are the industrial processes for preparation of poly(vinyl butyral)? Describe the process, showing all chemical reactions.
22. How can the Schotten-Baumann esterifications of poly(vinyl alcohol) are carried out? Explain.

Section 9.5

1. Discuss the vulcanization reactions of rubbers. Show all the chemical reactions.
2. Discuss ionizing radiation cross-linking of polymers.
3. Show the reaction of photocross-linking of poly(vinyl cinnamate) and explain the mechanism.
4. Show the reactions of photocross-linking of polymers bearing azide groups.
5. Draw examples of polymers with pendant benzoin and furoin groups.
6. Explain the mechanism of photocross-linking by $2\pi + 2\pi$ type dimerization. Give examples.
7. Discuss typical ultraviolet light-curable coating compositions by free radical and by cationic mechanisms.
8. Why are photoinitiators preferred to photosensitizers in UV-curable materials?
9. Discuss with the help of chemical equations the mechanism of photoreduction of aromatic ketone photoinitiators hydrogen donors and by electron donors.
10. Discuss photoinitiators for photocross-linking by cationic mechanisms, showing all reactions and products.
11. Discuss cross-linking reactions by electron beams.

Section 9.6

1. What is meant by microporous and macroreticular supports.
2. Discuss some applications of polymeric reagents. Show examples.
3. How are enzymes immobilized? Discuss, showing chemical reactions.
4. Discuss nonenzymatic catalysts.

Section 9.7

1. What is the mechanism of free-radical graft copolymer formation by chain-transferring technique. Explain by examples and discuss advantages and disadvantages.
2. Discuss free-radical grafting reactions to polymers with double bonds. Give examples and show reactions.
3. How can macromonomers be used to form graft copolymers? Give several examples.
4. How can polymerizations be initiated from the backbones of the polymers? Explain and give examples.
5. Discuss photochemical preparation of graft copolymers.
6. How is high-energy radiation used to form graft copolymers?
7. Discuss formations of graft copolymers by ionic chain-growth and step-growth polymerizations.

Section 9.8

1. Discuss advantages of block copolymers over polymer blends.
2. How can block copolyesters be formed? Explain with chemical equations.
3. How can block copolyamides be formed? Explain as in Question 2.
4. How can polyurethane-polyamide and polyamide-polyester block copolymers be formed? Explain and show chemical reactions.
5. What are polyurethane ionomers? How are they prepared?
6. Describe the technique for preparation of block copolymers of poly(α-olefins).
7. How do block copolymers form in simultaneous free radical and ionic chain-growth polymerizations? Explain and give examples.
8. Discuss formations of block copolymers by homogeneous ionic copolymerization.
9. How can block copolymers form by mechanochemical techniques?

Section 9.9

1. What is meant by polymer degradation and what are the various causes?

Section 9.10

1. What is the common technique for studying thermal degradation of polymers?
2. Explain the two thermal degradation processes in chain-growth polymers?

3. Describe the thermal degradation of polyolefins.
4. Describe the thermal degradation of polybutadienes.
5. What is the thermal degradation process in polystyrene and polystyrene-like polymers?
6. How do the methacrylic and acrylic esters degrade thermally?
7. What happens when polyacrylonitrile is heated? Describe
8. Discuss the thermal degradation of poly(vinyl chloride)
9. Discuss the thermal degradation of fluorocarbon polymers
10. Discuss the thermal degradation of poly(vinyl acetate)

Section 9.11

1. Can the step-growth polymers degrade in the same manner as the chain-growth polymers?
2. How do the polyoxides degrade thermally?
3. Discuss the thermal degradation of polyesters.
4. Discuss the thermal degradation of polyamides.
5. Discuss the thermal degradation of the epoxy resins
6. How do the polyimides and the polyquinoxalines degrade thermally?
7. Discuss the thermal degradation of polysulfones
8. How do cellulosic materials degrade thermally?

Section 9.12

1. How does hydrolytic degradation of polymers take place?

Section 9.13

1. Describe oxidative degradation in hydrocarbon polymers
2. Describe oxidative degradation of polystyrene
3. Describe oxidative degradation of poly(ethylene terephthalate)
4. How do the polyamides degrade oxidatively?

Section 9.14

1. What is meant by photo-degradation of polymers?
2. Describe photolysis of polyethylene.
3. Describe photo-degradation of polybutadiene and poly(*p*-methylstyrene)
4. How does poly(methyl methacrylate) degrade at elevated temperature under the influence of ultraviolet light?
5. Describe photo-degradation of poly(vinyl acetate) and poly(vinyl chloride)
6. What is the mechanism of photo-degradation of aromatic polyesters?

Section 9.15

1. What causes photo-oxidative degradation and how does it take place in polyolefins?
2. How does commercial polypropylene degrade photo-oxidatively?

Section 9.16

1. If you had to select polymeric materials for use near a nuclear reactor, what types of materials would you select? Explain.

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Chapter 10
Polymeric Materials for Special Applications

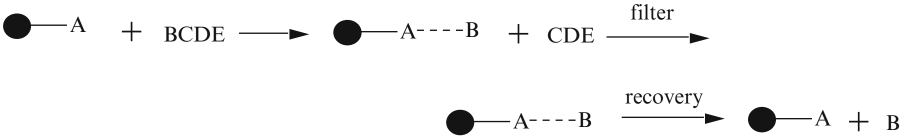
10.1 Polymer Supports for Reagents, Catalysts, and Drug Release

Supports are materials that are used for immobilization of various reagents, catalysts, drugs for release. Many of them are specially prepared macromolecules. Reagents and catalysts on support find applications in organic syntheses, biochemical reactions, special separations, and analyses. They also find uses in medicine for drug release, etc. An advantage of immobilized polymeric reagents in chemical reactions is that they can be separated, often easily by filtration, from the products of these reaction. Cross-linked polymeric reagents have an additional advantage in that several different polymeric reagents can be used simultaneously without the functional groups being accessible to each other for interaction. Reactions of some compounds in solution require high dilutions. Immobilization, however, may permit the same reactions to be carried out at relatively high concentrations. Immobilization can also be very useful in syntheses that consist of many steps, where the undesired by-products from each step can simply be washed away. This avoids lengthy isolation and purification procedures [2]. Also, by immobilizing on a polymer, the macromolecule may provide microenvironmental effects to the attached species for the reactions. These may include special electronic and steric conditions that could be different from those existing in bulk or in solution.

The chemical uses of polymeric reagents were originally classified by Patchornik according to the general type of reaction [1].

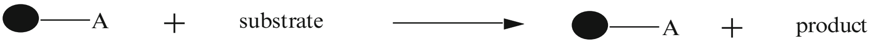
These are as follows:

1. Polymer-attached reagents are used in ***special separations*** to selectively bind one or a few species out of complex mixtures:



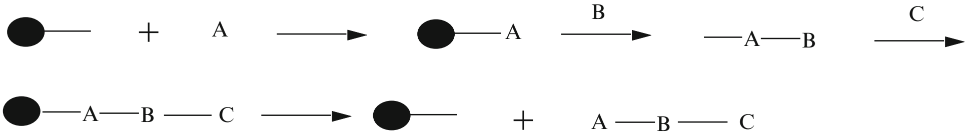
The polymer-bound compound is separated from the mixture and then released.

2. The polymer with a ***catalyst*** attached. Such catalysts can be enzymes, inorganic compounds, or organometallic compounds:



A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_10,

3. The polymeric reagent can also be used as ***transfer agents***. Low molecular weight reactants transfer the functional moiety with the aid of the polymeric agent. This leaves the products in pure form after filtration and solvent removal.
4. The polymers are used as ***carriers*** or **as *blocking groups*** in syntheses [1]:

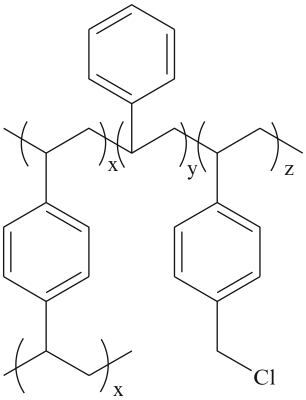


10.1.1 Support Materials

Many different support materials were developed [3, 4] since the original use by Merrifield of a polystyrene-based support material for polypeptide synthesis [5]. The work of Merrifield is described in Chap. 8 (see section on proteins). Beads of copolymers of styrene with divinyl benzene are available commercially and have been widely used as supports for many reactions. Many other polymeric materials are also used. These can be various other type of copolymers of styrene or with other polymers. The list includes cellulose, starch, polyalkanes, polyamides, poly(glycidyl methacrylate), polyisobutylene, polynorbornene, polyacrylamide, and others. In some instances, even glass was used. The more prominent support materials are presented below.

10.1.1.1 Materials Based on Polystyrene

Cross-linked polystyrene (copolymer with divinyl benzene) was the original support material used by Merrifield for polypeptide syntheses. The material is actually a terpolymer of styrene, chloromethyl styrene, and divinyl benzene.



Copolymers of styrene and divinyl benzene supports have since received many uses and have undergone many chemical modifications for various reactions as reagents and catalysts. The material can be functionalized in many ways. Thus, it can be nitrated, chloromethylated, sulfonated, lithiated, carboxylated, and acylated. The greatest use has been made of the chloromethylated and lithiated derivatives. These two derivatives can react with nucleophilic and electrophilic reagents, respectively, resulting in a wide range of functionalized polymers. For various modification reactions of polystyrene, see Chap. 9.

Two types of cross-linked polystyrene are often favored. One is a polymer that is cross-linked by only 1–2% of divinyl benzene. The material, though fairly strong mechanically, swells and expands significantly in volume when dispersed in proper solvents. It is called ***micro porous***. A copolymer with up to 20% divinyl benzene is the second type. It is prepared in the presence of large quantities of diluents to retain the products in expanded form. As a result, the structures are ***macro porous*** or ***macro reticular***. The advantages of micro porous over macro porous structures are faster reactions, less fragility, and easier handling. Although, macro reticular supports are less often used, they have the advantage of being useful in almost any solvent.

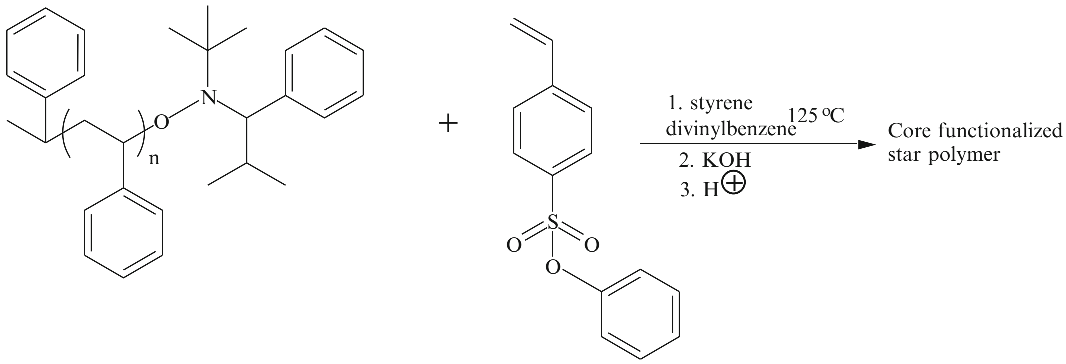
As a variation of the process, Fréchet and coworkers introduced ***reactive filtration*** [6]. In place of beads, they used discs of cross-linked polystyrene that were cut from a rod of the material. On the surface of these discs, they grafted 2,2-dimethylazlactone. These discs were then used in a filtration to efficiently scavenge excess amines from a reaction mixture. Subsequently, Frechet and coworkers also used such discs in a flow through acylation reaction [7].

To improve the access to the functional groups, Lee and coworkers developed a process of placing most of the functional groups on the outer surface of the polystyrene beads [7]. This was done by surface aminomethylation of preformed cross-linked commercially available polystyrene beads. Such bead usually range in size from 100 to 400 mesh (in.) in diameter and can be functionalized by surface reactions or by surface grafts. This yielded materials with a lower number of functional groups, but with the majority of them being accessible. Lee and coworkers then utilized the beads in a solid peptide synthesis [7].

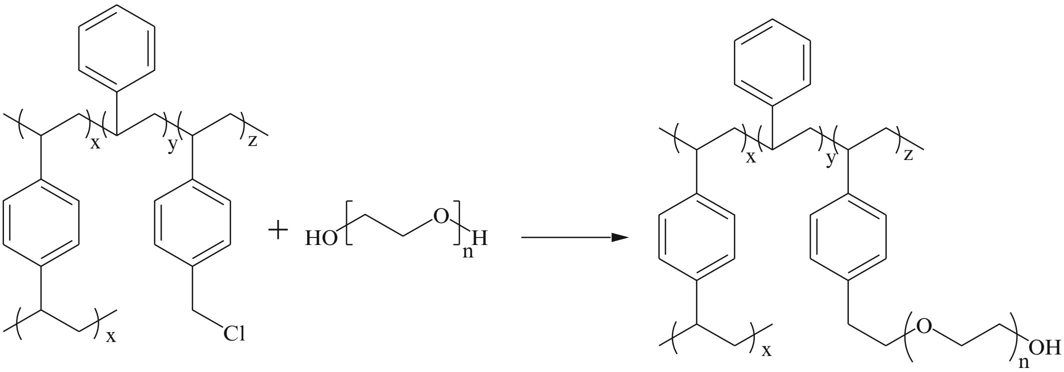
Lee and coworkers also prepared beads with *N*-heterocyclic carbene ligands located on the outer shell. In this preparation, they used beads formed in a suspension polymerization [8, 9].

Fréchet and coworkers [7] reported a variation of the strategy by attaching functional groups to cross-linked polystyrene in the interior of a soluble star polymer matrix. In this process, the catalytic groups are core-confined through the use of low molecular weight macroinitiators that form the surface of the final polymer. Presumably, this allows using simultaneous incompatible reagents, like acids and bases, because they are physically isolated from one another.

Lu and Toy [10] illustrated a similar approach: by showing how core-functionalized star polymers are prepared to form sulfonic acid-functionalized core material:

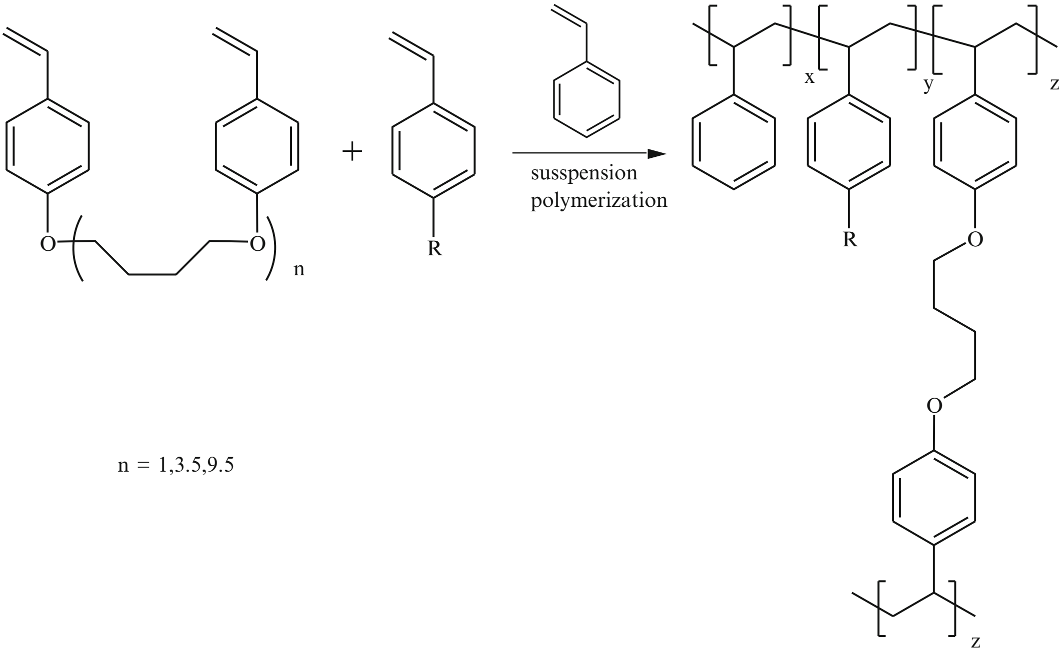


There is a drawback, however, of using the polymer described above, because many functional groups end up imbedded inside the resin and access to them requires the type of solvents that can thoroughly swell the resin. Many polar solvents, however, fail to swell cross-linked polystyrene adequately, yet may be required for specific reactions. That led to modifications, such as, the use of polar cross-linking materials, like oligomers of glycols. One example is a cross-linked polystyrene-poly(ethylene glycol) composite, known as ***Tentagel*** [10]. It can be illustrated as follows:



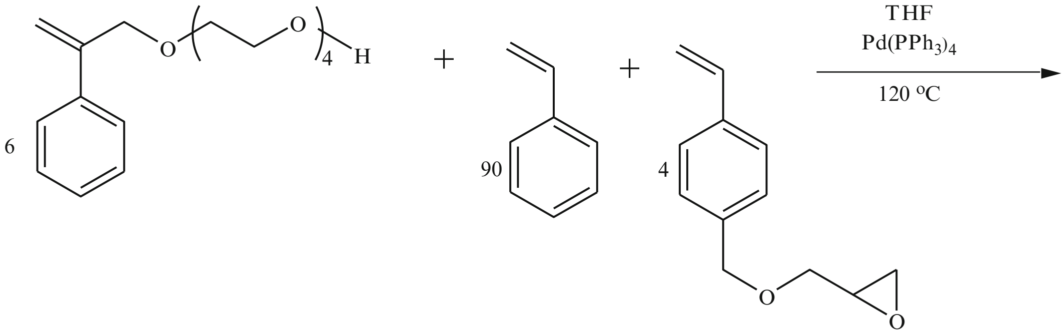
Another example is work by Bradley and coworkers who incorporated short oligomer (polyethylene glycol) groups into the backbone of the cross-linked polystyrene [11]. The oligomer poly (ethylene glycol) in this preparation also acts as a spacer to separate the polystyrene backbone from locations of the reactions. The material was used efficiently in a solid phase peptide synthesis.

Toy et al. [12] demonstrated that by replacing divinyl benzene with more flexible compounds usually increases their mechanical stability and allows them to absorb more solvent. In addition, when the cross-linked compounds contain oligomers of such materials as ethylene glycol, the compatibility with polar solvents increases. Subsequently, Janda and coworkers used polytetrahydrofuran in suspension polymerization of styrene to prepare general solid support resins for organic syntheses [13].



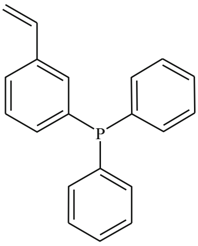
The material became known as **Janda Gel** [13]. The preparation of this gel with *n* equal to one is illustrated above [14].

An interesting application of cross-linked styrene resins that are similar to the Janda gel was developed by Kobayashi and coworkers, who used such materials to encapsulate metal catalysts [15]. The technique used was to first entrap the metal catalysts by coacervation with linear polystyrene that was functionalized both by epoxide groups and oligo poly(ethylene glycol). The polymer becomes cross-linked upon heating through reaction of the epoxide groups with polyethylene glycol entrapping the metal:

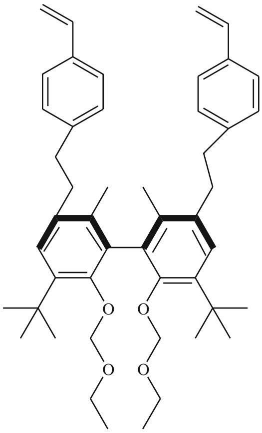


The above solid catalysts were used successfully to catalyze various reactions, like the Suzuki–Miyura reaction [15], such as aminocarbonylation, amidation, and the Heck reactions [16]. Polymers containing scandium triflate, ruthenium, platinum, or gold were prepared to perform Mukayama aldol, alcohol, and sulfide oxidation, hydrogenation, and indole syntheses [17].

Incorporation of some of the metals, like palladium, is improved by incorporating phosphine ligands into the polymer. One such ligand can be illustrated as follows [19]:

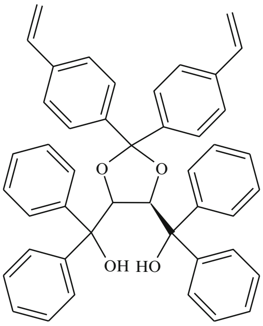


Hoveyda, Schrock, and coworkers [19] reported using chiral cross-linking compounds immobilized on heterogeneous polystyrene resins. The chiral moiety was then used as a ligand in asymmetric catalyses. In one application, they used the material to prepare a recyclable chiral molybdenum olefin metathesis catalyst that was used in enantioselective ring opening and ring-closing metathesis reactions. The material can be illustrated as follows:



The products that were isolated possessed only slightly lower enantiomeric excess than those obtained with the corresponding small molecule catalyst.

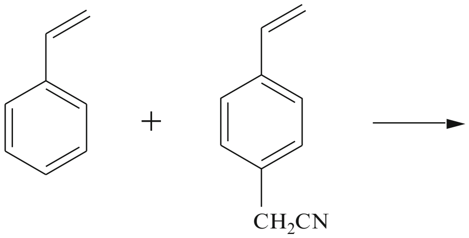
In a similar manner, Sellner et al. [20] prepared a variety of polystyrene beads with embedded α,α,α,α-tertiaryl-l,3-dioxolane-4,5-dlmethanol groups. They were subsequently used to form an immobilized catalyst with recyclable chiral titanium Lewis acid for addition of Bu_2Zn to benzaldehyde.

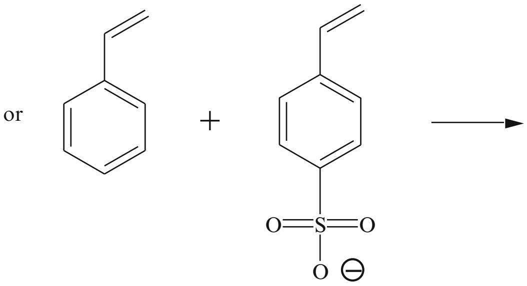


They also reported preparations of various cross-linkers containing tertiary aryl groups with polymerizable carbon-carbon double bonds [20].

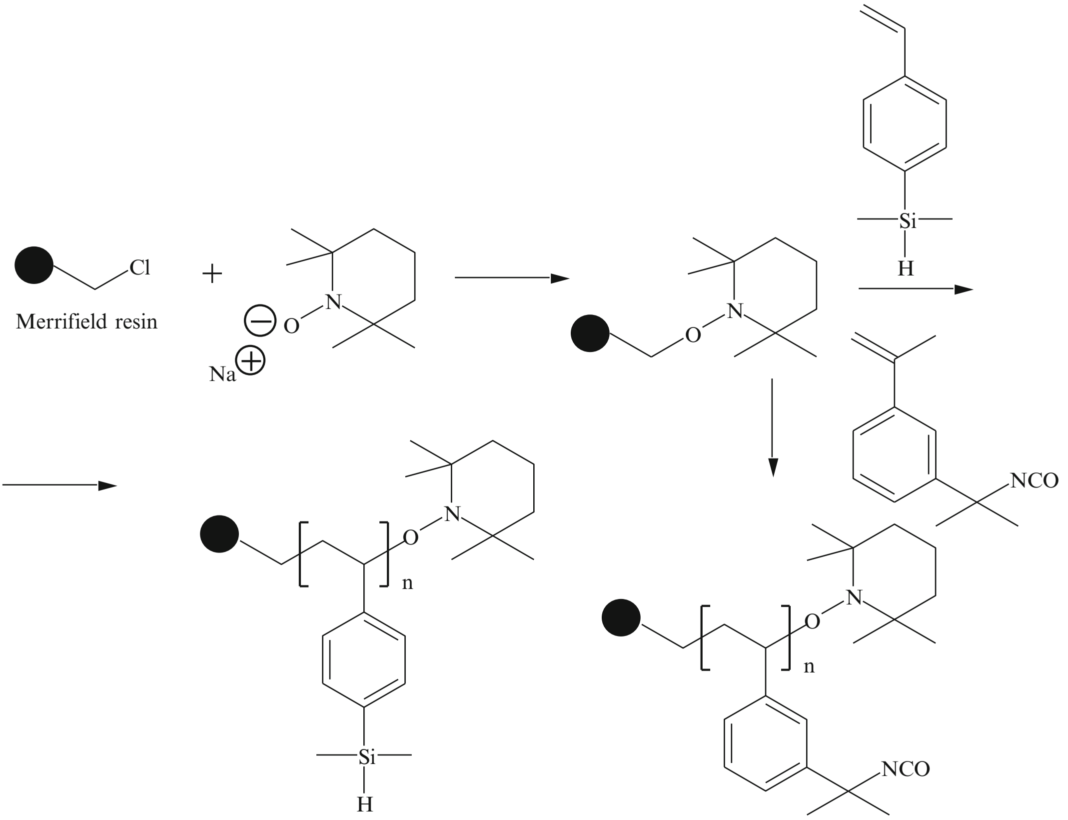
Itsuno et al. [21] synthesized a cross-linked polymer support with a chiral 1,2-diamine for enantioselective ruthenium transfer hydrogenation catalysis of aromatic ketones.

A variation on the process was to functionalize polystyrene by incorporating groups like hydroxy, acetoxy, or nitrile onto the backbone of polystyrene, through copolymerization of monomers [22]. Following are two examples:



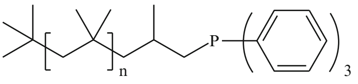


Similar to the work by Frechet who grafted functional groups to heterogeneous polystyrene (see above), Hodges used living free-radical polymerization to prepare what he referred to as **Rasta resin** [23]. The Merrifield resin was first functionalized with reduced TEMPO to form a resin core. With the help of Rhodamine dye, it was confirmed that the grafts and associated functional groups were located on the exterior of the resin beads [2]. The product was then used in free-radical polymerization with various styrene monomers [4]. It was also shown that such resins could be prepared efficiently using microwave-initiated polymerization [22]. Fontaine extended this concept by using atom transfer radical polymerization initiators to attach poly(2-vinyl-4,4-dimethyl-5-oxazollne) to form grafts that are efficient nucleophilic scavenging [25, 26]. Preparation of Rasta resin can be illustrated as follows:

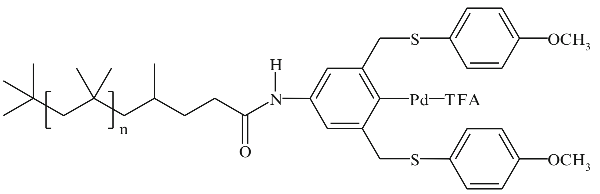


10.1.1.2 Support Materials Other Than Polystyrene

Barett et al. [27] as well as Hanson and coworkers [28] used low molecular weight polyisobutylene to form polyisobutylene-supported catalysts:

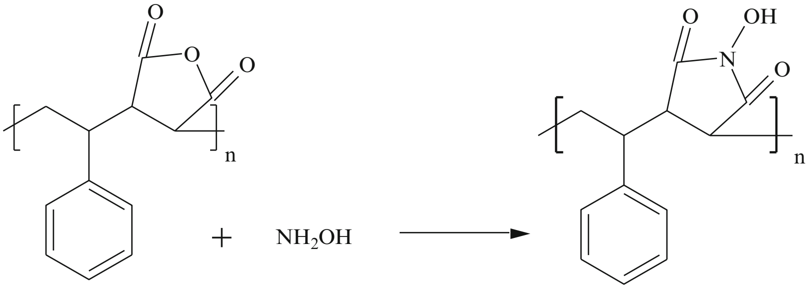


and

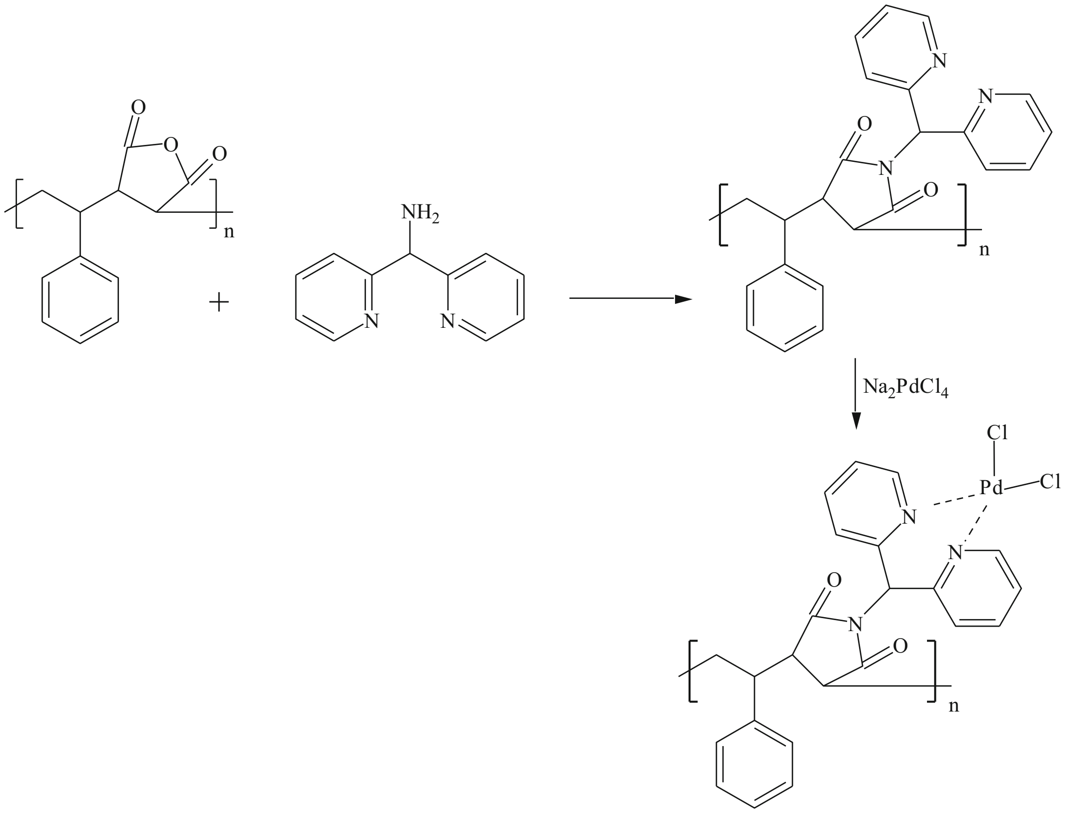


An advantage of using polyisobutylene is solubility in a variety of nonpolar solvents at ambient temperatures. Also, the terminal double bond of polyisobutylene can be readily transformed into various useful groups for attachment of catalysts or reagents. Thus, polyisobutylene was used as a catalyst support for anchoring a sulfur-cation-sulfur Pd(II), as shown above. These catalysts were used to perform allylic substitution, Heck, and Sonogashira reactions [26]. Polyisobutylene was also used to support chiral bisoxazoline ligands for copper-catalyzed cyclopropanation reactions [27]. Other uses included catalysis of self-separating atom transfer radical polymerization [28], RCM catalysis [29], and catalysis of a chromium-based polycarbonate polymerization [30]. It is important to note that these polyisobutylene-supported catalysts exhibited close to or similar activity to their unanchored counterparts. In addition, they were readily recovered and reused without appreciable loss of activity.

Nájera and coworkers [34] used a commercial poly(styrene-*alt*-maleic anhydride) copolymer as support material. The copolymer was first reacted with hydroxylamine and then converted to a polymer-supported *N*-hydroxy succinimide. The product was then used in a peptide-coupling reactions. Low levels of racemization were reported. Addition of hexane allowed the removal of the polymeric material by filtration.

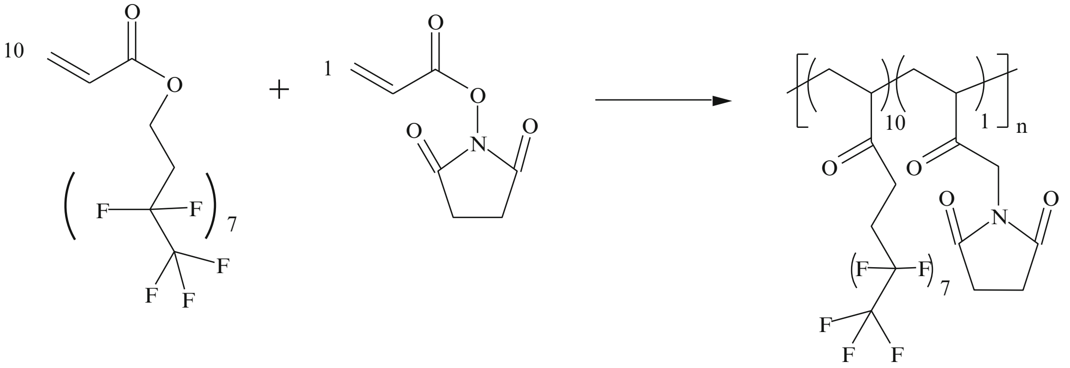


The polymeric imide could then be reacted with primary amines or ammonia to form ammonium salts for a subsequent reactions with a carboxylic acid in the presence of a coupling reagent. It could then be converted to amides or functionalized as a uranium salt for use as polymer-supported peptide coupling. In addition, the anhydride was also reacted with di(2-pyrldyl)methylamine and formed a recoverable palladium catalyst for cross-coupling reactions that could take place in water.

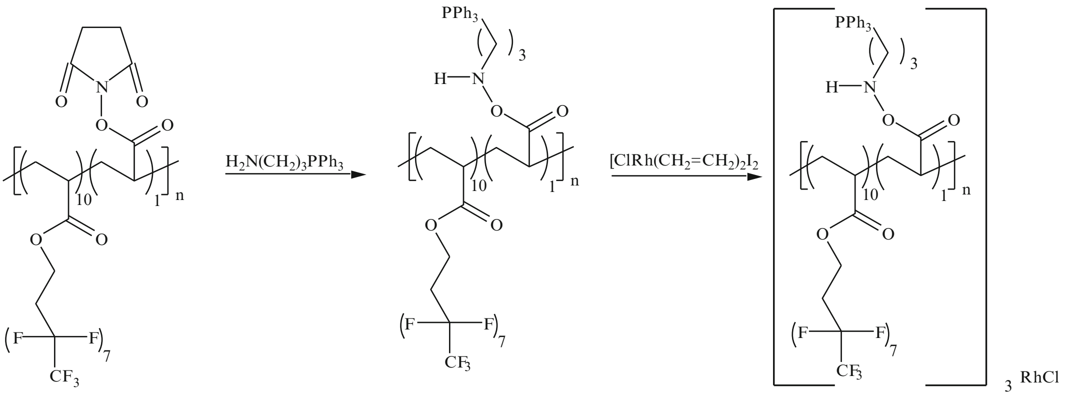


Acrylic Polymers as Support Materials

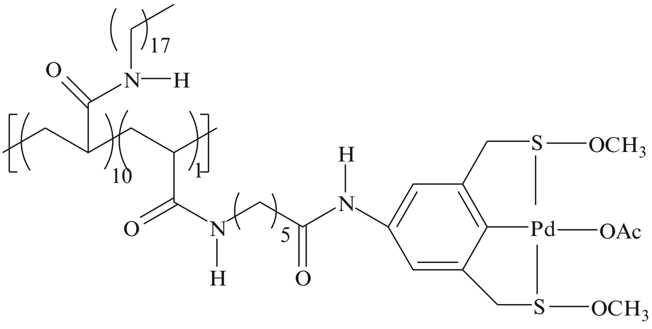
Various acrylic polymers and copolymers are also utilized as support materials. For instance, a copolymer of a fluoroacrylate monomers was prepared by Bergbreiter and coworkers to form a support material that is selectively soluble in fluorinated solvents [28–32].



The resulting polymer was then converted to a rhodium hydrogenation catalyst:



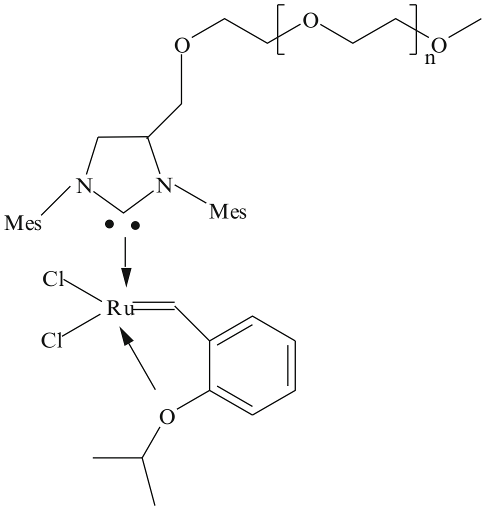
Numerous papers were also published on use of polyacrylamide and copolymers as support materials. Following is an example [33–36].



Bergbreiter reported using this material in mechanistic studies of the Heck reaction [33].

Polyether-Based Supports

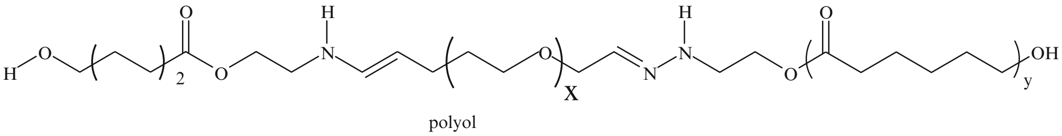
Tentagel, described above, is in wide use today in solid phase syntheses. Polyethylene glycol has also been attached to various other polymers to form support resins. For instance, Fréchet and coworkers [37] used cross-linked methacrylate esters of ethylene glycol oligomers in a suspension polymerization to synthesize hydroxyl group functionalized beads. These beads swell well in a variety of polar solvents. Another example is that of Grubbs attaching a ruthenium metathesis catalyst to polyethylene [38]:



10.1.2 Special Gels for Drug Release

Metyjaszewski et al. reported [39] preparation of nanostructured hybrid hydrogels for tissue engineering and drug delivery applications. They incorporate poly(oligo (ethylene oxide) monomethyl ether methacrylate) nanogels of size 100–200 nm into a larger 3D matrix, such as hyaluronic acid gel. The macroscopic hydrogel acts as a 3D matrix regulator for the drug release. In this work, polymerizable poly(oligo (ethylene oxide) monomethyl ether methacrylate) nanogels were covalently incorporated into a 3D network via a photo-polymerization process. The introduction of disulfide moieties into the polymerizable groups resulted in releasable nanogels from cross-linked 3D network under reducing environment.

Tan, Fu, and coworkers [40] reported preparation of a pH-sensitive biodegradable polyurethane for drug release:



A series of pH-sensitive polyurethanes were synthesized using pH-sensitive macrodiol, shown above, and a tripeptide chain extender. The obtained polyurethane had a number average molecular weights of 4,500–6,200. The material cleaves in acid media (pH 4–6) and degrades in enzymatic solution.

McCormick and coworkers [41] reported the synthesis of a temperature-responsive triblock copolymer, consisting of α-methoxypropyl (ethylene oxide)-*b*-poly(*N*-(3-aminopropyl)methacrylamide)-*b*-poly(*N*-isopropylacrylamide). At room temperature, the polymer is hydrophilic and exists as individual molecule in aqueous solution. Increasing the solution temperature above a lower critical solution temperature leads to self-assembly into micelles. The PAPMA portions were cross-linked with terephthaldicarboxaldehyde at pH 9.0 to generate shell cross-linked micelles with cleavable imine linkages. The release of a model hydrophobic drug, prednisolone 21-acetate, was studied at specific pH and temperature conditions. The drug was released at pH 6.0 as hydrolytic cleavage of the imine cross-links within the swollen micelles occurred.

10.1.3 Utilization of Support Materials

Following are examples of more prominent utilizations of support materials.

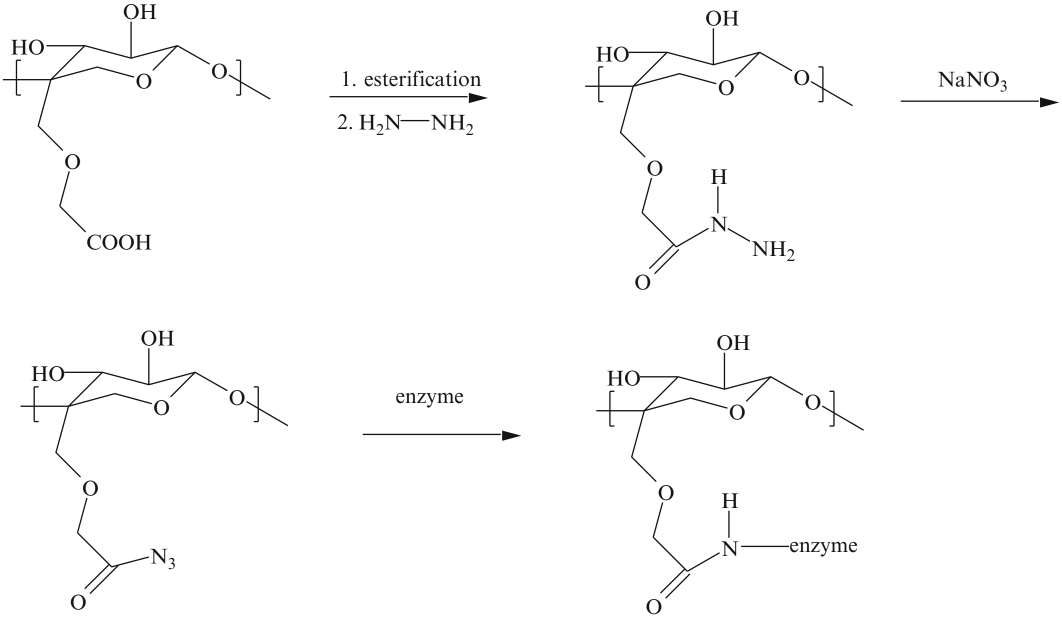
10.1.3.1 Immobilized Catalysts

It may be more accurate to refer to many of them as catalysts attached to polymers. Such catalysts can be inorganic compounds, like, for instance, Lewis acids attached to organic polymers. They can also be organic or biochemical catalysts. Perhaps the biggest group among such attached catalysts are *immobilized enzymes*. They are used in industrial processes as well as in research laboratories. Immobilization often improves stability, and in some rare cases, activity over a broader range of pH and temperatures. Another advantage is elimination of enzyme contamination of waste streams. On the other hand, immobilized enzymes can often be less active after immobilization.

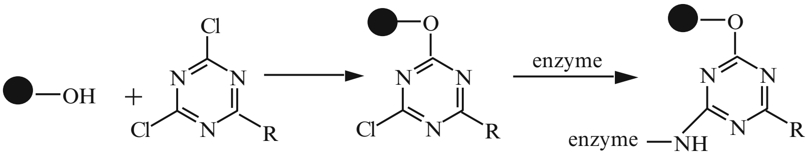
Immobilized Enzymes

Several major techniques of enzyme immobilization are used. One important one is covalent bonding of the enzyme to a support material. Such attachment usually consists of reacting some functional group of the enzyme, not active in the enzymatic process, with a functional group on another polymer that is the carrier. Hydrophilic groups are preferred for reactions with enzymes in aqueous media.

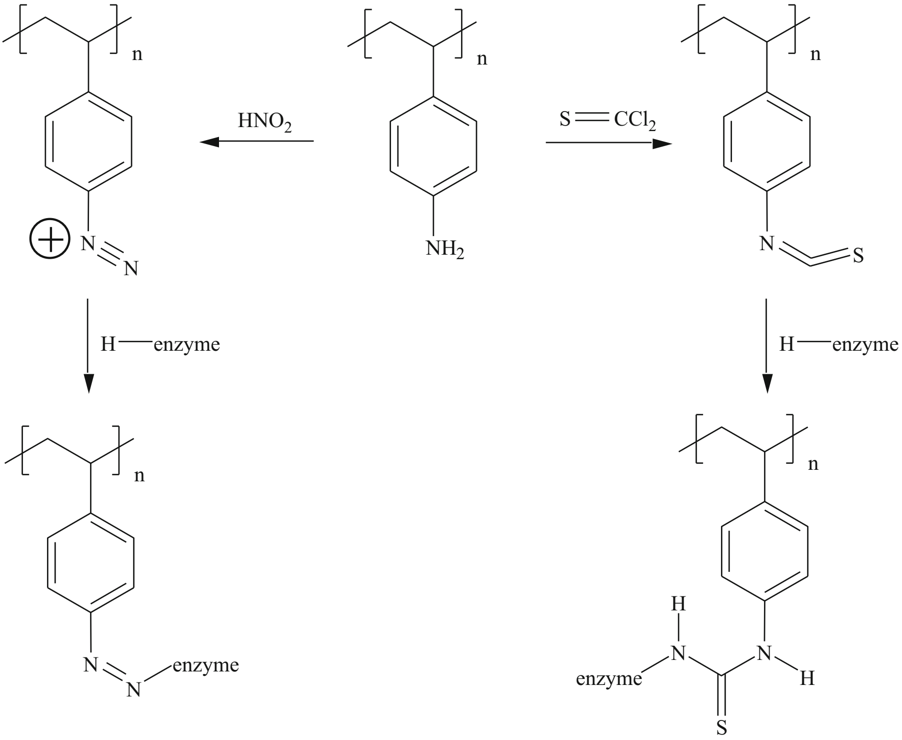
An immobilization of an enzyme on cellulose with azide groups [42] attached can serve as an illustration. Carboxymethyl cellulose is the starting material:



In other techniques, the protein may be bound by some copolymer of maleic anhydride, where the anhydride groups react with some available amine groups on the enzyme [42]. Other techniques may utilize cyanuric chloride attached to polysaccharides for immobilization [42]:



Polyaminostyrene can be diazotized or treated with thiophosgene and then used in enzyme immobilization [43]:

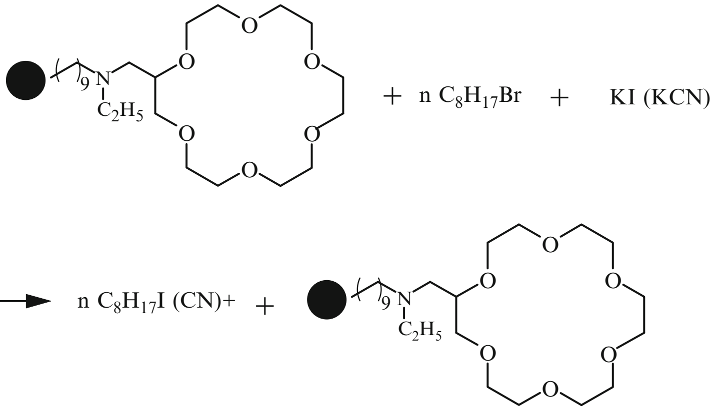


Because epoxy groups on carrier molecules are capable of reacting with an amine or a carboxylic acid groups of the enzymes, they can be used in enzyme immobilization. A variation on the technique is to react a vinyl monomer that contains an epoxy groups, like glycidyl methacrylate or glycidyl acrylate, with the enzyme first. The product is then polymerized or copolymerized through the vinyl portion [44]. As stated earlier, in many cases, immobilization of enzymes is accompanied by some loss of activity. In some instance, the loss in activity can be severe. A special technique, however, was developed [45], where the enzyme called protease is immobilized on a polymer with amino glucose units to form covalently bonded carbohydrate-protein conjugates. In aqueous solution, the conjugated enzymes show about the same catalytic activity as native enzymes. At elevated temperatures, however, they exhibit enhanced stability. In addition, they are capable of catalyzing reactions in organic solvents that denature and inactivate the native enzymes [45].

Hiroshi et al. reported [46] a high-performance immobilized lipase catalyst for polyester synthesis. A porous polypropylene was found to be a good support for immobilization of *Candida antarctica* lipase (enzyme). The immobilized lipase on polypropylene efficiently catalyzes ring opening polymerization of 15-pentadecanolide, polycondensation of divinyl sebacate, and 1,8-octanediol.

10.1.3.2 Immobilized Nonenzymatic Catalysts

There are also many uses for special nonenzymatic polymeric catalysts. For instance, polymer-bound crown ethers, cryptates, and channel compounds can be immobilized to act as polymeric phase-transfer catalysts. The catalytic activity is based on selective complex formation. An example is a use of polystyrene-attached oxygen heterocycles [18]-crown-6 or a cryptand[222] to catalyze replacements of bromine in *n*-octyl bromide by an iodine or by a cyanide group [47]:



A 95% yield is achieved. The catalytic activity, as a result of the complexation of the cations, results in an increased nucleophilicity of the anions.

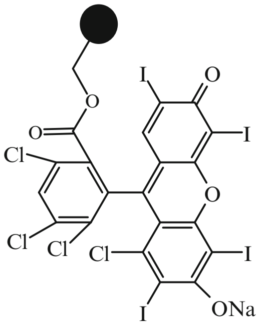
Interactions of ions and ion pairs with vinyl polymers of crown ethers were shown to be considerably more efficient than such interactions with unattached crown ethers [48]. Also, studies of diazo-4,7,13,16-tetraoxacyclooctadecane bound to polyacrylamide gel show an enhancement of cationic complexation when compared to ligands that are not bound to polymers [49]. On the other hand, polymer-bound crown ethers do not offer any advantage over unbound ligands in the Koening–Knorr reaction [50].

The catalytic properties and solute-binding capabilities of the pendant crown ethers and glyme ligands apparently depend on the spacing between the ligands. They also depend upon the structure and length of the chains connecting the ligand bound ions and the solvent [51]. In low polarity solvents, the ligands activate anionic reactants through modification of their ion pair structures.

Ion exchange resins have been used for a long time now to catalyze some reactions. This is mentioned, for instance, in Chap. 7 in the section on epoxy resins. Basic ion exchange resins can also be used in condensations of furfural with aliphatic aldehydes [52].

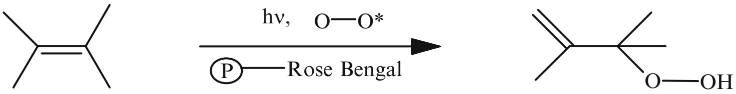
A still different kind of polymeric catalyst is one that has pendant photosensitizers attached. To be effective, the sensitizer portion must absorb light and undergo a transition from a singlet to a longer lived triplet state (see Sect. 10.4). It must then, without emitting radiation, activate a substrate molecule and return to the ground state. Some dyes function in this manner. An example is Rose Bengal. When it is attached to cross-linked polystyrene [53], it can be used to produce singlet oxygen.

The excited oxygen in turn hydroperoxidizes olefins. The structure of polymer-bound Rose Bengal can be illustrated as follows:

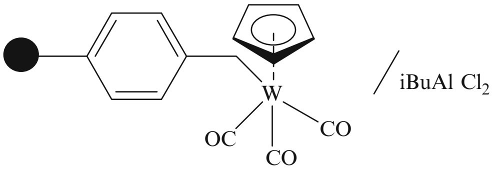


polymer bound Rose Bebgal

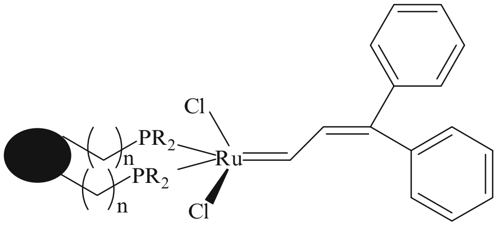
The photosensitized hydroperoxidation reaction of olefins [53] can be shown as follows:



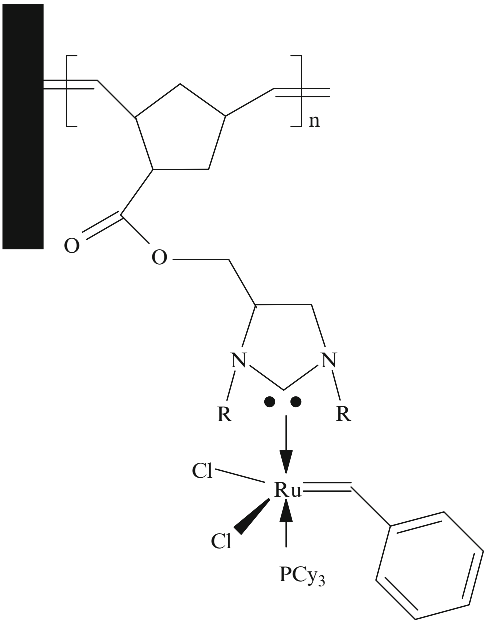
Metathesis catalysts including Grubbs ruthenium catalyst (see Chap. 5) are hard to separate from the reaction products. Chemists therefore sought ways to overcome this problem by immobilizing the catalyst on various supports. Buchmeister recently reviewed various polymer-supported metathesis catalysts [54]. A few are reported here. Early, Grubbs described a phosphine-derivatized polystyrene-supported catalyst [55]



Similarly, a Grubbs type ruthenium catalyst on a phosphine-derivatized polystyrene [56] can be illustrated as follows:

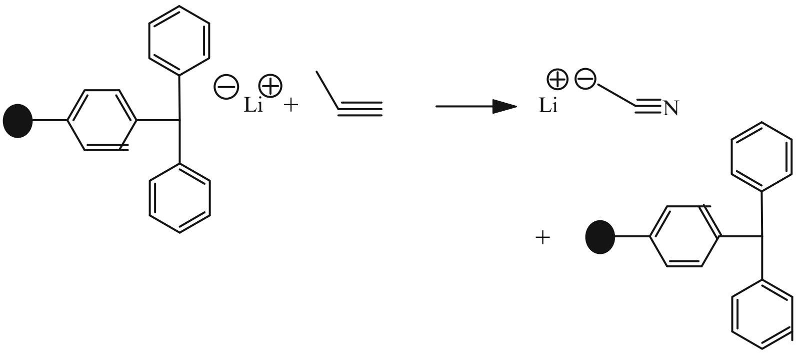


This catalyst, however, turned out to be considerably less active in ring opening metathesis polymerization of norborn-2-ene and in metathesis polymerization of *cis*-2-pentene. Better results were obtained when a ruthenium-based metathesis type catalyst was immobilized via an *N*-heterocyclic carbene [57]. Additional improvements in performance were obtained when the catalyst was immobilized on a monolithic silica rods:

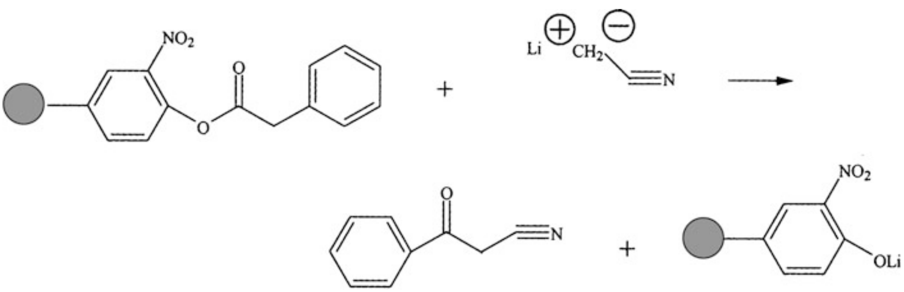


10.1.3.3 Immobilized Reagents

An example of such a reagent is use of immobilized triphenyl methyl lithium to transfer a charge and form a new carbanion:

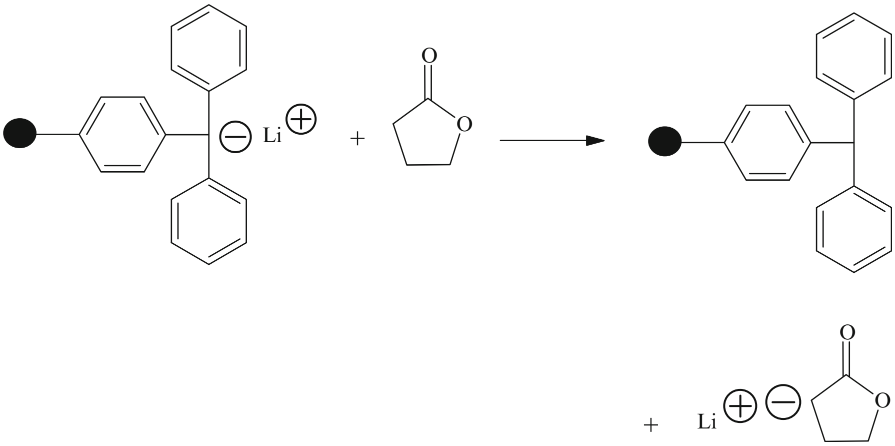


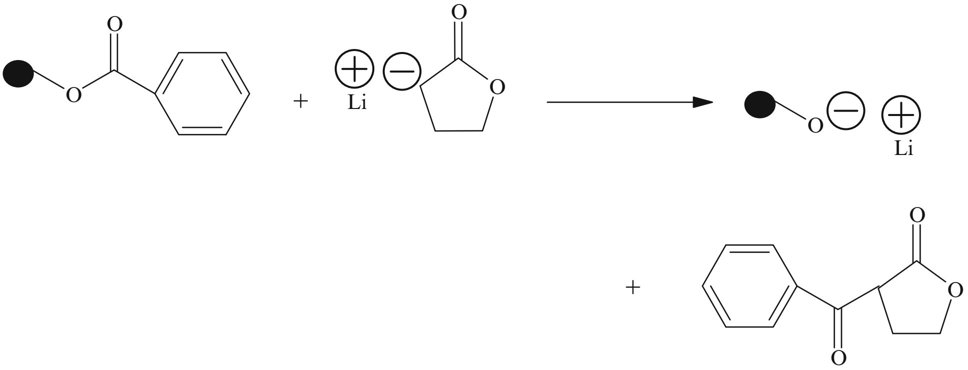
The carbanions in turn react with the ester groups and yielded the desired product:



The yield from the above reaction was found to be about 90%. This compares very favorably with a 27% yield obtainable without polymeric supports [58].

Another example is benzoylation of δ-butyrolactone. When an acylation reaction is being carried out on an ester in solution, the ester enolate must be completely formed before the acylating agent can be introduced. Otherwise, the acylating agent reacts with the base instead. During this period, however, the ester enolate can undergo self-condensation. Using polymer-attached reagents, however, benzoylation of δ-butyrolactone or similar compounds can be achieved in 95% yields [59]





By comparison, when the above reaction is performed in solution, without any support, the yield is only about 31% [59]. Patchornik termed the use of supports in this manner as "wolf and lamb chemistry" [58].

It appears unlikely that all organic reactions can benefit from use of polymeric reagents or catalysts. Nevertheless, such reagents and catalyst do appear to be promising for many applications. The fact that polymer-bound reagents and catalyst are more expensive, however, may preclude wider industrial utilization, except in special cases.

10.2 Electricity-Conducting Polymers

Most polymeric materials, as we usually know them, are insulators, yet conducting polymers were first prepared in 1862 by Letherby who formed polyaniline [60] by electro polymerization. It was only during the past 25–30 years, however, that organic polymers, capable of conducting electric current, created considerable interest [61]. Many polymeric materials were synthesized since. At present, it is not completely understood by what mechanism the electric current passes through them. We do know, however, that all conductive polymers, or intrinsically conducting polymers according to Inzelt [62], are similar in one respect. They all consist of extended π-conjugated systems, namely alternating single and double bonds along the chain.

One of the early known conductive polymers is polysulfurnitride $(SN)_x$, an inorganic material that tends to be explosive, but becomes superconducting at 0.3 K [63]. Since then many other conductive polymers evolved. The most investigated ones appear to be polyacetylene, polyaniline, polypyrrole, polythiophene, poly(phenylene sulfide), and poly(phenylene vinylene) and their derivatives. Many derivatives of these materials and other similar ones also been reported.

The mechanism of electro polymerization that is used to form many conductive polymers is also still not fully understood. According to Diaz et al. [64], the process involves a sequence of coupling steps, with each step being activated by two species. The polymer- forming process requires two electron per step It also includes partial oxidation of the polymer. Thus, the polymer formation and the polymer oxidation occur simultaneously. Diaz proposed a chain propagation process for the polymer formation. Although that is still accepted by many, his mechanism is now being questioned. Heinze et al. [65] suggest that the process of polymer formation consists of oligomer formation and oxidation followed by σ-coupling of chains.

All known conducting polymers have backbones of contiguous **sp**^{2}-hybridized carbon centers. In each of these centers, one valence electron resides in a $\mathbf{p}_z$ orbital. It is orthogonal to the other three sigma bonds. When the material is oxidized or reduced, that removes some of the delocalized electrons. The electrons then obtain high mobility. As a result, the conjugated p-orbitals form a one-dimensional electronic band. The electrons within that band become mobile when it is partially emptied. Depending upon the chemical structure, some polymer can also be self-oxidizing or reducing.

Structural disorder in these polymer molecules interferes with electron mobility. Thus, for instance, polyacetylene exhibits conductivity of 0.1–10 kS/cm. Stretch-orienting this polyacetylene, a process that aligns the chains and removes much of the disorder, increases conductivity to 80 kS/cm [66].

Polyacetylene can be shaped into a silvery looking film. The polymer is more thermodynamically stable in the *trans* form and converts from *cis* to *trans* when heated above 150°C. Partial oxidation of the film, with iodine or other materials, transforms it and increases its conductivity 10^9-fold. The process of transforming a polymer to its conductive form through chemical oxidation or reduction is called **doping**.

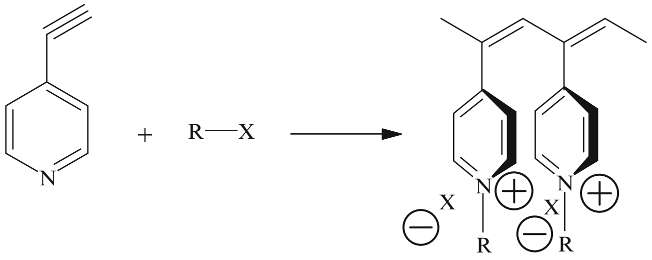
Two types of polyacetylene doping are possible:

$$(\mathrm{CH})_n + 1/2\mathrm{I}_2 \rightarrow (\mathrm{CH})_n^{\oplus}(\mathrm{I}_3)_{0.33}^{\ominus} \quad \text{oxidative doping (p - type)}$$

$$(\mathrm{CH})_n + x\mathrm{Na} \rightarrow (\mathrm{Na}^{\oplus})_x[(\mathrm{CH})_n^{\ominus}] \quad \text{reductive doping (n - type)}$$

The doping process can be reversed and conductive polymers can be undoped again by applying an electrical potential. It causes the dopant ions to diffuse in and out of the structure.

Improvements in preparations of polyacetylene came from several developments. One is the use of metathesis polymerization of cyclooctatetraene, catalyzed by a titanium alkylidine complex. The product has improved conductivity, though it is still intractable and unstable. By attaching substituents, it is possible to form soluble and more stable materials that can be deposited from solution on various substrates. Substitution, however, lowers the conductivity. This is attributed to steric factors introduced by the substituents that force the double bonds in the polymeric chains to twist out of coplanarity [67]. A family of substituted polyacetylenes were prepared [68] that were actually formed from ethynylpyridines by a polymerization reaction that takes place spontaneously by a quaternization process:



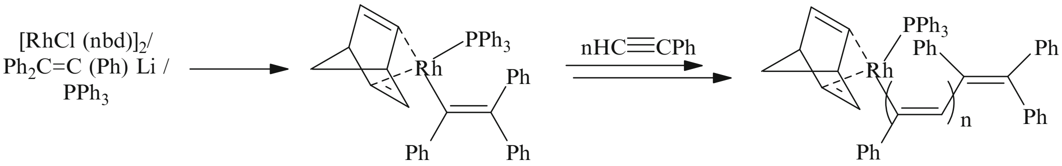
where X is a bromine or an iodine.

Like other substituted polyacetylenes, these materials are fairly stable in air and are soluble in polar solvents, also in water. The conductivity of these polymers is improved over previously reported substituted polyacetylenes to within the range of semiconductors.

Preparation of a highly conductive polyacetylene was achieved when Ziegler–Natta catalyst was used by Shirakawa in aged silicone oil at 150°C. It is believed that this reaction results in formation of polymers with less defects in the structures. The conductivity of these materials, when doped, actually approaches that of copper [62].

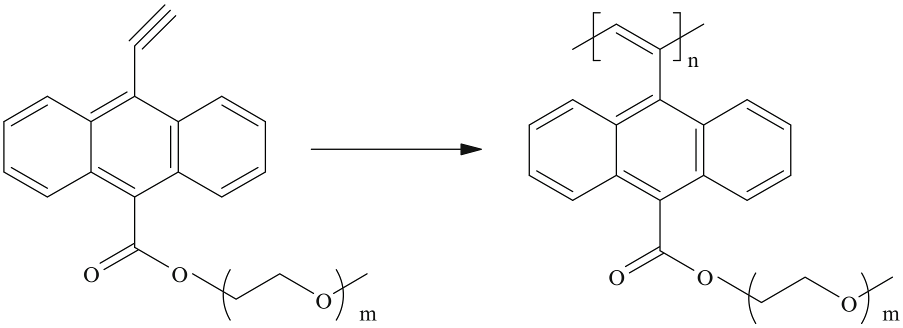
Considerable progress has been achieved in development of catalyst systems for living polymerization of various substituted acetylenes during the last 10 or 15 years [69]. Nowadays, there are available single-component catalysts based on stable carbene complexes and multicomponent catalysts based on $MoOCl_4$ and $WOCl_4$, both operating in metathesis mode, as well as Rh(diene) complexes operating in the Ziegler–Natta mode.

For instance, a living polymerization of phenyl acetylene and the synthesis of an end-functionalized poly(phenyl acetylene) by using Rh-based catalyst systems, $[RhCI(nbd)]_2/Ar_2C{=}C(Ph)Li/PPh_3$ ($Ar = Ph$, 4-Me_2-NC_6H_4), was reported [70]. Also, use of (triphenyl vinyl)lithium that has functional groups, such as the dimethylamino groups, results in formation of end-functionalized poly(phenyl acetylene)s, which quantitatively contained functional groups at the initiating chain end. The polymerization of phenyl acetylene by a catalyst prepared from $[RhCl(norbornadiene)]_2$, $Ph_2C{=}C(Ph)Li$, and PPh_3 proceeds smoothly in benzene to give quantitatively a yellow polymer with the number average molecular weight of 5,400 and the polydispersity ratio of 1.14. The reaction can be illustrated as follows:



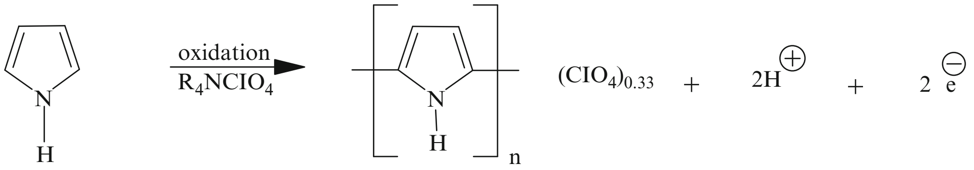
Masuda and colleagues reported [71] that they synthesized poly(anthryacetylenes)-bearing oligo oxyethylene units by using a transition metal catalyst, $WC1_6$, in 30 and 34% yields. The polymers were black solids. These polymers are soluble in chloroform, tetrahydrofuran, acetone, etc., but insoluble in alcohols, aliphatic hydrocarbons, etc. The UV–VS spectra of the polymers showed absorption maxima and band edges at around 570 and 750 nm, respectively, indicating that the polymer chains possess highly extended conjugation. These polymers exhibited blue emission

(emission maxima 470 nm) upon photo-excitation at 380 nm. One of the polymers ($n = 4$) showed a fairly large ionic conductivity (4.1×10 S/cm) at 80°C upon doping with $Li(CF_3SO_2)_2N$.

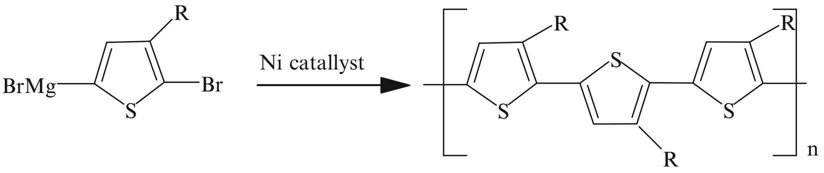


In 1979, it was demonstrated that **polypyrrole** can be formed as a film by electrochemical oxidative polymerization of the pyrrole monomer in acetonitrile. The polymers that form on the surface of the electrode can be peeled off as flexible, shiny blue-black films. Subsequently, in 1982 it was shown that thiophene can also be electro polymerized oxidatively at the anode. The method allows control over the oxidative potential during the polymerization, yielding doped films with optimized polymer properties. Both polypyrrole and **polythiophene** differ from polyacetylene in that both form during the polymerization in the doped form and that both are stable in air. They are, however, less conductive than the doped polyacetylene. The exact structures of polypyrrole and polythiophene prepared that way are still not fully established. The process of oxidative polymerization involves very reactive cation radical intermediates. Much of the coupling of the heterocyclic rings together is at the 2 and 5 positions. X-ray photoelectron spectroscopy shows that the polypyrrole formed in this manner has about 30% of the linkages at other than 2 and 5 positions. They might be in the 2 and 3 positions. This introduces "defects" into the hypothetically ideal chain and reduces the conjugation length and with it the conductivity.

The flexible films of polypyrrole that form upon electrochemical oxidation are not only stable in air and water, but may also be heated to 200°C without much change in electrical properties. The oxidative polymerization of pyrrole can be illustrated as follows:

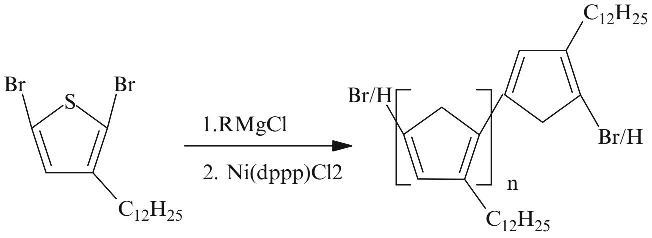


A regioselective synthesis of a highly conductive **poly(3-alkylthiophene)**s was reported [72]. Following synthetic procedure was used:



The iodine doped, unoriented poly(3-dodecyl thiophene)s exhibits average conductivity of 600 S/cm and a maximum conductivity of 1,000 S/cm [72].

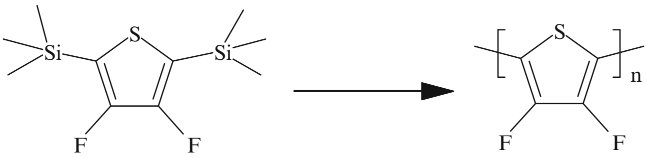
More recently, McCullough and coworkers [73] reported using the Grignard reaction to synthesize poly(3-dodecyl thiophene)



The molecular weights of the products were found by them to range from 10,000 to 50,000.

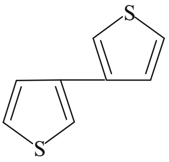
Earlier, McCullough et al. [74] reported that they have developed an end group functionalization method that enables the synthesis of many well-defined block copolymers that form nano wires with high electrical conductivity. They claim to have discovered that nickel-initiated regioregular polymerization of alkyl-thiophenes proceeds by a chain growth mechanism. They also observed that the degree of polymerization of poly(alkyl-thiophenes) increases with conversion and can be predicted by the molar ratio of monomer to nickel initiator. On the basis of their experimental results, they concluded that nickel-initiated cross-coupling polymerization is essentially a living system, with low polydispersities.

Irvin et al. [75] reported forming a poly(3,4-difluoro thiophene) by anodic polymerization:



Because of the very electron-poor nature of the monomer, electro deposition could only be accomplished with a strong Lewis acid, BF_3EtO.

Mendez and Weder improved considerably the conductivity of poly(3,4-diethylene, dioxythiophene) by cross-linking [76]. The polymers were oxidatively synthesized in the presence of four different oxidative cross-linkers,



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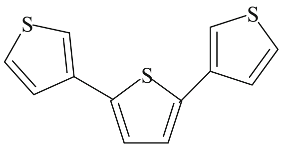

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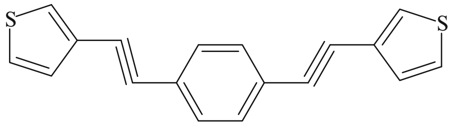
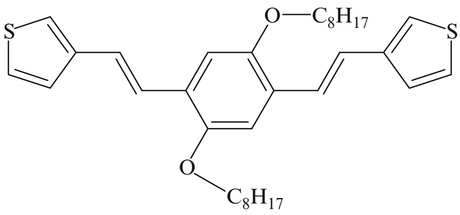
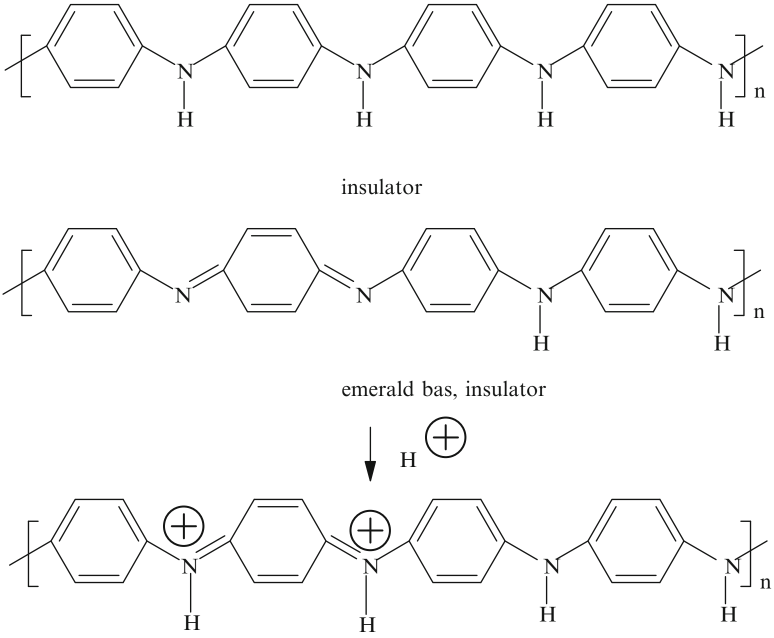




The cross-linking compounds were incorporated into the polymer in amounts of 0.5–2%. As a result, in a maximum case, the conductivity increased by as much 36%.

Polyaniline was first prepared at the beginning of the last century. Several oxidation states are known. The conductivity and the color of the material vary progressively with oxidation. Only one form, however, known as the emeraldine salt, is truly conducting. The material can be prepared readily by electrochemical or chemical oxidation of aniline in aqueous acid media. Common oxidants, such as ammonium peroxydisulfate, can be used. Flexible emeraldine films can be cast from solutions of *N*-methylpyrrolidone and made conductive by protonic doping. This is done by dipping the films in acid or by exposing them to acid vapors. The process results in protonation of the imine nitrogen atoms:

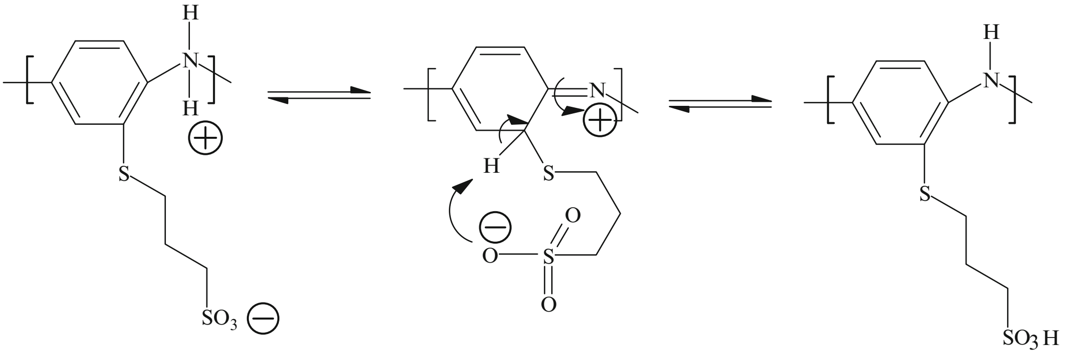


The conductivity of the emeraldine salt increases with decrease in pH of the acid used to dope it. In this respect, polyaniline, in its emeraldine form, differs from other conductive polymers because it does not require partial oxidation or reduction for doping. Protonation of the imine nitrogens is sufficient to make it a very conductive material.

A different method of synthesizing polyaniline was reported [77]. It uses an enzyme, horseradish peroxidase, in the presence of hydrogen peroxide to polymerize aniline. To prevent reactions at the *ortho* positions of the phenyl rings that yield insoluble branched materials, a polyelectrolyte template, like sulfonated polystyrene, was used. The polyelectrolyte aligns the monomers, dopes the polyaniline to the conducting form, and forms an irreversible complex with the polyaniline to keep it water-soluble [77]. The conductivity of the complex increases with increasing polyaniline to sulfonated polystyrene molar ratios. Conductivities of 0.005 S/cm are obtained with the pure complex and increase to 0.15 S/cm after additional doping by exposure to HCl vapor [77].

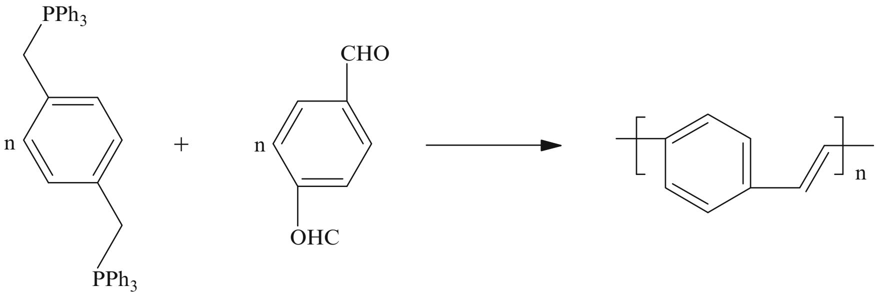
Lee reported [78] a new synthesis of polyaniline, where aniline hydrochloride monomer acts as a surfactant. The organic phase serves to diffuse water away from water-insoluble oligomers. As a result, the chains grow, because the monomer radicals can meet the active polymer chain ends at the organic aqueous interfaces. This results in formation of a polymer with high structural integrity. This enables the electrons or holes to travel in a perpendicular direction.

Han et al. [79] reported preparation of highly conductive and thermally stable, self doping propylthiosulfonated polyanilines. The polymer was illustrated as follows:

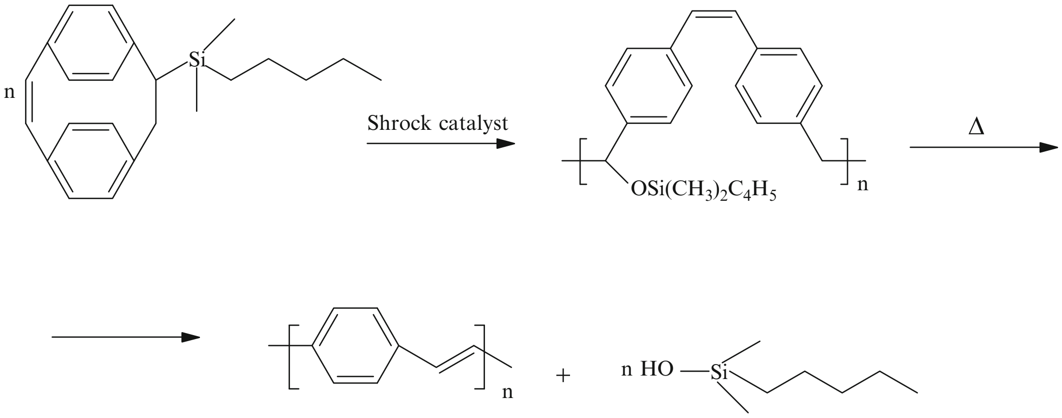


The material was found to be a better conductor than sulfonated polyaniline and more thermally stable.

Poly(phenyl vinylene) can be synthesized by several routes. One of them is step growth polymerization [80] by the Witting reaction:

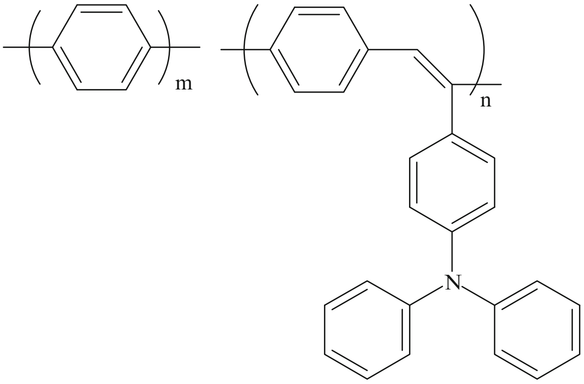


There are several other routes to poly(phenyl vinylene). One of them is through a metathesis ring opening polymerization:



The polymer can be doped with iodine, acids, and ferric chloride. Alkoxy-substituted poly(phenyl vinylene) is easier to oxidize and exhibits higher conductivity.

Natori et al. reported [81] the synthesis of a copolymer that consists of p-phenylene, p-phenylene vynelene, and styryl amine:



Orientation of the films yields large increases in conductivity. Thus, films of doped, oriented poly (phenylene vinylene) [81] not only have the strength of high-performance polymers, but also their conductivities measure as high as 10^4 S/cm. This is approximately 1,000 times greater than that of the unoriented films.

Another interesting material consists of the doped forms of covalently linked siloxane-phthalocyanin (Pc) complexes, $[Si(Pc)O]_n$. In these polymers, the planar phthalocyanin units are apparently stacked face-to-face and form columns, due to the silicon-oxygen-silicon bonds. The polymers appear to be intrinsically metallic systems. The principal pathways of conductivity are perpendicular to the phthalocyanin planes. The extended π–π systems that form result from face to face are a pathway for the electron [67].

There are numerous applications for conducting polymeric materials. These applications include use in electronics, in organic solar cells that convert light to electricity and others.

10.3 Photonic Polymers

The term photonic polymer describes a wide variety of polymeric materials that respond to light in one manner or another. These can be rearrangement upon irradiation with light of a certain wavelength, or conductivity of electricity upon irradiation, or dimerization and others. What they all have in common is that they all required irradiation with light, often but not always of a specific wavelength to undergo a change. To understand the mechanism of these reactions, it is first necessary to look into the nature of light and how it reacts with matter.

10.3.1 The Nature of Light

Photochemical reactions involve interactions of light with matter. They either induce chemical changes, or they induce luminescence and conversions of electronic and other forms of energy into heat. For practical purposes, the photochemical reactions that are discussed here are limited to those that take place in the presence of light that ranges from ultra-violet to infra-red.

Light, independent of the source, travels in vacuum with a velocity equal to 2.9979×10^{10} cm/s. But that is only true in a vacuum. Within any medium, the light moves with a velocity of:

$$C' = C/(\varepsilon\mu)^{1/2}$$

where ε is the dielectric constant of the medium and μ is the magnetic permeability.

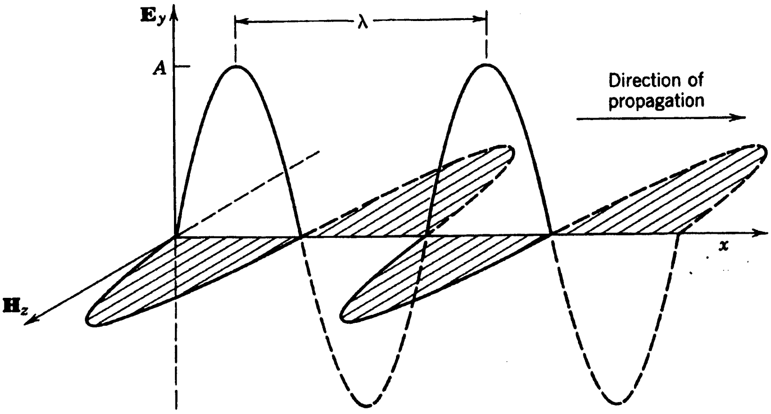


Fig. 10.1 The instantaneous electric, $\mathbf{E}_y$ and magnetic $\mathbf{H}_x$ field strength vectors of a light wave as a function of position along the axis of propagation (from Calvert and Pitts [82])

Our concept of light is that it also consists of packets of energy that travel in waves. In each packet, there is a range of energies. These energies cannot be represented by one wavelength, but rather by a whole spectrum of wavelengths. The energy of each particular wavelength in the wave-packet is a discrete unit, a *quantum*. Electromagnetic radiation is described in terms of a transverse plane wave involving associated electric and magnetic fields. Experimental data suggest that the electric vector **E** and magnetic vector **H** which describe the respective field strengths are aligned in planes at right angles to one another, with both planes perpendicular to the direction of propagation of the wave. This was illustrated by Calvin and Pitts [82], as shown in Fig. 10.1.

A convenient model for the variation of the field strength as a function of time K and distance x along the axis of propagation is one that can be described in Cartesian coordinates by the sinusoidal functions in the following equations:

$$\mathbf{E}_y = A\ \sin 2\pi(x/\lambda - vt)$$

$$\mathbf{H}_z = (\varepsilon\mu)^{1/2} A\ \sin 2\pi(x/\lambda - vt)$$

In these equations, $\mathbf{E}_y$ is the electric field strength vector lying in the xy plane and increasing along the y-axis, $\mathbf{H}_z$ is the magnetic field strength vector lying in the xz-plane and increasing along the z-axis, A is the amplitude of the electric vector (the *intensity* of the wave is proportional to A^2), ε is the dielectric constant, and μ is the magnetic permeability of the medium through which the light wave is transported. In a vacuum, $\varepsilon = \mu$ and they are approximately unity in air. The length of the wave, that is, the distance between adjacent maxima in the vectors measured at any instant along the direction of wave propagation (the x axis) is λ, while v is the frequency or number of complete cycles of vector position change per second. The relationship between λ and v is:

$$C/v = \lambda$$

where C is the velocity of the radiation. The frequency v is independent of the medium through which the radiation travels. Wavelength λ and velocity C, on the other hand, depend on ε and μ of the medium.

Ordinary light is not polarized. It consists of many electromagnetic vectors that are undulating in fixed, though randomly oriented with respect to each other, planes. When the light is polarized in a plane, it is believed that all the waves have their electric vectors oriented in the same direction. When the light is polarized elliptically, then it is believed that two plane waves of equal wavelength and frequency and with identical directions of propagation have the electric vectors perpendicular to one another and out of phase, as shown in Fig. 10.1.

The degree of polarization of light p is usually expressed by the equation

$$p = \frac{I_{\|} - I_{\perp}}{I_{\|} + I_{\perp}}$$

where $I_{\parallel}$ and $I_{\perp}$ represent the intensities of light transmitted by an analyzer parallel and perpendicular to the plane of maximum polarization of ht incident light.

The above-described model is incomplete and even called naive by some. Mathematically, however, it can successfully account for many observations concerning light, and this theory has been used successfully to describe many phenomena associated with optics.

10.3.2 Quantum-Mechanical Description of Light

In order to better understand the emission and absorption of light by molecules, it is necessary to look at the quantum-mechanical concept of the nature of light. In this concept, light is considered to be a *beam of photons* whose energies are quantized. Detailed description of quantum mechanics and spectroscopy is beyond the scope of this book. Here will only be presented the major conclusions necessary for better understanding of light.

In the quantum theory of radiation [93], all electromagnetic radiation are considered to be beams of particles. As stated above, they are called photons. Each photon has an energy **E** that is defined by the Planck relationship,

$$\mathbf{E} = h\upsilon = hc/\lambda$$

where h is the proportionality constant, called Planck's constant. It is equal to 6.6256×10^{-27} erg s/quantum. The quantum theory has explained very many phenomena associated with interactions of light with matter. One of them is the photoelectric effect. This effect was discovered early by Hertz. He found that short wavelength radiation incident on a metal surface caused instantaneous emission of photoelectrons. The classical electromagnetic wave theory fails to explain these phenomena. Einstein, in 1905, derived an equation that is based on the phenomenon that, when a quantum of light of energy $h\upsilon$ is absorbed by the metal, an electron is emitted. This energy relationship is described by the following equation:

$$m_{\mathrm{C}}\upsilon/2 = h\upsilon - \omega_0$$

where ω_0 is the minimum energy necessary to remove an electron, and $m_c\upsilon/2$ is the kinetic energy of the electron emitted.

10.3.3 Interaction of Light with Organic Molecules

If monochromatic light passes through a uniform thickness of an absorbing homogeneous medium with the absorbing centers acting independently of each other, then the energy of light that is absorbed follows the Lambert-Bouguer law. According to this law of physics, the light absorbed is independent of the intensity of the incident light and the intensity of radiation is reduced by the fraction that is proportional to thickness of the absorbing system. In addition, Beer's law states that absorption is proportional to the number of absorption centers. The two laws are usually combined and expressed as follows:

$$\mathrm{d}I/\mathrm{d}l = kcI$$

where I is the intensity of the radiation, l is the length of the optical path, through the absorbing medium, c is the concentration of the absorbing centers, and k is proportionality constant. While there are no know exceptions to the Lambert-Bouguer law, there are deviations from Beer's law due to partial ionization, molecular association and complexation, and fluorescence.

Portions of organic molecules or whole molecules that have π bonds can absorb light radiation, provided that it is of the right wavelength. Particular groupings or arrangements of atoms in molecules

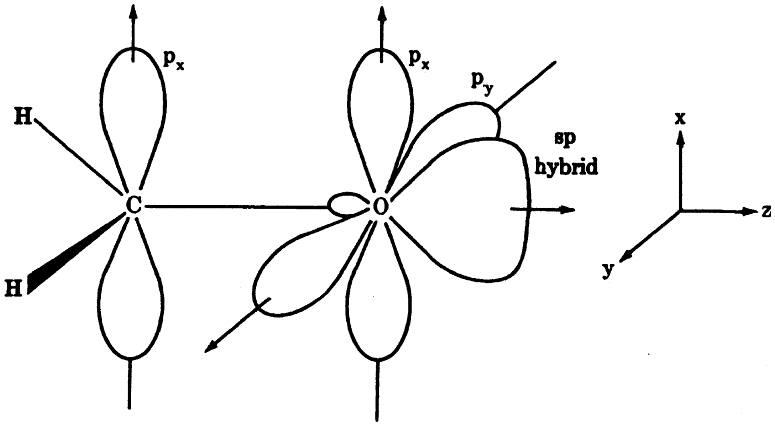


Fig. 10.2 The orbitals of formaldehyde (from Jaffe and Orchin)

give rise to characteristic absorption bands. Such groups of atoms, usually containing π bonds, are referred to as *chromophores*. Examples of such molecules with π bonds are compounds that contain carbonyl or nitro groups and aromatic rings. A molecule that serves as an example of carbonyl arrangement, one that is often referred to, is a molecule of the formaldehyde. In this molecule, the carbon atom is linked to two hydrogens and to one oxygen by σ bonds. The hybrid sp^2 orbitals bond one electron of carbon with one of oxygen in an sp orbital. In addition, there are two unbonded n electrons on oxygen that point away from the carbon atom. The orbitals of formaldehyde, the simplest of the carbonyl compounds, were illustrated by Orchin and Jaffe [88], as shown in Fig. 10.2.

As described above, the molecule has σ and π bonded skeleton, shown above. The carbon atom is attached to two hydrogen atoms by a single bond and to the oxygen atom by a double bond. This bonding of the carbon to the two hydrogens and one oxygen atoms is by means of sp^2 hybrid orbitals. The orbitals are approximately at 120° angles from each other. In the ground state of the molecules, the pair of electrons that form a bond is paired and has opposite or antiparallel spin. In this state, the formaldehyde molecule is planar. The Pauli exclusion principle [83] states that no two electrons can have identical quantum numbers. That means that if two electrons are in the same orbital and three of their quantum numbers are the same, the fourth quantum number, the spin quantum number, must be different. The total spin quantum number of a molecule is designated by a letter J and the sum of the spins of the individual electrons by a letter S. The spin quantum number of a molecule J is equal to $[2S] + 1$.

This arrangement of electrons in the p orbital can generate π bonding and π* antibonding orbitals. Absorption of light energy by a chromophore molecule results in formation of an excited state and an electronic transition from the ground state to an excited state. Such light may be in the ultraviolet or in the visible region of the electromagnetic spectrum, in the range of 200 μm to approximately 780 μm. Promotion of electrons out of the σ bonding orbitals to the excited states requires a large amount of energy and rupture of bonds in the process. On the other hand, the electronic transition to promote one of the n electrons on the oxygen atom in formaldehyde to the *antibonding* or the *nonbonding* orbital, $n \rightarrow \pi^*$ level requires the least amount of energy. The name, *antibonding*, as one might deduce, is a type of orbital where the electrons make no contribution to the binding energy of the molecule. In formaldehyde, this $n \rightarrow \pi^*$ transition to the excited state gives rise to an absorption band (at about 270 μm). This is a relatively weak band and it suggests that the transition is a forbidden one (forbidden does not mean that it never occurs, rather than it is highly improbable). It is referred to as a symmetry forbidden transition. The reason for it being forbidden is crudely justified by the fact that the π* is in the xz plane (see Fig. 10.2). The n electrons in the p orbital are in the xz plane and perpendicular to the π* orbital. Because the spaces of the two orbitals overlap so poorly, the likelihood of an electronic transition from one to the other is quite low. As stated above, in the ground (normal) state of the molecules, two electrons are paired. The pairing means that these electrons have opposite or anti-parallel spins. After absorbing the light energy, in the singlet excited

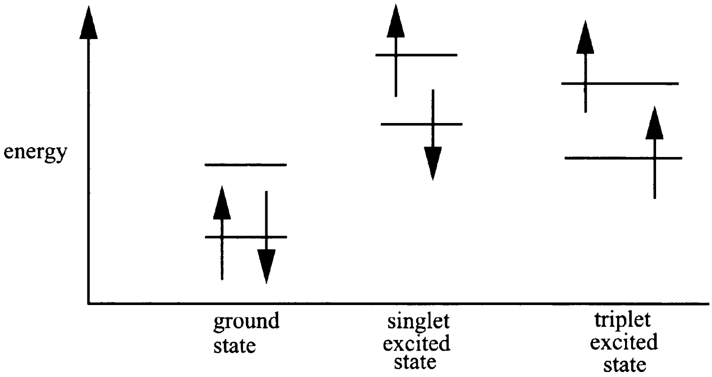


Fig. 10.3 Illustration of the singlet and the triplet states (from Ravve [91])

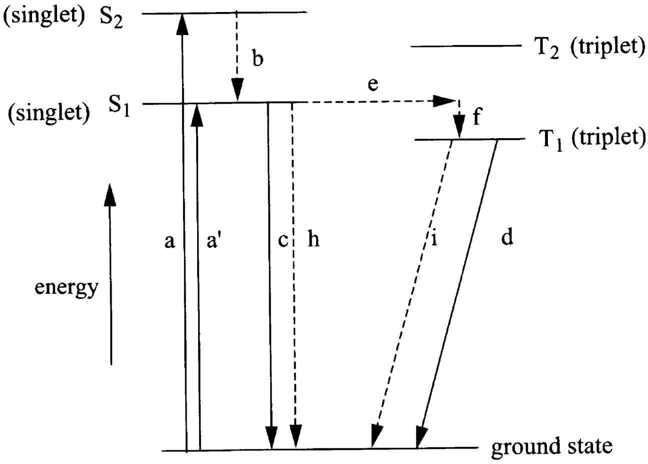


Fig. 10.4 Illustration of energy transitions (from Ravve [91])

state the two electrons maintain anti-parallel spins. The n → π* excitation, however, can lead to two excited state, a singlet (S_1) and a triplet (T_1) one with an absorption band (at about 250 μm). Intersystem crossing to a triplet state from the singlet results in a reversal of the spin of one of the electrons and an accompanying loss of some vibrational energy. This is illustrated in Fig. 10.3.

The intersystem crossing from the singlet to triplet states can occur with high efficiency in certain kinds of molecules, particularly in aromatic and carbonyl-containing compounds. Electron–electron repulsion in the triplet state is minimized because the electrons are farther apart in space and the energy is lower in that state than that of the corresponding excited singlet one. Solvents can exert a high influence on the n → π* transitions. While the intersystem crossing is a forbidden transition (see above), it can actually occur with high frequency in aromatic or carbonyl compounds.

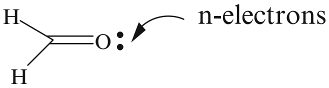
The chemical mechanism of photo-excitation of organic molecules has been fully described in various books on photochemistry [82, 84, 85, 87]. It will, therefore, be discussed here only briefly. The transitions are illustrated here in a very simplified energy diagram that shows the excited singlet state and the various paths for subsequent return to the ground state in Fig. 10.4.

The energy diagram (Fig. 10.4) represents energy states of a molecule that possesses both n and π* electrons. S_1 and S_2 are the singlet excited states. T_1 and T_2 are the excited **triplet** states. Solid lines represent electronic transitions. They are accompanied by absorption or emissions of photons. Radiationless transitions are represented by doted lines. The above diagram shows the lowest singlet state S_1, where the electrons are spin-paired, and the lowest triplet state T_1, where the electrons are spin-unpaired. The electron is excited by light of a particular wavelength into an upper singlet level, S_2. Relaxation follows via an internal conversion process to S level. The excess energy is dissipated by vibrational interactions giving rise to evolution of heat. At the S_1 level, there are three possible ways that the excited state becomes deactivated. The return to the ground state from the triplet one requires again an inversion of the spin. In Fig. 10.4, *a* and *a′* represent the energies of light absorbed, *b*, *h*, and *I* the energies of internal conversion, *c* represents return to the ground state by way of fluorescence, and *d* return by way of phosphorescence.

The Franck and Condon principle states that during an electronic transition the various nuclei in the molecule do not change their position or their moment [90]. What it means is that electronic transitions are much more rapid (10^{-15} s) than nuclear motions (10^{-12} s) so that immediately after the transitions the nuclei have nearly the same relative positions and velocities that they had just before the transitions. The energy of various bonding and antibonding orbitals increases for most molecules in the following order,

$$\sigma < \pi < \mathrm{n} < \pi^* < \sigma^*$$

In molecules with heteroatoms, such as oxygen or nitrogen, however, the highest filled orbitals in the ground state are generally nonbonding, essentially atomic, n orbitals. This, for instance, is a case with ketones and aldehydes. These molecules possess electrons that are associated with oxygen and are not involved in the bonding of the molecules. The n electrons in formaldehyde can be illustrated as follows:



As explained above, in the triplet state the spin of the excited electron becomes reversed. This results in both electrons having the same spin. From purely theoretical approach, such an electronic configuration is not allowed. Due to the fact that the excited electron cannot take up its original position in the ground state until it assumes the original spin, the triplet state is relative long-lived. For instance, in benzophenone at 77°C the lifetime can be 4.7×10^{-3} s. Orchin and Jaffe wrote [88] that the triplet state has a lifetime of 10^{-3} s. By comparison, the lifetime of a singlet state is about 10^{-8} to 10^{-7} s. Also, in the triplet state the molecule behaves as a free-radical and is very reactive. The carbon atom has a higher electron density in the excited state than in the ground state. This results in a higher localized site for photochemical activity at the orbital of the oxygen. Because the carbonyl oxygen in the excited state is electron-deficient, it reacts similarly to an electrophilic alkoxy radical. It can, for instance, react with another molecule by abstracting hydrogen.

At higher frequencies (shorter wavelength) of light, if the light energy is sufficiently high, $\pi \rightarrow \pi^*$ transitions can also take place. All aromatic compounds and all conjugated diene structures possess delocalized π systems. Because there are no n electrons, all transitions in these systems are $\pi \rightarrow \pi^*$. In general, the excited states of molecule are more polar than the ground states. Polar solvents, therefore, tend to stabilize the excited state more than the ground state. As shown in Fig. 10.4, the triplet state is lower in energy than the corresponding singlet state. This is due to the fact that the electron–electron repulsion is minimized, because they do not share each other's orbitals according to the Pauli exclusion principle. Thus, less energy is required for the triplet state.

The chemical reactivity of organic molecules is determined principally by the electron distribution in that molecule. When the electron distribution changes, due to absorption of light and subsequent transitions, photochemical reactions take place while the molecule is in an electronically excited state. The phenomenon of light absorption, formation of the excited states, and subsequent reactions obey four laws of organic photochemistry, as was outlined by Turro [87]:

1. Photochemical changes take place only as a result of light being absorbed by the molecules.
2. Only one molecule is activated by one photon or by one quantum of light.
3. Each quantum or photon which is absorbed by a molecule has a given probability of populating either the singlet state or the lowest triplet state.
4. In solution, the lowest excited singlet and triplet states are the starting points for the photochemical process.

The relationship between the amount of light or the number of photons absorbed and the number of molecules, that, as a result, undergo a reaction, is defined as the quantum yield. It is defined as the number of molecules involved in a particular reaction divided by the number of quanta absorbed in the process [1, 3].

Another fundamental law of photochemistry was formulated by Grotthus and Draaper [82, 83]. It states that only the light that is absorbed by a molecule can be effective in producing photochemical changes in that molecule. There is also a fundamental law of photochemistry that states that the absorption of light by a molecule is a one-quantum process, so that the sum of the primary processes, the quantum yield, must be unity [82, 83]. Also, the law of conservation of energy requires that the sum of the primary quantum yields of all processes be equal to unity. Mathematically this can be expressed as:

$$\Phi_{\text{total}} = \sum_i \Phi_i = 1$$

where Φ is the quantum yield. The quantum yield of photochemical reactions is important because it sheds light on the mechanisms of the reactions. The number of molecules involved in a particular photoreaction can be established by an analytical kinetic process and the number of quanta absorbed can be measured with the aid of an actinometer. The quantum yield can also be expressed in general kinetic terms [1]:

$$\Phi_i = \varphi_{\text{ES}}\varphi_R P_i \quad \text{or} \quad \Phi_i = \sum_i \varphi^i_{\text{ES}}\varphi^j_R P^j_i$$

The above equations signify that a quantum yield of a particular photo process is the product of two or three distinct probabilities. These are: φ_{ES} is the probability that the excited state will undergo the primary photoreaction necessary for the process. The probability that any metastable ground state intermediate will proceed to stable products is P_i and the probability that the excited state will undergo the primary photoreaction necessary of the process is φ_R.

The concept that matter can only acquire energy in discrete units (quanta) was introduced in 1900 by Max Planck [83]. The corollary of the quantization of energy is that matter itself must be quantized, i.e., constructed of discrete levels having different potential energies. Occupying these particular levels are electrons that obviously possess the energy of the level which they occupy. In a molecule, the intramolecular motions of the electrons and the associated molecular electronic levels must be taken into account. There are, in addition to electronic levels, modes of vibration and rotation that are also quantized. In other words, the absorption of a photon of light by any molecule is a reaction that must promote transitions between quantum states. This requires two conditions. These are: (1) for a molecular state m with energy E_m, there must be a state n of higher energy, E_n, so that $h\upsilon = E_n - E_m$; (2) there must be specific interaction between the radiation and the light-absorbing portion of the molecule that results in a change in the dipole moment of the molecule during the transition. If we designate the wave functions of the states m and n as ψ_m and ψ_n respectively, then the transition moment integral that may not equal to zero is:

$$R_{mn} = (\Psi_m / P\Psi_n)$$

where P is the electric dipole operator. It has the form of $P = e\sum r_i$, where e is the electronic charge and r_i is the vector that corresponds to the dipole moment operator of an electron i.

The increase in the energy of a molecule as a result of absorbing a quantum of radiation can be expressed in the relationship [85]:

$$\Delta E = hC/\lambda$$

where λ is the wavelength of the interacting radiation. All reactions that are photochemical in nature involve electronically excited states at one time or other. Each one of these states has a definite energy, lifetime, and structure. The property of each state may differ from one to another and the excited states are different chemical entities from the ground state and behave differently. The return to the ground state from the excited state, shown in Fig. 10.4, can take place by one of three processes [85]:

1. The molecule returns directly to the ground state. This process is accompanied by emission of light of a different wavelength in the form of fluorescence.
2. An intersystem conversion process takes place to the T_1 state, where the electron reverses its spin. The slower decay of excitation from the triplet state to the ground state is accompanied by emission of phosphorescence.
3. The molecule uses the energy of excitation to undergo a chemical reaction

As explained above, in the triplet state the spin of the excited electron becomes reversed. This results in both electrons having the same spin. From purely theoretical approach, such an electronic configuration is not allowed. Due to the fact that the excited electron cannot take up its original position in the ground state until it assumes the original spin, the triplet state is relative long-lived. For instance, in benzophenone at 77°C the lifetime can be 4.7×10^{-3} s. Orchin and Jaffe wrote [88] that the triplet state has a lifetime of 10^{-3} s. By comparison, the lifetime of a singlet state is about 10^{-8} to 10^{-7} s. Also, in the triplet state the molecule behaves as a free-radical and is very reactive. The carbon atom has a higher electron density in the excited state than in the ground state. This results in a higher localized site for photochemical activity at the n orbital of the oxygen. Because the carbonyl oxygen in the excited state is electron-deficient, it reacts similarly to an electrophilic alkoxy radical. It can, for instance, react with another molecule by abstracting a hydrogen.

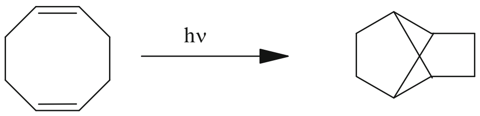
At higher frequencies (shorter wavelength) of light, if the light energy is sufficiently high, $\pi \rightarrow \pi^*$ transitions can also take place. All aromatic compounds and all conjugated diene structures possess delocalized π systems. Because there are no n electrons, all transitions in these systems are $\pi \rightarrow \pi^*$. In general, the excited states of molecule are more polar than the ground states. Polar solvents, therefore, tend to stabilize the excited state more than the ground state. As shown in Fig. 10.4, the triplet state is lower in energy that the corresponding singlet state. This is due to the fact that the electron–electron repulsion is minimized, because they do not share each other's orbitals as stated by the Pauli exclusion principle Thus, less energy is required for the triplet state.

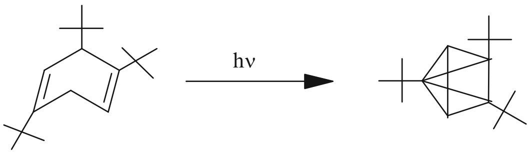
This dissipation of the excitation energy can also be illustrated as follows:

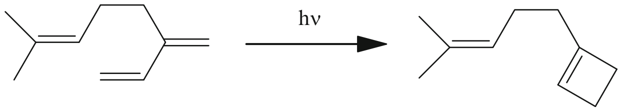
$$\begin{tikzcd}
 & & A_0 + \text{fluorescence} \\
A_0 \quad + \quad \text{light} \arrow[r] & A^* \arrow[ur] \arrow[r] \arrow[dr] & A_0 + \text{heat} \\
 & & \text{chemical reaction}
\end{tikzcd}$$

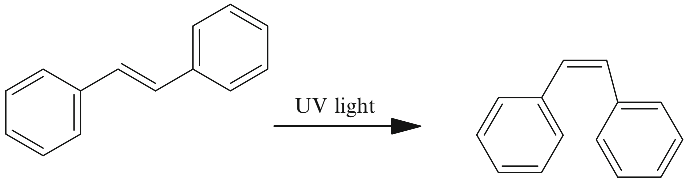
where A_o represents any organic molecule and A* represents the same molecule in an excited state.

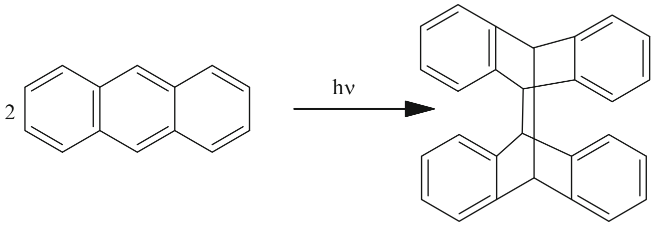
In the process of energy dissipation from the singlet and return to the ground states, the light emission by fluorescence is at a different wavelength than that of the light that was absorbed in the excitation. This is because some energy is lost in this process of the electron returning from its lowest excited state to the ground state. The energy, however, may also, depending upon the structure of the molecule, be dissipated in the form of heat, as shown above. And, also, a third form of energy dissipation can occur when the molecule undergoes a chemical reaction. Depending, again on the molecular structure, the chemical reactions can be rearrangement, isomerization, dimerization (or coupling), fragmentation, or attack on another [90–92] molecule. Some examples of such reactions are:

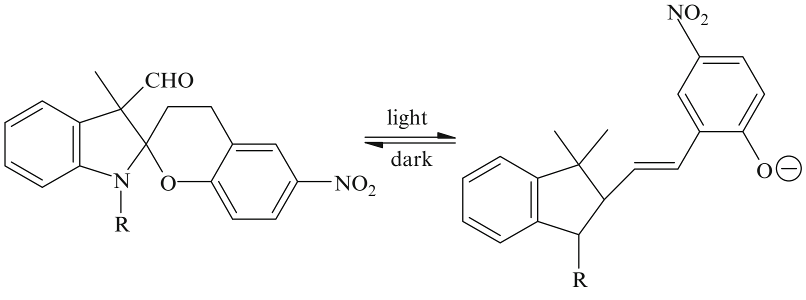




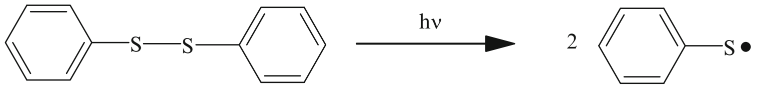








Many other examples can be found in the literature. Most familiar isomerization reaction is that of *trans*-stilbene to *cis*-stilbene, shown above. It was observed that the quantum yield of stilbene *cis-trans* isomerization decreased with an increase in viscosity of the medium [89]. In addition, it was also found that in a polymeric matrix, the photo-isomerization is not inhibited, provided that it occurs above the glass transition temperature of the polymer. An example of a fragmentation of a molecule is the decomposition of disulfides upon irradiation with ultraviolet light of the appropriate wavelength:



The same reaction takes place in peroxides. Ketones and aldehydes cleave by the mechanism of the Norrish reaction.

10.3.4 Energy Transfer Process

Photosensitizers are used in many photonic applications. To understand how they function, it is necessary to understand the energy transfer process. The term ***energy transfer*** [92, 93] refers specifically to **one-step** ***radiationless transfer*** of electronic excitation from a ***donor*** molecule to another, qualified, ***acceptor*** molecule, from one chromophore to another one. This excludes what is referred to as ***trivial energy transfers*** that result from the donor emitting light that is subsequently absorbed by an acceptor. Based on the energy and spin conservation laws, there are two a priori requirements for efficient energy transfer: (1) the process must be thermoneutral or exothermic to occur with highest efficiency, because the activation energies have to be low due to short lifetimes of electronically excited state, and (2) no net spin changes should occur. If a donor molecule was in the triplet state at the time of the energy transfer process, the acceptor molecule is then also promoted to the triplet state. Transfer of singlet to singlet energy should be possible, but it occurs less frequently, because of the shorter lifetimes of the singlet states [92, 93].

Energy transfer is thus a process by which excitation energy passes from one photo-excited molecule, often referred to as a ***sensitizer*** and in this case designated as S*, to another adjacent molecule in its ground state, often referred to as a ***quencher***, in this case designated as Q. The quencher must have a thermodynamically accessible excited state, one whose energy is lower than that of S*. A donor molecule must possess sufficiently long lifetime to be an efficient sensitizer. The reaction of energy transfer can be illustrated as follows:

$$S^* + Q \rightarrow S + Q^*$$

$$S^* \rightarrow S_0 + hv$$

where * designates an excited state. In the process of energy transfer, S* returns (or relaxes) to the ground state S. Energy transfer is further categorized as involving singlet (paired electron spins) or triplet (unpaired electron spins) states. Symmetry rules, as explained above, require a singlet S* to produce a singlet Q* and a triplet S^{3+} to produce a triplet Q^{3+}.

The quenching reaction of the excited state was expressed in a equation by Stern–Volmer. The reaction shown below is based on a quenching reaction that is accompanied by a release of heat:

$$S^* + Q \rightarrow Q^* + S_0 \quad (k_2)$$

$$S^* \rightarrow S_0 + \text{heat} \quad (k_3)$$

The equation is written as follows:

$$\Phi_0/\Phi_Q = \{k_1 + k_2[Q] + k_3\}/(k_1 + k_3)$$

In experimental studies of energy transfer, it is convenient to express the experimental results in another form of the Stern–Volmer equation, as follows,

$$\Phi_0/\Phi_Q = 1 + k_q\tau[Q]$$

where

Φ_0 is the quantum yield for a particular process in the absence of a quenching molecule
Φ_Q is the quantum yield of the quenched process
k_q is the bimolecular rate constant for the quenching process
τ is the lifetime of the state in the absence of a quenching molecules. It is equal to $1/(k_1 + k_3)$, and
[Q] is the concentration of the quenching molecules

Two processes were proposed to explain the mechanism of energy transfer. In the first one, energy transfers result from the interactions of the dipole fields of the excited donors and ground state acceptor molecules (long-range: Forster (dipole–dipole)) [86, 90]. This is referred to as the ***resonance transfer mechanism***. Such transfer is rapid when the extinction coefficients for absorption to the donor and acceptor-excited states involved in the process are large (10^4–10^5 at the maximum). When the dipolar interactions are large, resonance transfers are possible over distances of 50–100 Å. Close proximities of donors and acceptors, however, are required for weakly absorbing molecules. In the second mechanism [90] (short-range: Dexter (exchange)), the excited donor and acceptor are in very close proximity to each other, (up to ≈15 Å) such that their electronic clouds overlap slightly. In the region of the overlap, the location of the excited electron is indistinguishable. It may be at any one instant on either the donor or on the acceptor molecule. Should the pair separate when the excited electron is on the acceptor molecule, energy transfer has been achieved by the mechanism of electron transfer, discussed in the next section.

Both absorption and emission processes may be intramolecular, localized in a single molecule. On the other hand, they can also involve whole crystals that may act as absorbers and emitters. Such energy transfers can manifest themselves in different ways that include sensitized fluorescence or phosphorescence, concentration depolarization of fluorescence, photo-conduction, and formation of triplet acceptor molecules.

Intermolecular energy transfer can be electronic and vibrational and can take place in solid, liquid, and gaseous phases. In addition, the sensitized excitation of Q by S* has to take place within the time that the molecule S remains in the excited state. In summary, theoretical and empirical considerations suggest two modes of transfer, described above:

1. Only when the two molecules are in very close proximity to each other and their centers are separated by the sum of their molecular radii will transfer take place.
2. When the two molecules are at distances that exceed their collision diameters, resonance transfer or long range electronic excitation takes place though Coulombic interactions.

The transfers that take place by mechanism 1 are limited by diffusion of molecules in solution and should be affected by the viscosity of the medium. Transfers by mechanism 2, on the other hand, should be much less sensitive to the viscosity of the medium. It was shown by Foster [86] that the rate constant of resonance-energy transfer (mechanism 1), as a function of distance, is:

$$\text{Rate constant } (\mathrm{S}^* \rightarrow \mathrm{Q}^*) = 1(R_\mathrm{o}/R)^6/\tau S$$

where τS is the actual mean lifetime of S*, R is the separation between the centers of S* and Q, and R is the critical separation of donor molecules and the acceptor molecule. The efficiency of energy transfer was expressed by Turro et al. [94] as follows:

$$\Phi_\mathrm{et} = k_\mathrm{et}[\mathrm{S}^*][\mathrm{Q}]/\{k_\mathrm{et}[\mathrm{S}^*][\mathrm{Q}] + k_\mathrm{d}[\mathrm{S}^*]\}$$

The transfer by long-range excitation or mechanism 2 can be in the form a ***singlet–singlet*** transfer, a ***triplet–singlet transfer***, and a ***triplet–triplet transfer***. Due to the fact that the lifetime of triplet state of molecule is longer than the singlet one, it is more probable to be the one to participate in energy transfer. Molecules that undergo intersystem crossing with high efficiency, like benzophenone, are efficient triplet sensitizers. Such molecules must possess high energy in the triplet state and a lifetime of at least 10^{-4} s.

The two types of intermolecular energy transfers can be expressed as follows:

$$\text{Forster(dipole-dipole) long - range: } k_\mathrm{SQ}(R) = k_\mathrm{S}^0(R_0^\mathrm{SQ}R)^6$$

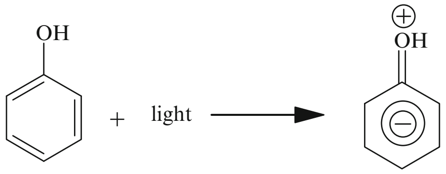
$$\text{Dexter(exchange) short - range: } k_{SQ}(R) = k_{SQ}^0 \exp(-\alpha R)$$

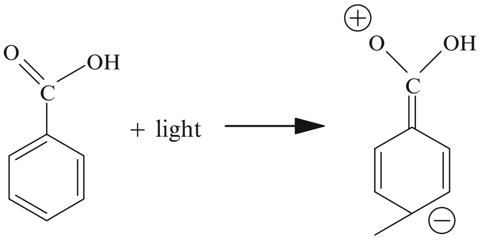
The nomenclature that was developed in connection with energy and charge transfer processes is as follows, an ***eximer*** is a transient dimer formed by the combination of an excited (usually aromatic) molecule and a second similar (usually unexcited) molecule. Such a dimer bonds only in the excited state and promptly dissociates in losing its excitation energy. The term ***exiplex***, explained by Birks [92], describes a complex between two molecules, one a donor and the other one, an acceptor, which subsequently dissociate in a deactivation process. One of the components of the ***exiplex***, either the donor or the acceptor, is in excited state while the counterpart, acceptor or donor, is in the ground state. An ***eximer*** is then just a special case in which the two constituent molecules are identical. While numerous charge-transfer complexes can form between certain molecules in the ground state, a number of compounds can form only charge–transfer complexes when either the donor or the acceptor is in an excited state. Formation of eximers was observed in a number of aromatic polymers, such as polystyrene, poly(vinyl naphthalenes), poly(vinyl toluene), and others [93].

An ***exterplex*** is composed of three molecules and often takes an important role in photophysical and photochemical processes. Polymers with pendant aromatic chromophores and dimeric compounds often show efficient ***exterplex*** formation due to high local chromophore concentration in their structure. It was observed that ***exiplex*** emission spectra from a chromophore is usually broad, structureless, and red-shifted to the corresponding monomer fluorescence. The extend of such a shift is a function of the distance between the two components of the complex. It is also strongly affected by the polarity of the media. Martic et al. [95] obtained emission spectra of the exiplexes of anthracene and *N*,*N*, dimethyl-*p*-toluidine in toluene and in polystyrene. While the maximum band of the emission spectra in toluene at 30°C is at 616 nm, in polystyrene it is shifted to 400 nm. The exiplex emission spectra in a copolymer of styrene with 4-*N*,*N*-diaminostyrene is at 480 nm. The maxima of the emission spectra are temperature-dependent. The maxima shifts in toluene solution to shorter wavelength and in polystyrene it is the opposite, and it shifts to longer wavelength with an increase in temperature. The maxima approaches common value at the glass transition temperature of polystyrene. Similar results were reported by Farid et al. [96] who studied formation of ***exiplexes*** of 4-(1-pyrenyl)butyrate in different solvents and in polymers.

Chemical and physical changes take place in molecules when they absorb energy and reach an excited state. This is particularly true of carbonyl compounds. There is a change, as already stated, in the dipole moments of the molecules. This is due to the fact that dipole moments depend upon the distribution of the electrons. In carbonyl compounds, this change is particularly large. Also the geometry of the molecule changes from the ground to the excited states. In addition, the chemical properties of the molecules change. Thus, phenol, for instance, is a weak acid, but in the excited state it is a strong acid. This can be attributed to the $\pi \rightarrow \pi^*$ transition where one of the pair of π electrons is promoted to an antibonding orbital.

By the same reason, the acid strength of benzoic acid is less than in the excited state because the charge in this case is transferred to carbonyl group. The excited states of both phenol and benzoic acid can be illustrated follows [93]:





10.3.5 The Electron Transfer Process

This process is particularly important in such photonic applications as solar cells. Simple migration of energy is a thermodynamically neutral process. It allows the excitation energy deposited at a site in a solid or in a concentrated solution to move to another position by transferring the excitation energy in the absence of an intermediate quencher. Electron transfer, however, is a process by which an electron is passed from an electron-rich donor to an electron-deficient acceptor [95]. This reaction is substantially accelerated when the donor or acceptor is excited. Electron transfer from an excited state donor molecule D* to a ground state acceptor A generates a radical cation $D^{+\bullet}$ and a radical anion $A^{-\bullet}$. The resulting radical ion pair exists as a charge-separated pair of ions:

$$D^* + A \rightarrow D^{+\bullet} + A^{-\bullet}$$

The oxidized and reduced species are usually highly energetic, storing a substantial fraction of the energy absorbed from the photon. The charge separation that occurs in such a photo-induced electron transfer provides a way to convert the excitation energy of the excited molecule to a chemical potential in the form of a radical ion pair.

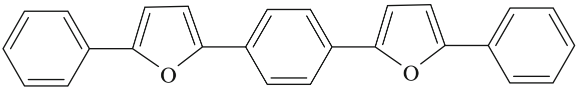
Electron migration can also be a movement of an electron either to a neutral electron donor from an oxidized one $(D + D^\bullet \rightarrow D^\bullet + D)$ or from a reduced acceptor to a neutral one $(A^\bullet + A \rightarrow A + A^\bullet)$ [93]. These thermoneutral processes that are called ***hole*** and ***electron migrations***, respectively, permit further spatial charge separation between an excited donor, D*, and a reduced acceptor, $A^\bullet$. This separation is beyond one that is initially produced in an ion pair by photo-induced electron transfer. After the absorption of light by a to a sensitizer, the energy migrations or the energy transfer move the excited state site where the excitation energy is converted to a radical ion pair by photo-induced electron transfer. A kinetic competition then takes place between the rates of several possible next steps. These steps can be chemical reaction of the radical ions, or they can be further charge migrations by ***sequential electron or hole transfers***, or actually nonproductive charge recombination, called ***back-electron transfer***. The back-electron transfer regenerates the ground states of both the donor and the acceptor.

10.3.6 The Charge Transfer Processes in Polymers

Charge transfer in polymers is either electronic (transfer of electrons or of positive charges alone) or it is ionic (transfer of protons or larger charged species). Electronic conduction can be also of two types. One type is conduction due to diffusion of electrons that are not localized on any particular molecule (this is usually found in liquids or in gases). The other type can be by conduction due to positive or negative charges that are localized on any particular part of the molecules. Such charges can be exchanges between like polymeric molecules (or between segments of single polymeric molecules).

This can occur without any net energy loss (***resonant charge transfer***). It was shown experimentally that the electrical conductivity in many polymeric materials, subjected to short irradiation pulses, consists initially of a "prompt" component. That means that very rapid transfer of a considerable amount of charge takes place over a comparatively short distance (≈100 Å). The movement of the charge is then terminated as a result of trapping in "shallow" traps [90, 93, 97]. This is followed by a "delayed" component that is very temperature-dependent and probably indicates a thermally activated charge-hopping process between the shallow traps. This continues until terminated (after ≈1 μm) by trapping in deep traps or by recombination [90, 93, 97].

There is a major difference between *eximers* of polymers and those of small molecules. The difference is that at least in some polymers a large part of the excitation of the excimer site appears to be a result of singlet energy migration [93]. Also, in polymeric materials with a number of identical chromophores, either in the backbone or as pendant groups, when photons are absorbed, the excited states cannot be considered as localized. In simple cases of rigid lattices, the excitations are distributed over the entire volume of the material as a wave-like linear combination of local excitations [87, 90, 91, 93]. They are referred to as ***tight-binding excitations*** [90, 91, 93]. As one might expect, excimer formations in polymers depend upon the properties of the chromophores and upon their location on the polymeric chain [90]. In addition, polymer tacticity, conformation, and distance between chromophores can greatly affect the formation of eximers. Also, it is possible to distinguish between two different types of energy transfers in polymeric materials. The transfer of excitation can take place either from or to large molecules from small ones. Thus, for instance, a polymer transfer of the excitation energy can be localized from a chromophore on one polymeric chain to another. An example of a transfer to a small molecule is an energy transfer from a polymer, like polystyrene to a scintillator molecule, like 1,4-bis[2-(5-phenyloxazolyl)]benzene shown below [95]:



More than that, transfer can also take place from one group of atoms, or from a chromophore, located on a polymeric chain in one section of the molecule, intramolecularly, to another one located at another section of the same polymer. Thus, in copolymers from monomers with two different chromophores groups, the energy absorbed by one group of chromophores can be transferred to the chromophores from the other group. This can take place by either Foster or exchange mechanism. The possibility of energy transfer from one chromophore to an adjacent different chromophore in polymeric chains depends to a large extent upon the lifetime of the excitation and its alternative modes of deactivation. For this reason, the most readily observed form of energy migration is one that occurs through the mechanism of the triplet [88, 90, 93, 97].

Intermolecular energy transfer from one polymeric material to another while the molecules are in solution or in the melt can also take place [17]. This was demonstrated on an ***intramolecular excimer*** and ***exiplex*** formation in solutions of polyesters containing naphthalene or carbazole moieties in their chemical structures [98].

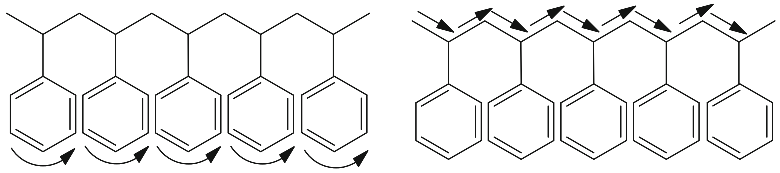
In general, the migrations of energy in polymers are somewhat more complex, because chain folding and conformations are additional factors that enter into the picture. The separation between interacting units can be affected by the composition of the polymer, the geometry of the polymeric chains, and the flexibility of the backbones [99].

There are two limiting cases for the effects of polymer folding on energy transfer efficiency. Folding of a polymer before excitation into a conformation in which the sensitizers are held within a hydrophobic pocket improves the efficiency of energy migration. This takes place with a large number of intramolecular hops or when bond interactions intervene between the sensitizer and the ultimate trap [93]. If the polymers are flexible, however, they can also bend after photo-excitation to bring otherwise distant chromophores close enough so that energy can hop from one to the other, skipping intervening units and thereby considerably shortening the effective migration distance along an individual polymer chain [93]. For flexible polymers in solvents that promote folding, this motion can take place even faster than excited state decay [99].

Intramolecular singlet energy migration can also proceed via electronic coupling through the bonds that form the polymer backbone. In a random walk, the excitation energy migrates without directional control, moving back and forth along a chain or across space. Through-space interactions between pendant chromophores are also common in polymers with large numbers of absorbing units [18]. One should also include movement of excitation across folds or loops that can form in polymeric chains. Such folds can be the result of packing into crystalline domains or simply from temporary collisions.

In principle, the excitation can be localized for some finite time (however small) on a particular chromophore before it is transferred to another one in the chain. Guellet [94] defines *intramolecular energy migration* as any process that involves more than one exchange of excitation energy between spectroscopically identical chromophores attached by covalent bonds to a polymeric chain [12]. He further terms "energy transfer" as a single step migration between two chromophores, while one that involves several or more chromophores as "energy migration" [93].

The polymers with multiple sensitizers offer several routes for energy migration. This can be illustrated as follows [99]:



Route A Route B

A very common arrangement is for the photosensitive groups to be aligned outside of a spiral arrangement of the polymeric chain in close enough proximity to each other for energy transfer. Also, as mentioned earlier, folding of a polymer before excitation into such a conformation that the sensitizers are held within a hydrophobic pocket improves the efficiency of energy migration when a large number of intramolecular hops. Efficiency of energy migration is also helped through-bond interactions that intervene between the sensitizer and the ultimate trap [99]. Also, as mentioned before, flexible polymer frameworks can bend the polymeric chains in such a manner as to bring otherwise distant chromophores close enough together so that after excitation the energy can hop from one to another. In such a case, the energy migration can skip intervening units and thereby considerably shorten the effective migration distance along a single polymer chain. As stated above, for flexible polymers in solvents that promote folding, this motion can be even faster than excited-state decay [99].

Intermolecular energy migration can also occur between two different polymeric molecules. Thus, for instance, Turro et al. [95] investigated inter- and intramolecular energy transfer in poly(styrene sulfonate). They found that excimer formation between adjacent phenyl groups is a dominant reaction both along a single chain and between two different chains [95]. At low densities of excited states, singlet energy transfer between a sensitizer and its nearest quencher (perhaps on another chain) dominates, whereas at high excited state densities, energy migration takes place through the series of donors [99].

Guellet quotes Webber, who reported that he used the following equation (that he called crude but useful) to obtain rough estimates of the energy migration diffusion rate along the polymer backbone [94]:

$$k_q = 4\pi N_0 (D_Q + k_g) PR / 1{,}000$$

where D_Q is the normal diffusion constant of the quencher and k_g is the energy migration diffusion rate along the polymer.

In some aromatic vinyl polymers, excimer emission can occur after an initial excitation of an aromatic chromophore. This is followed by intramolecular singlet energy migration, either along the polymer chain, or intermolecularly along the chromophores. Here too, it can be through different chains in a polymer that is in bulk form and the chains are in close proximity to each other. The process generally continues until the excitation is trapped at some chain conformation that is suitable for excimer formation. Such a chain conformation is referred to as ***eximer-forming site***. If the polymer is in solution and viscosity is low, interconversion of chain conformations proceeds fairly rapidly. In such cases, the lifetimes of any particular conformation are limited by the collision processes as well as by the magnitude of the rotational barriers with respect to thermal energy [93]. In the solid state, however, the rotational freedom of the polymeric chain is considerably reduced. Large-scale conformational changes are unlikely. There still is the possibility, however, that adjacent chromophores will be in a marginal eximer-forming site [94].

10.3.7 The Antenna Effect in Polymers

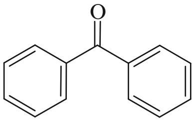
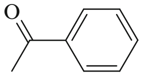
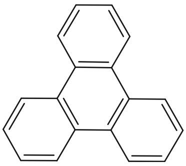
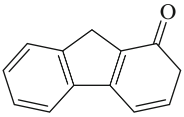
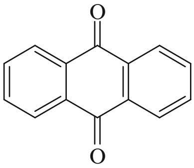
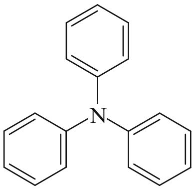
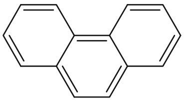
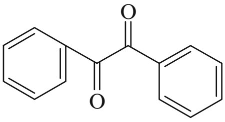
It was originally observed by Schneider and Springer [101] that efficient fluorescence occurs from small amounts of acenaphthalene that is copolymerized with styrene. Fox et al. [100] observed the same effect in a copolymer of styrene with small amount of vinyl naphthalene. The emission of naphthalene fluorescence is much higher than from solution of a mixture of the two homopolymers. It was suggested by both groups that this phenomenon is due to energy migration between styrene sequences to the naphthalene moieties. Guellet and coworkers carried out quantitative studies of this phenomenon with various polymers that contained naphthalene or phenanthrene as the donors and anthracene as the trap [94]. This effect is similar to one observed in ordered chlorophyll regions of green plant chloroplasts (antenna chlorophyll pigments). It was, therefore, named the ***antenna effect***.

Guellet [94] demonstrated that the effect is not entirely due to energy migration among the chromophores that form the antenna, but rather a combination of migration and direct Forster energy transfer to the trap [94]. It was concluded that energy migration and transfer in such systems are primarily due to long-range Forster transfer by dipole-dipole mechanism (discussed earlier). In the absence of any trap in the polymer, the energy will migrate along the backbone of the polymer chain until it is deactivated by some other processes. In the presence of a singlet energy trap, the lifetime of the excitation will be reduced and the length of energy migration will be reduced. The difference between this form of energy transfer and one observed in solid aromatic polymers is that the photon energy is collected within a single polymer molecule and all energy transfer is intramolecular. The antenna effect permits collection of the photon energy from the entire region of space (the hydrodynamic volume of the polymer) and transmitting it to the traps located on the polymer chain. The efficiency is relatively independent of concentration and can be very efficient even in dilute solutions [93].

10.4 Photosensitizers

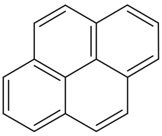
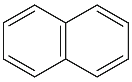
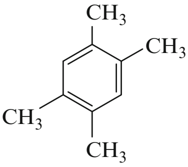
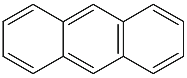
As explained in Sect. 10.3, photosensitizers are molecules that absorb the energy of light and act as donors by transferring this energy to acceptor molecules. The molecules that receive the energy may in turn undergo various reactions, such as polymerizations, isomerizations, couplings, and others. Many different molecules can act as photosensitizers, but the most useful ones are various aromatic compounds. In Table 10.1 are listed some common photosensitizes that appeared in various publications

Table 10.1 Some often used photosensitizers

Photosensitizer	Chemical structure	Φ
Benzophenone		1.0
Acetophenone		0.99
Triphenylene		0.95
Fluorenone		0.93
Anthraquinone		0.88
Triphenylamine		0.88
Phenanthrene		0.76
Benzil		0.87; 0.92

(continued)

Table 10.1 (continued)

Photosensitizer	Chemical structure	Φ
Pyrene		0.40
Naphthalene		0.40
Durene		
Anthracene		

From various literature sources. Φ represents the quantum yield of triplets

in the literature. The process of photosensitization and energy transfer involves formation of charge transfer complexes. A good photosensitizer, therefore, is not only a molecule that readily absorbs light energy, but also one that readily transfers it to another molecule. Some compounds are capable of forming such transfer complexes in the ground state, but many more form *exiplexes* in the excited state. Others can form complexes between a compound in the ground state and another one in the excited state and are called ***excimers*** or ***excited dimers***. The difference between the excited state of a dimer and an exiplex is that the dimers possess binding energy in the ground state, while exiplexes lack any binding energy in the ground state. This is described in Sect. 10.3.1. The emission spectra from two molecules that are capable of forming ***exciplexes*** depend upon the distances between the two molecules. An equation for the excited state wave function of a one-to-one exciplex that forms from a donor molecule D and an acceptor molecule A was written by Guellet as follows [94]:

$$\Psi_{\mathrm{E}} = \alpha\Psi_1(\mathrm{D}^+\mathrm{A}^-) + \beta\Psi_2(\mathrm{D}^-\mathrm{A}^+) + \gamma\Psi_3(\mathrm{D}^*\mathrm{A}) + \delta\Psi_4(\mathrm{DA}^*)$$

The first two terms on the right side of the above equation correspond to charge resonance states and the last two to the excitation resonance states. Thus, a photosensitizer, as explained in Sect. 10.3, can act in two ways, by energy transfer and by electron transfer. To be exact, one may feel that a true photosensitizer is one that acts by energy transfer alone. This, however, is not always the case. Also, in the event of electron transfer, the process can lead to photo-induced decomposition via electron transfer [102].

The rate of absorption of light by a sensitizer that corresponds to excitation from the ground state to the excited singlet can be expressed as [94]:

$$I_{\mathrm{abs}} = \mathrm{d}[\mathrm{S}_0]/\mathrm{d}t - \mathrm{d}[\mathrm{S}_1]/\mathrm{d}t$$

The measurement of fluorescence and phosphorescence spectra of photosensitizers is very important in providing information about the energy of the excited states. It also allows identification of the phenomena.

The process of energy transfer requires that the excited donor diffuse to the proximity of an acceptor within the time period of its excited lifetime. This is subject to the viscosity of the medium and the efficiently of the collision process and the range r in which the collisions can occur. The observed rate constant for energy transfer k_{ET} is governed by the molecular rate constant k_{diff} for diffusion-controlled reaction. This is defined by the Debye equation:

$$k_{\mathrm{diff}} = 8RT/3{,}000\eta$$

$$k_{\mathrm{ET}} = \alpha k_{\mathrm{diff}}$$

where α is the probability of energy transfer. R is the universal gas constant, T is the temperature in Kelvin, η is the viscosity of the medium in poise. The Schmoluchowski [94] equation defines the diffusion constant in terms of the diffusion coefficient of the sensitizer and the acceptor:

$$k_{\mathrm{diff}} = 4\pi/1{,}000(R_{\mathrm{s}} + R_{\mathrm{a}})(D_{\mathrm{s}} + D_{\mathrm{a}})N_{\mathrm{a}}/2)\{1 + [R_{\mathrm{s}} + R_{\mathrm{a}}/(\tau_0(D_{\mathrm{s}} + D_{\mathrm{a}})/2)^{0.5}]\}$$

where D_{s} and D_{a} are the diffusion coefficients of the sensitizer and the acceptor R_{s} and R_{a} are the molecular radii of the sensitizer and the acceptor, N_{a} is the Avogadro number, and τ_0 is the lifetime of the excited state of the sensitizer.

10.5 Photocross-linkable Polymers

Some photocross-linking of polymers can be traced back to ancient days, when pitch was photocross-linked for decorative purposes [102]. In modern times, wide varieties of photocross-linkable polymers were developed. The early practice of photo imaging relied mainly upon the photodimerization reactions. These reactions are common, photo-induced, reactions of organic chemistry, namely intermolecular cyclization. This reaction of cyclization that takes place between two reactive species, with one of them electronically excited, is actually predicted by the Woodward–Hoffmann rule [104]. In contrast, the reactions of thermally excited ground states of molecules proceed by different pathways. Many polymers were synthesized that possess pendant groups capable of photocyclization intermolecularly to be used in the photo-imaging technology. Photocross-linking technology today, however, also uses coupling reactions of radicals, chain growth polymerizations that result in photocross-linking, and some ionic reactions. The light-induced polymerizations of multifunctional monomers that transform liquid resins into solid polymers almost instantly and selectively in the illuminated areas are now versatile processes. They can, however, be achieved in a variety of ways. Thus, for instance, Decker discussed work in the less explored areas of photo-curing, namely laser-induced ultra-fast polymerization and UV curing of binary polymer systems [105]. By using highly sensitive acrylate photoresists, relief images of micronic size can be obtained by fast scanning with a focused laser beam. Also, polymer networks of different architectures can be obtained by UV irradiation of various monomer blends, e.g., acrylate-epoxide, acrylate-vinyl ethers, acrylate-polyene, vinyl ether-maleate, and thiol-polyene [104]. This does not mean, however, that photocross-linking of polymers is now unimportant technologically or scientifically. The fact that considerable research still continues in the field is a direct indication of that.

The light cross-linkable reaction, like all cross-linking reactions, results in ***gelation*** and the extent of gelation is important in this process. This extent is tied to the quantity of the functional groups in the reaction mixture. Carothers equations relate the critical extent of the gelation, p_{c}, at the gel point to the functionality of the reactants:

$$p_c = 2/f_{\text{ave}}$$

where f_{ave} is the functionality. This equation, however, was written for reaction mixtures that contain two different functional groups in stoichiometric proportions to each other. All the functional groups, however, for various reasons, might not participate in photocross-linking reactions. Even though these reactions may involve identical groups, this equation probably would not apply.

A statistical approach was developed by Flory [107, 108] and by Stockmayer [109] to derive an expression for predicting the extent of reaction at the gel point. It is expressed as

$$p_c = 1/[r(f_{wA} - 1)(f_{wB} - 1)]^{0.5}$$

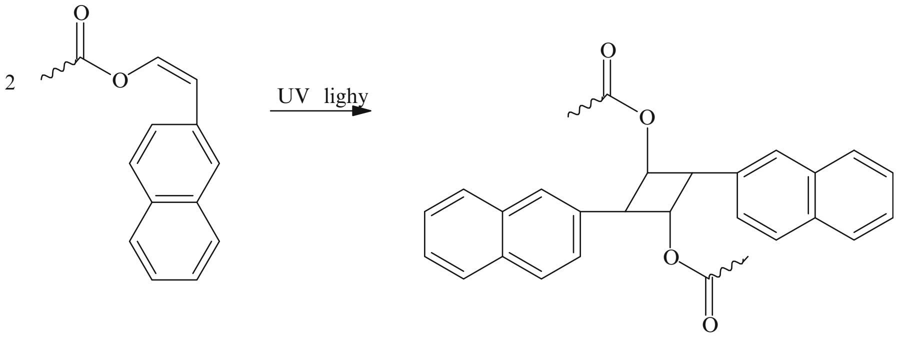
where f_{wA} and f_{wB} are weight average functionalities of A and B functional groups. Here the functionalities are defined as,

$$f_{wA} = \sum f_{Ai}^2 N_{Ai} \Big/ \sum f_{Ai} N_{Ai} \quad \text{and} \quad f_{wB} = \sum f_{Bi}^2 N_{Bi} \Big/ \sum f_{Bi} N_{Bi}$$

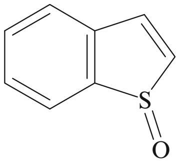
When the cross-linking, however, takes place by cyclization through dimerization of pendant groups, it appears that the gelation should probably be treated instead as a case of multiple dimerizations.

10.5.1 Polymers That Photocross-link by Formation of Cyclobutane Rings

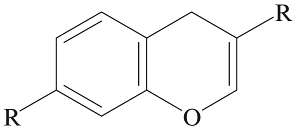
Many of the photocross-linkable polymers for photo-imaging in use today react by a 2π + 2π type dimerization with the accompanying formation of the cyclobutane rings [108, 109]. The formation of the cyclobutane ring can be simply shown on the photocross-linking reaction of poly(naphthyl vinyl acrylate), a polymer that also undergoes this type of dimerization [110]:



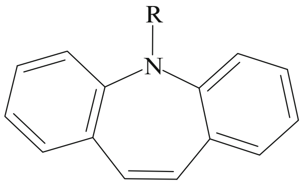
The naphthalenes become bonded to cyclobutane ring in 1,2 and 1,3 positions. Many polymers with other functional groups can also photocross-link by 2π + 2π addition. Following is an illustration of some of these groups [111, 112]:



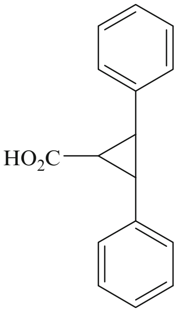
banzothiophene oxide

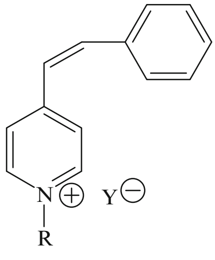


coumarin

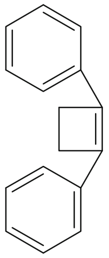


dibenzazepene

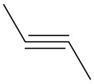




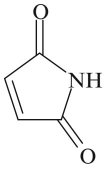
stilbazole



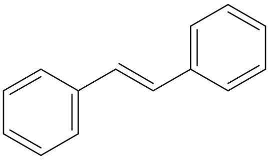
diphenylcyclobatane



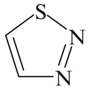
alkyne



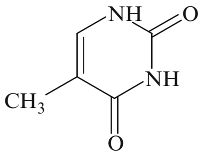
maleimide



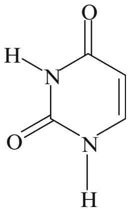
stilbene



1,2,3-thiadiazole

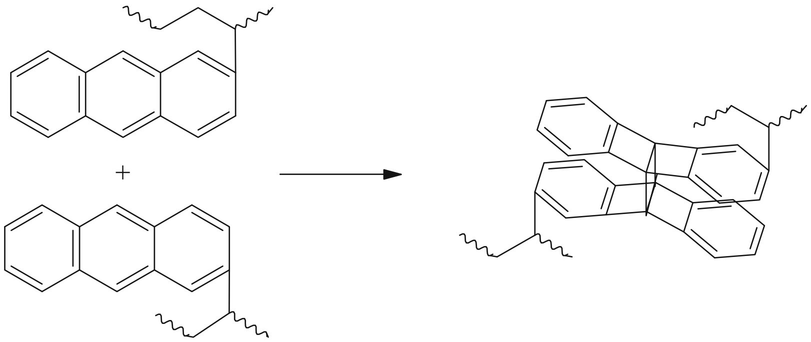


thiamine



uracil

Pendant groups with anthracene moieties, however, are believed to cross-link by a 4π + 4π type cycloaddition [114]:



Many photo-dimerizations of functional groups, like the ones shown above, require the presence of photosensitizers. These compounds may be selectively excited to their triplet state by sensitizers with the right type of energy levels. For efficient energy transfer to occur, the triplet energy of the donor should be approximately 3 kcal/mole greater than that of the acceptor [113, 114]. This type of sensitization is believed to be diffusion controlled [115].

Trecker [116] lists the steps of the sensitized dimerization reaction as follows:

Excitation: S (sensitizer) $+ h\nu \rightarrow S^*$
Energy loss: $S_3^* \rightarrow S$
Sensitization: $S_3^* + D \rightarrow {}^\bullet S - D^\bullet$
Dimerization: ${}^\bullet S - -D^\bullet + D \rightarrow S + {}^\bullet D - D^\bullet$
Dimer: ${}^\bullet D - D^\bullet \rightarrow$ dimer(s)

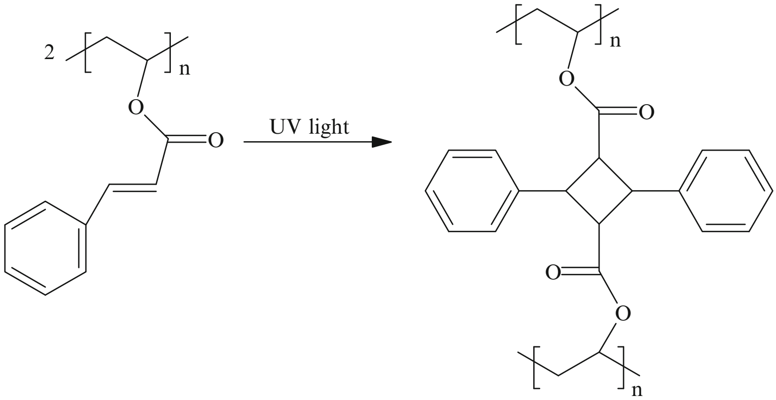
The quantum yield expression for this scheme of dimerization is shown as follows [115]:

$$1/\Phi = 1/\phi\alpha + k_3/\phi\alpha k_4(D)$$

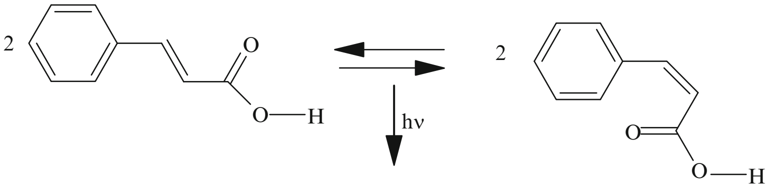
where Φ represents the quantum yield of dimer formation, ϕ is the efficiency of sensitizer intersystem crossing, D is the initial concentration of the reactive groups, and k's are the specific rate constants for the reactions shown in the above scheme.

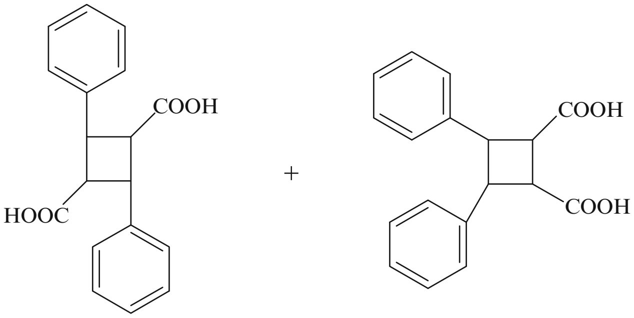
10.5.1.1 Polymers with Pendant Cinnamoyl Functional Groups

Minsk et al. [117] may have been the first to synthesize a photocross-linkable polymer, namely poly (vinyl cinnamate). The photochemistry of this compound is similar to the photo-cyclization of cinnamic acid that is discussed bellow in this section. It is interesting that the reaction of cyclization of cinnamic acid can take place even in the solid crystalline stage. This illustrates that the reaction requires very little molecular motion. Similar reactions occur in polymeric materials that are functionalized with cinnamate groups. The photocross-linking of poly(vinyl cinnamate) is illustrated below:



Much earlier, well before Minsk, in 1895, Bertram and Kursten [118] recognized that solid cinnamic acid undergoes a chemical change when exposed to light. Following this, Ruber [119] established that the change is a dimerization of the acid to form a cyclobutane derivative. This dimerization results in formation of truxillic and truxinic acids:





truxillic acid truxinic acid

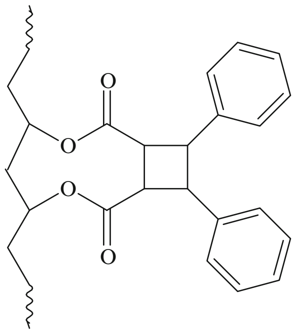
Schmidt and coworkers [120, 121] studied the reaction mechanism and came to the following conclusions:

1. Photo-dimerization of cinnamic acid and its esters is controlled by the crystal lattice.
2. Dimerizations are possible when olefinic double bonds of the two neighboring molecules in the crystals are 4.1 Å or less apart.
3. Dimerizations are not possible when the double bonds are 4.7 Å or more apart.

The dimerization reaction takes place upon irradiation with light of a wavelength longer than 300 nm. It was demonstrated subsequently [122], however, on poly(vinyl cinnamate) that the adducts dissociate again upon irradiation with light of 254 nm. Photo-dimerization and formation of cyclobutane groups were demonstrated to be enhanced as a result of sensitized irradiation [123].

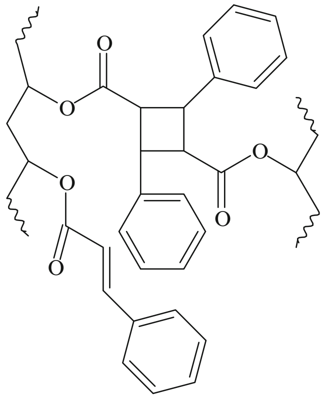
When dealing with poly(vinyl cinnamate), it is reasonable to assume that the degree of order in the relationship of one cinnamic group to another is much lower than is found in a crystal lattice of cinnamic acid. On the other hand, it should be higher than in solutions of cinnamic acid, where the groups are far enough apart so that very little photo-dimerization takes place. Photocross-linking of poly(vinyl cinnamate) can include the following reactions [124]:

1. Truxinic acid type dimerization in irradiated poly(vinyl cinnamate) that can occur intramolecularly. It can be shown as follows:



This is accompanied by formation of both folded and parallel chains

2. Truxillic acid type intermolecular dimerization in irradiated poly(vinyl cinnamate), on the other hand, can be illustrated as follows:



dimerization of this type would be accompanied by formation of folded chains.

Reactions of formations of folded and parallel chains are similar with the exception that the reacting cinnamic groups are further apart in folded chains and come together only by virtue of chain folding. Chains located parallel to each other but at the right distance can also conceivably yield truxinic acid type dimerization. This would be similar to the arrangements in crystal lattices. Formation of a truxillic dimer, like in reaction 2, shown above, requires favorable folding or two different chains. Also, there is accompanying possibility that the double bonds may simply polymerize by a chain propagating reaction [125]. This was observed with some cinnamate esters [125]. Attempts were made to determine the reaction products of photocross-linked poly(vinyl cinnamate) by first hydrolyzing it, and then by isolating and identifying the acids. The results showed that α-truxillic acid does form. Formation of β-truxillic acid, however, was not demonstrated. In addition, among the reaction products there is also a large quantity of unreacted cinnamic acid. This indicates that only a small portion of the double bonds participate in the reaction. Also, it should not be forgotten that only small changes in unsaturation in polymer molecules, as a result of cross-linking, can have a profound effect on solubility.

Studies [126] of electronic structures in photo-isomerization and photo-dimerization of cinnamic acid showed that phosphorescence of cinnamic groups occurs at about 20,000/cm. Also, it was demonstrated when photosensitizers are present, the critical distance between donor, sensitizer, and acceptor molecules (cinnamic acid) is about 10 Å [126]. Although all the details of incipient photocross-linking of poly(vinyl cinnamate) have to date still not been fully worked out, most accept that all three mechanisms take place. These are: dimerizations to truxillic and truxinic acid type structures and polymerizations through the double bonds. The excited states of the molecules can be produced by direct irradiation and also through intersystem crossing from an appropriate photosensitizer [126].

Several criterions were derived from proper selection of sensitizers [127, 128]. These are:

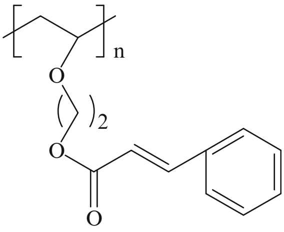
1. The triplet state must be at the energy level close to 50–55 kcal/mole for the cinnamate moiety.
2. The quantum yield of the ratio of phosphorescence to fluorescence should be higher than unity.
3. The mean lifetime of a triplet state must be greater than 0.01 s. The photosensitizing activity (characterized by the triplet state) of derivatives of cinnamic acid is beyond the phosphorescence of the cinnamate group (at about 20,000/cm, as stated above). An energy transfer diagram for poly (vinyl cinnamate) photosensitization with a sensitizer like 2-nitrofluorene was published [128]. The rate of dimerization obeys first-order kinetics. In addition, polymers consisting of flexible segments exhibit higher rates of photo-dimerization than do those composed of rigid segments.

Table 10.2 Effectiveness of sensitizers on relative speed of cross-linking of poly(vinyl cinnamate)

Sensitizer	Relative speed	Sensitizer	Relative speed
(None)	1	4-Nitroaniline	100
Naphthalene	3	3-Nitrofluorene	113
Benzanthrone	7	4-Nitromethylaniline	137
Phenanthrene	14	4-Nitrobiphenyl	200
Crysene	18	Picramide	400
Benzophenone	20	4-Nitro-2,6-dichlorodimethylaniline	561
Anthrone	31	Michler's ketone	640
5-Nitroacenaphthene	84	*N*-Acyl-4-nitro-1-nathylamine	1,100

From ref. [131] and other sources

It was also demonstrated that greater photosensitivity can be obtained by separating the cinnamic group from the polymer backbone by introducing –CH_2–CH_2–O– spacers as follows [129, 130]:

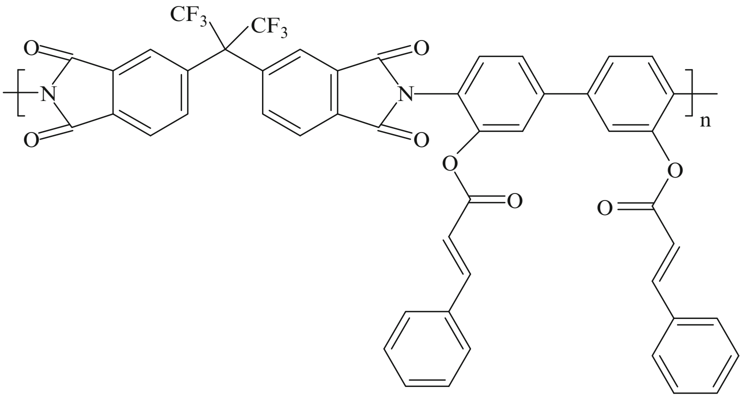


In addition, Tsuda and Oikawa carried out molecular orbital calculations of the electronic structures in the excited states of poly(vinyl cinnamate) [131, 132]. They based their calculations on the reaction of intermolecular concerted cycloaddition that take place according to the Woodward–Hoffmann's rule. This means that the cyclobutane ring formation takes place if a nodal plane exists at the central double bond in the lowest unoccupied MO(LLUMO) and not in the highest occupied MO (HOMO) of the ground state cinnamoyloxy group. This is within the picture of Huckel MO or Extended Huckel MO theory. The conclusion is that the concerted cycloadditions occur favorably in the lowest triplet state T_1 and in the second excited singlet state S_2 [132].

The effectiveness of photosensitizers in accelerating the cross-linking reaction of poly(vinyl cinnamate) is illustrated in Table 10.2.

Some 4 decades after the original development of poly(vinyl cinnamate) into a useful photocross-linkable polymer, a novel optical property of the polymer was observed. When the material is irradiated with linearly polarized light, it exhibits polarization holography [133, 134]. The exposure of thin films of poly(vinyl cinnamate) to linearly polarized ultraviolet light causes uniaxial reorientation into liquid crystal layers [135–142]. Poly(vinyl cinnamate) and its derivatives have the ability to align in thin films the liquid crystal moieties in the direction that is perpendicular to the polarization axis of the linearly polarized ultraviolet light [143–145]. Schadt et al. [136] suggested that the surface-settled homogeneous alignment of nematic liquid crystals results from photo-dimerizations of the cinnamate moieties and formation of cyclobutane rings (as shown earlier) with an azimuthally oriented order. This, he feels, determines the direction of the liquid crystal alignment [140]. Ichimura et al. [141] suggested a different photo-alignment process. They claimed that the photo-induced homogeneous liquid crystalline alignment is caused by polarization of photo-chromophores at the uppermost surfaces of the substrates due to repeated A/Z photo-isomerizations, similarly to azobenzenes [140–149]. This was also shown to take place with stilbenes [140]. In addition, it was demonstrated by them [149] that both photo-isomerization and photo-dimerization contribute to liquid crystalline alignment. Photo-regulation in a polymethacrylate with *o*-cinnamate side chains displays preferential formation of *Z*-isomer. Dimerization, on the other hand, takes place more favorably in other polymers, including poly(vinyl cinnamate) [150].

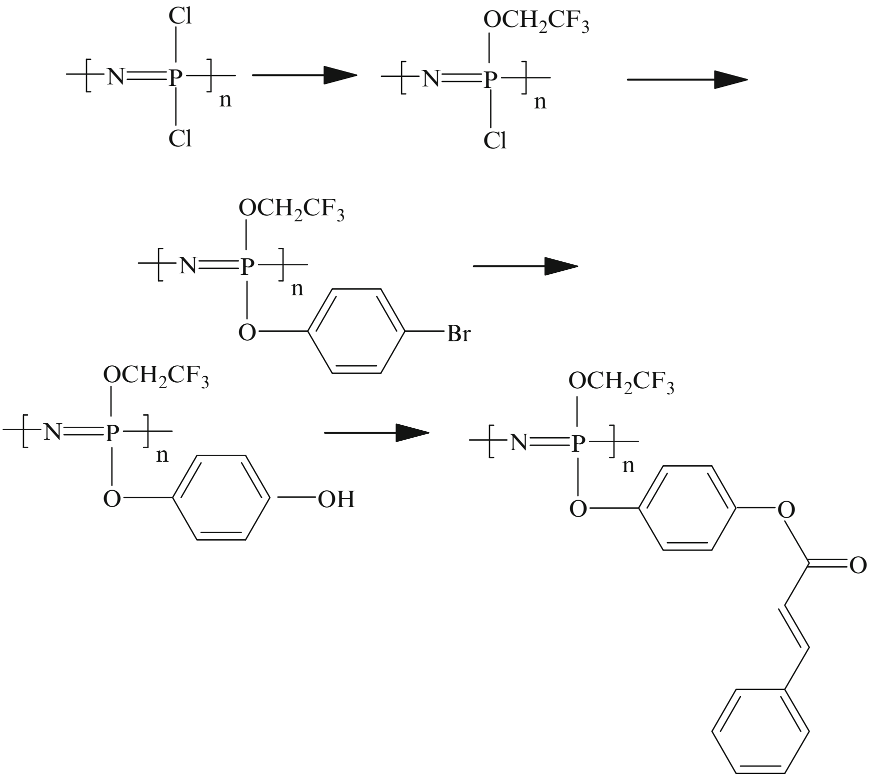
The liquid crystals alignment in films prepared from materials with cinnamate group after irradiating the films with linearly polarized UV light is quite uniform. All the aggregate structures, lamellar crystals, produced by the photocross-linking reaction were found to be square in shape [151]. This has application in flat panel liquid crystal displays. It led others to synthesize polymeric materials that could be useful in photo-alignment. Lee et al. [152] synthesized a soluble photo-reactive polyimide with cinnamate chromophore side groups. The polymer, poly(3,3′-bis(cinnamoyloxy)-4,4′-biphenylene hexafluoroisopropylidene diphthalimide), has a reasonably high molecular weight and forms good quality films through conventional solution spin-casting and drying.



The polymer is thermally stable up to 340°C and positively birefringent. The photochemical reactions of the polymer in solution and in films, as well as its molecular orientations, are induced by exposure to linearly polarized ultraviolet light. As one might expect, the cinnamate chromophores undergo both photo-isomerization and photo-dimerization. Also, exposure to UV light induces anisotropic orientations of the polymer main chains and of the cinnamate side groups in the films. The irradiated films homogeneously align nematic liquid crystal molecules along a direction at an angle of 107° with respect to the polarization of the linearly polarized ultraviolet light. This coincides with the orientation direction of the polyimide chains. Thus, the liquid crystal alignment process is principally governed in irradiated polyimide films by the polymer main chains and the unreacted cinnamate side groups [151].

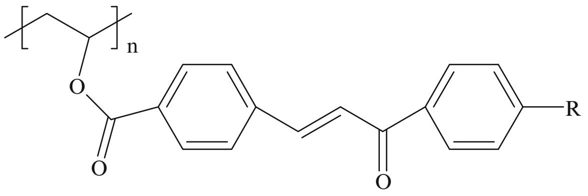
Nagata and Hizakae [153] reported preparation of a series of photocross-linkable biodegradable polymers by condensation of dichlorides of 4,4′-(adipoyldioxy)dicinnamic acid and alkane diols of various methylene lengths. They also used various poly(ethylene glycols) with molecular weights ranging from 200 to 8,300.

Among other interesting polymers with cinnamate functional groups are high polymeric phosphazenes that bear cinnamate groups [154]. A typical polymer synthesis is a follows:

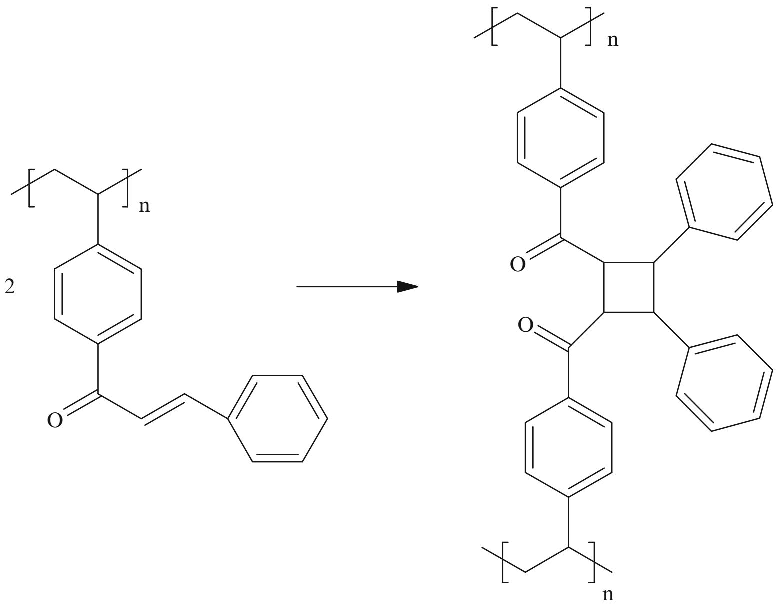


10.5.2 Polymers with Functional Chalcone Groups

Pendant chalcone groups on polymers behave similarly to pendant cinnamate groups. Thus, photocross-linkable polymer can be formed, for instance, from poly(vinyl alcohol) by a reaction with 4′-substituted-4-caboxychalcone in homogeneous dimethyl formamide solution, using 2,4,6-trinitrochlorobenzene as the condensing agent [155].



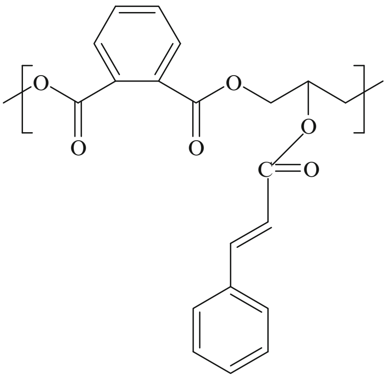
The photosensitivity of this polymer is in the range of 1–5 mJ/cm^2, according to Watanabe et al. [155]. When the R group shown above is p-Br, m-NO_2, or $(CH_3)_2N$, the cross-linking is via formation of biradicals derived from the double bonds of the cinnamoyl groups and an abstraction of protons from the neighboring methyne or methylene groups. This reaction of dimerization can be illustrated as follows [156]:



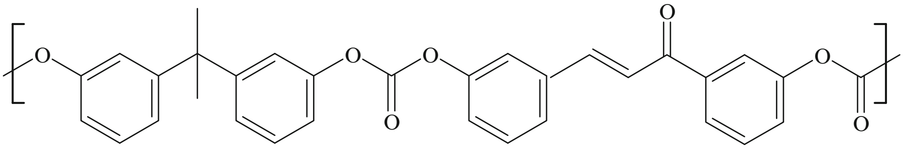
Formation of polymers by reaction of free-radical polymerizable methacryloyl groups and a photocross-linkable pendant chalcone units was also reported [157]. The photocross-linking reaction takes place in thin films and in solutions upon irradiation with high pressure mercury lamps. The reaction can be monitored through changes in the UV absorption spectrum. The rates of photocross-linking in solutions were reported to be faster than in films. Photocross-linking in the presence of a triplet photosensitizer shows no significant changes in the rate of disappearance of the double bonds. This particular polymer with a pendant chalcone unit was found to photocross-link at a high rate even in the absence of a photosensitizer and is of interest as negative photoresist [158].

10.5.3 Polymers with Functional Groups Similar to Cinnamates

As stated earlier, the photocross-linking reactions of poly(vinyl cinnamate) and the reversibility of cross-linking depends upon irradiation with light of the proper wavelength. In addition, some intramolecular cyclizations also take place. Because the reactions found extensive commercial applications, a number of other polymers that resemble poly(vinyl cinnamate) were developed. Following are two examples of such functional groups [159]:



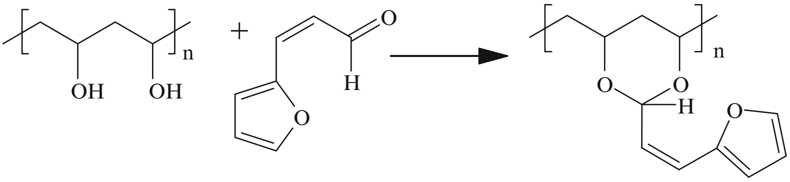
polyester



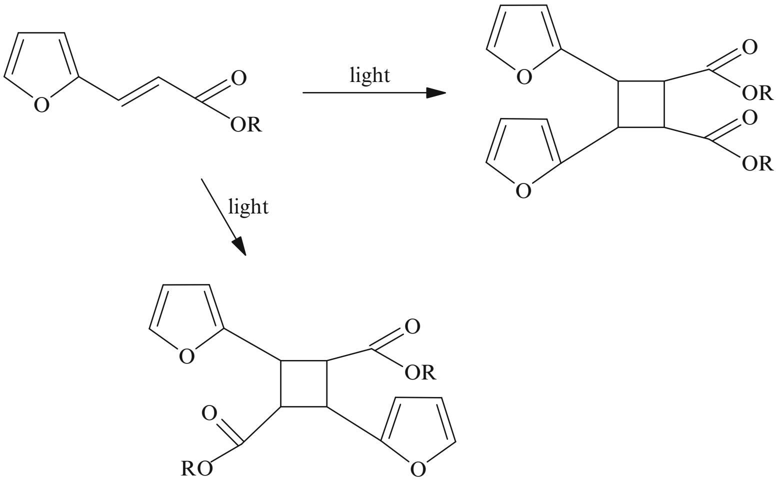
polycarbonate

10.5.4 Polymers with Pendant Furan Groups

Tsuda [160] attached 2-furylacrolein to a polymeric backbone by the following reaction:



In the presence of photosensitizers, this polymer was found by Tsuda to cross-link at a considerably faster rate than does poly(vinyl cinnamate) [160]. He showed that the cross-linking reaction also results in formation of cyclobutane derivatives. The cross-linking is illustrated on 3-furfurylacrylic ester:



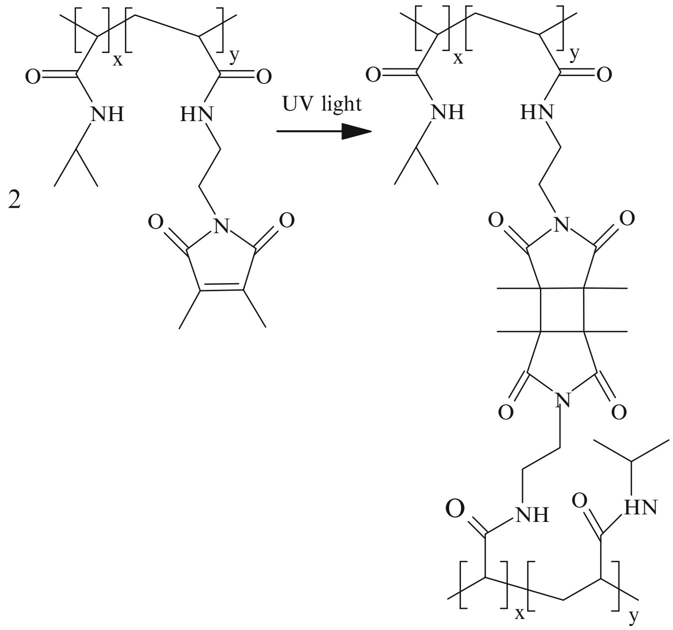
Tajima, Arai, and Takeuchi [161–163] studied the effects of singlet oxygen on photocross-linking of poly(furfuryl methacrylate). The singlet oxygen was generated by fullerene C_{60}. The reactions were carried out in 1,1,2,2-tetra-chloroethane solutions that contained the polymer and fullerene C_{60}. Gelation occurs when exposed to visible light in the presence of photosensitizers. These solutions gel after several hours and subsequently solidify completely [163].

It is interesting to note that fullerines are also effective in causing sensitization of poly(furfuryl methacrylate) and are effective in causing cross-linking upon with UV irradiation [164]. This is attributed to their long-lasting ability to sensitize oxygen even when they themselves undergo oxidation The sensitivity of poly(furfuryl methacrylate) increases linearly when the concentration of C_{60} is increased from 5×10^{-5} to I $\times 10^{-3}$ mol/L. Saturation of sensitivity in the high C_{60} concentration regions was observed to be due to deficiency of oxygen molecules in the resist films. It was concluded that the dissolution rate of oxygen from the atmosphere into the resist film is lower than its consumption rate [164].

Preparation of photocross-linkable furan-containing polyimides was also reported [165]. It was also found that the polymer cross-links with the aid of singlet oxygen. Formations of fine pattern images can be formed. This was taken as clear evidence of the successful photolithography in this photo-curable system that uses C_{60} as the photosensitizer [165].

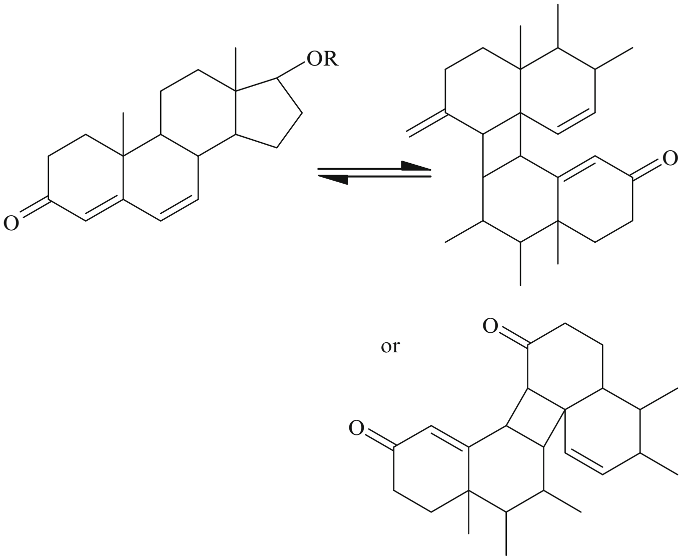
10.5.5 Polymers with Pendant Maleimide Groups

Preparation of photocross-linkable *co*- and terpolymers of *N*-isopropylacrylamide, 2-(dimethylmaleimido) *N*-ethylacrylamide as the photosensitive component, and 3-acryloylaminopropionic acid or *N*-(2-(dimethylamino)ethyl)-acrylamide as ionizable comonomers was reported [166]. Here too, cross-linking takes place through formation of cyclobutane moieties:

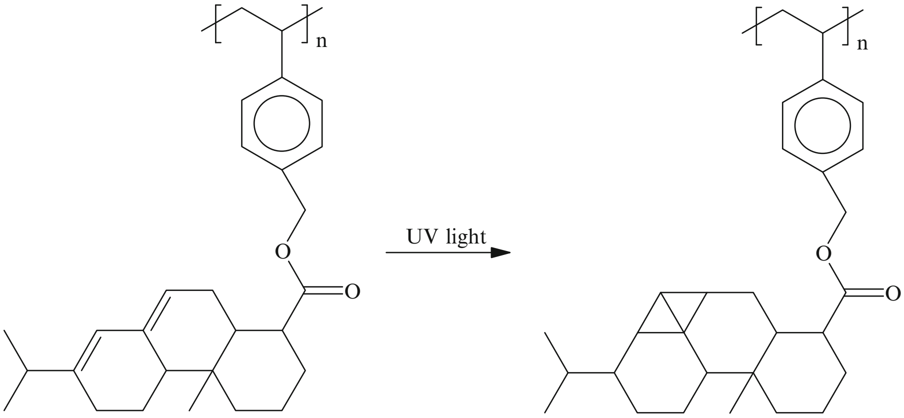


10.5.6 Polymers with Pendant Abietate and Dibenzazepine Groups

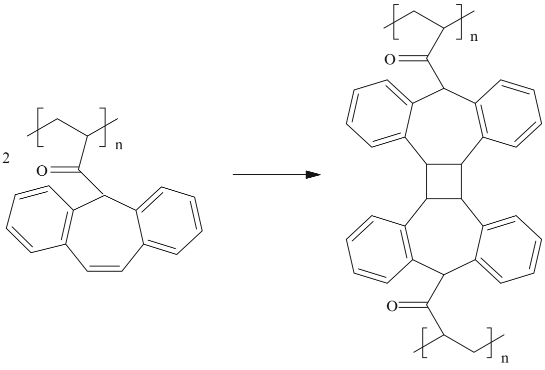
Poly(vinylbenzyl abietate) in the film state is cross-linkable via photo-dimerization of the conjugated carbon-carbon double bonds of the abietic acid moieties [166]. What the photo-dimerization product looks like is not clear. Formation of a cyclobutane rings in photo-dimerization of steroids was represented as follows [166]:



Also, judging from the photoreaction of cholestra-3,5-diene [166], one might expect some internal cyclization:

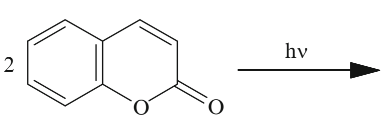


The cyclodimerization reaction of dibenzazepine was reported by Hyde et al. [167]. When attached to a polymer, the cross-linking reaction can be visualized as follows:



The cross-linking can result from either direct absorption of the light or in the presence of triple sensitizers like Michler's ketone [168]. The $2\pi + 2\pi$ addition leads to a formation of a cyclobutane cross-link.

Coumarin photo-dimerization is a known reaction [169]:

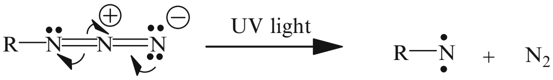


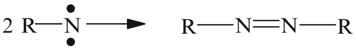
This was utilized by Tian et al. [168] to prepare a new class of liquid crystal homopolymers of poly {ll-[4-(3-ethoxycarbonyl-coumarin-7-oxy)-carbonyl-phenyloxy]-undecyl methacrylate} containing a coumarin moiety as a photocross-linkable unit. The preparations included polymers of various chain lengths. Also, liquid crystalline-coil diblock and liquid crystalline-coil-liquid crystalline triblock copolymers with polystyrene as the coil segment were formed. The polymers were reported to have been synthesized with the aid of atom transfer radical polymerization. The dimerization of the coumarin moieties takes place upon irradiation with light of $\lambda > 300$ nm to yield cross-linked network structures.

Lee et al. [169] reported the preparation of new soluble and intrinsically photosensitive poly(amide-*co*-imide)s containing *p*-phenylenediacryloyl moiety. The copolymers were formed from *p*-phenylenediacryloyl chloride, aromatic dianhydrides, and two equivalents of aromatic diamines. The products were subsequently imidized by reactions with the poly(amide-*co*-amic acid), acetic anhydride, and pyridine. The polymers were stable up to 350°C, showed good solubility in polar aprotic solvents, and became insoluble after the irradiation due to the photo-dimerization of phenylenediacryloyl moiety. The photo-reactivity increases with the irradiation temperature [169].

10.5.7 Polymers That Cross-link by Dimerization of Nitrenes and by Other Combinations of Free-Radicals to Form Covalent Bonds

The aromatic azide groups photo-decompose into nitrenes when irradiated with UV light: The nitrenes, that form, possess two unpaired electrons, similarly to carbenes, and dimerize readily into *azo* groups

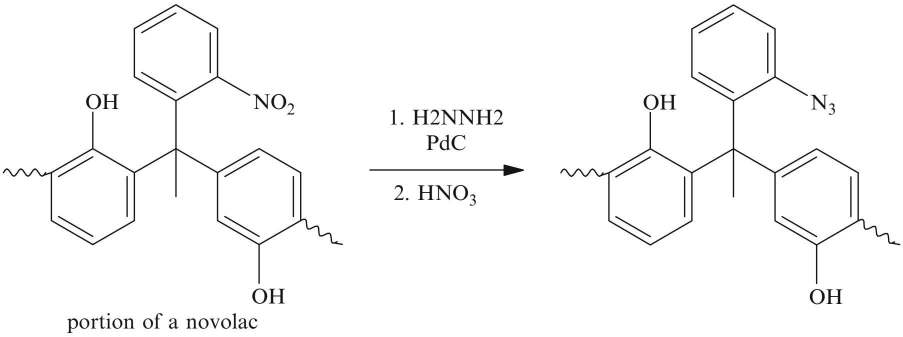




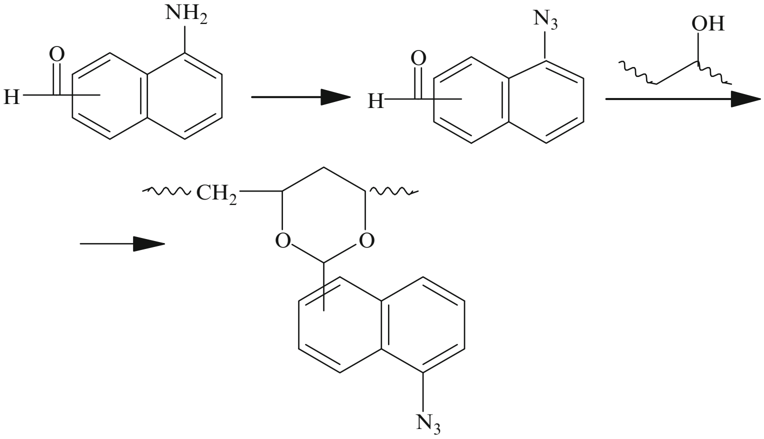
This reaction is utilized in photocross-linking.

10.5.8 Polymers with Pendant Azide Groups

Both azide and sulfonyl azide groups are photo-reactive and decompose into active nitrene groups and nitrogen upon irradiation. The dissociation of the azide moiety follows almost every transition from an excited n → π* state to a high vibrational level of the ground state [170, 171]. Introductions of pendant azide and sufonyl azide groups into polymeric structures are possible in a variety of ways and many publications describe different approaches. Thus, Tsuda and Yamaoka [81] introduced azide groups into a phenolic novolac resin by the following scheme:



Tsunoda and Yamaoka [173, 174] also condensed formyl-1-naphthyl azide with poly(vinyl alcohol). All steps in the synthesis were not disclosed. The preparation was illustrated as follows:



Preparations of azide derivatives from styrene-maleic anhydride copolymers, cellulose, and gelatin by attaching aromatic azide compounds are described in the literature [175]. Most of the resultant polymers cross-link rapidly when exposed to light of 260 μm wavelength. Also, as much as 90% of the hydroxy groups of poly(vinyl alcohol) can be esterified with *p*-azido-benzoyl chloride. These reactions must be carried out in mixtures of chloroform and aqueous sodium hydroxide [175]. Earlier, Merrill and Unruh [175] described formation of derivatives from poly(vinyl alcohol) and attachment of aromatic azide groups.

Most of these azide polymers photocross-link at a faster rate than does poly(vinyl cinnamate), when exposed to light of 260 μm. In addition, they responded well to photosensitization. Also, it was observed [50] that the 4-isomer of azidophthalate shows greater speed increase than does the 3-isomer. In general, the poly(vinyl alcohol) derivatives were reported to exhibit higher cross-linking speeds than do other azide functionalized polymers [176].

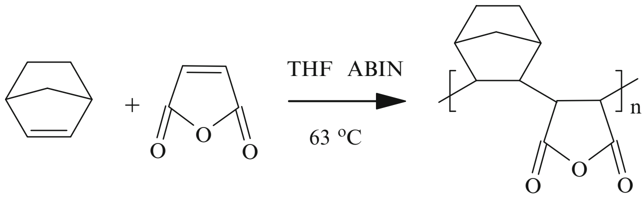
The reaction product of *p*-azidobenzoyl chloride with polyvinyl alcohol was investigated by Tsuda and coworkers [179]. In the polymer studied by them, over 90% of the hydroxy groups were esterified. The photocross-linking reaction was followed by observing changes in the ultraviolet and infra-red absorption spectra. It was shown that the simple photochemical reaction occurs stochiometrically upon irradiation. Also an absorption band was observed at 1,500/cm in the infra-red region of the irradiated and cross-linked polymer. This band is due to N=N stretching vibration of the *azo* group. Based on that, Tsuda concluded the cross-linking reaction takes place by dimerization, as expected [179].

There are reports in the literature that photosensitive azide polymers formed from polymers substituted with isocianate groups [176, 177]. The preparation and properties of many other polymers containing pendant aryl azide groups were described by Delzenne and Laridon [178]. The polymers were prepared by interfacial polycondensation of azido-substituted acid chlorides with diols and diamines. Also, in one experiment, a cinnamate moiety was combined with an azide group, together in one pendant functional structure [178]. It was found, however, that addition of the azide groups to the cinnamate side chain does not increase reactivity. A marked wavelength dependence was observed on $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions that occurs in both functional groups [179].

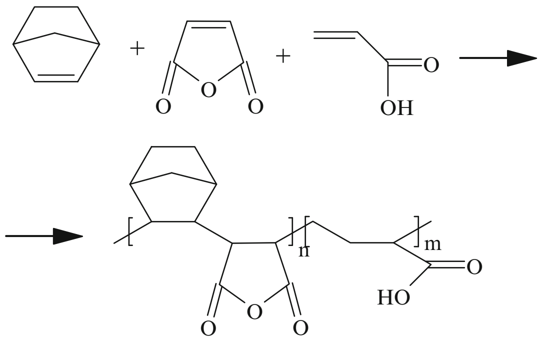
10.5.9 Polymers Designed to Cross-link Upon Irradiation with Laser Beams

To accommodate the needs of photolithography, some polymers were developed that cross-link upon irradiation with an Ar-F excimer laser source at 193 nm [180]. To this end were synthesized cycloolefin-maleic anhydride-alternating copolymers. This material was formed by free-radical copolymerization of norbornene and maleic anhydride:

(A)



(B)



To render the polymers soluble in aqueous base, acrylic acid terpolymerization was also carried out as shown in (B) above.

10.6 Photo-Responsive Polymers

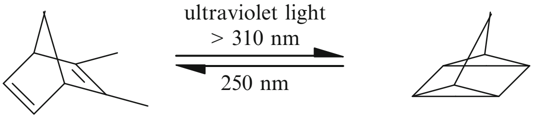
Photo-responsive polymers are materials that are able to respond to light irradiation by undergoing reversible changes in their chemical structures and/or their physical properties. Also, photochromism refers to the photo-induced reversible transformations in chemical compounds between two electronic states characterized by different absorption spectra [181]. There are many ways in which the photo-responsiveness of polymers can manifest itself. One might observe changes in viscosity of polymeric solutions, in contraction of polymeric chains, in sol–gel transitions, in electrical conductivity, or even in color changes as a result of irradiation with light of an appropriate wavelength. Another interesting manifestation of photo-responsiveness in some special polymers is a change in the permeability to gases in films. These changes can and are utilized in many ways. Thus, for instance, structural changes due to isomerization are employed to align liquid crystals and photoconductivity is utilized in xerography. Over the last 2 or 3 decades, the photo-responsive materials have grown in practical and scientific importance, because such materials are useful in many applications.

10.6.1 Polymers for Harvesting the Sun's Energy

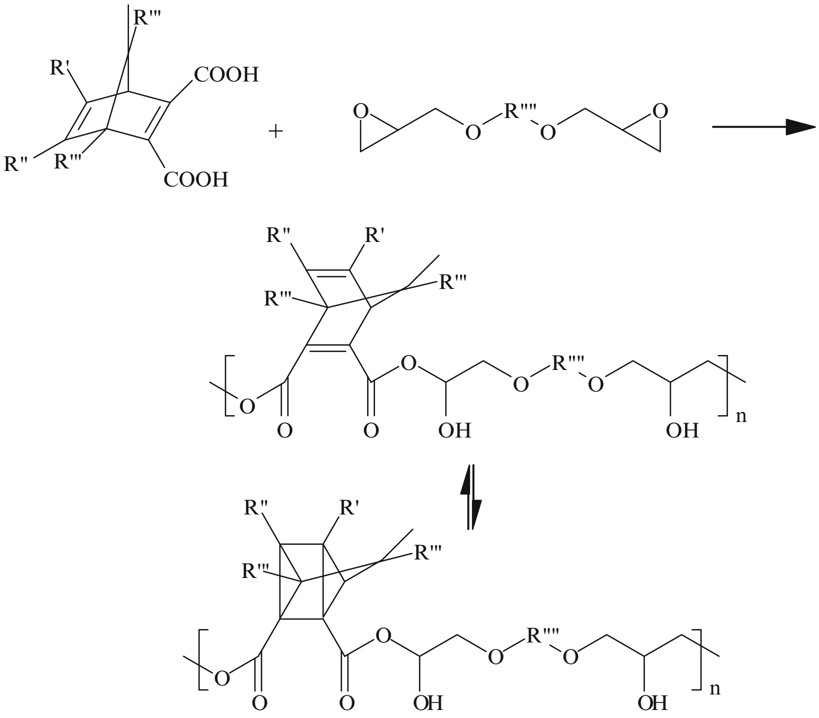
The goal of harvesting light energy has led to research in polymeric materials that could potentially mimic photosynthesis or harvest the sun's heat. In such materials, the choice of chromophores is the most critical variable. The location of the chromophores on the polymeric chains and the tacticity of the polymers are also very important. Weber pointed out, for instance, that among a number of chromophores attached to polymeric chains, naphthalene and carbazole form very stable *eximers*, while phenanthrene and diphenyl anthracene do not [182]. At present, many polymeric materials are utilized in the vast areas of nonsilver-based imaging, information storage, remote sensing, electroresponsive materials for displays, and others. Fox and Cozzens had to conclude, however, that none compare in efficiency to naturally occurring photon-harvesting polymers for photosynthesis [183].

10.6.1.1 Polymers with Norbornadiene Moieties

One approach to harvesting light energy is to utilize pendant groups that reversibly absorb light energy, rearrange, and then release this absorbed energy as heat in a rearrangement back to the original structure. To that end, research is going on in various laboratories to develop systematically derivatized polymer arrays than can collect and convert light energy. Among these, photo-rearrangements from norbornadiene to quadricyclane and back are of considerable interest, because photo-energy can be stored as strain energy (about 96 kJ/mol) in a quadricyclane molecule and later recovered [184]

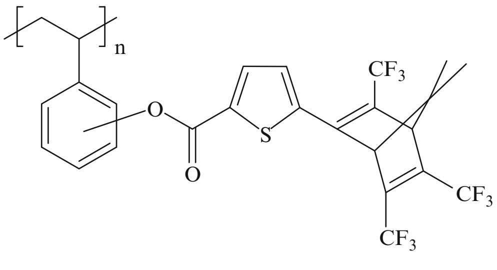


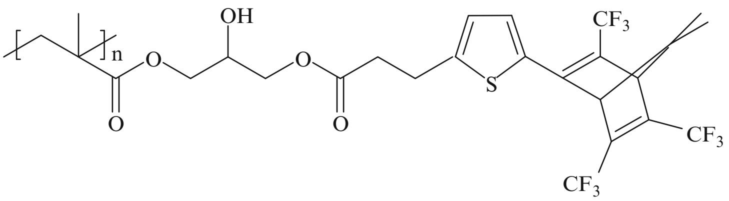
This photo-isomerization reaction is referred to as a ***valence isomerization***. It is a reaction in which electron reshuffling occurs and the nuclei move to make or break new π and σ bonds. A number of polymers were, therefore, prepared with the norbornandiene moieties either in the backbone or as pendant groups. Among them are polyesters that were synthesized with donor-acceptor norbornadiene residues in the main chain [184] by polyaddition of 5-(4-methoxyphenyl)-1,4,6,7,7-pentamethyl-2,5-norbornadiene-2,3-dicarboxylic acid or 5,6-bis(4-methoxyphenyl)-7,7- dimethyl-2,5-norbornadiene-2, 3-dicarboxylic acid, with bis(epoxide)s. This preparation of and the accompanying photo-rearrangements can be illustrated as follows:

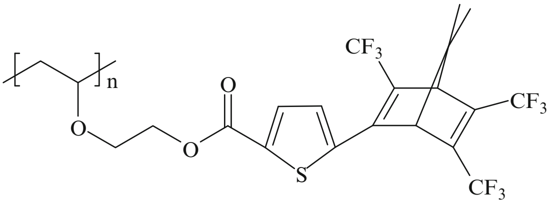


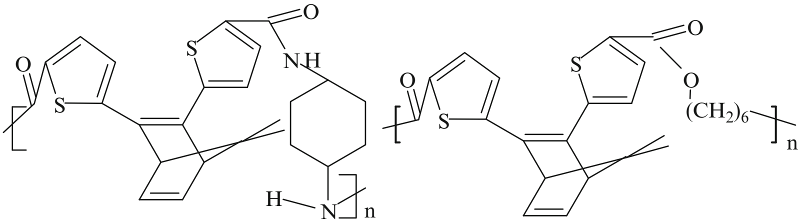
The photo-rearrangements of the norbornadiene residues in the resulting polyesters were observed to proceed smoothly to the quadricyclane groups. Also, it was found that the norbornadiene residues in these polyesters show resistance to fatigue in repeated cycles of the interconversions [184].

The goal to utilize photochemical valence isomerization between norbornadiene and quadricyclane for solar energy collection and storage was reported by others [185]. Nagai et al. synthesized five different polymers with trifluoromethyl-substituted norbornadiene moieties in the side chains and in the main chain [185]:



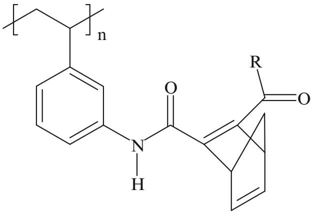






All of the above polymers exhibit large absorption bands in the visible region of the spectra and the norbornadiene moieties in these polymers isomerize very rapidly. In addition, the norbornadiene moieties also exhibit efficient fatigue resistance [185].

Kawatsuki et al. [186] synthesized styrene polymers with pendant norbornadiene groups attached via amide linkages:



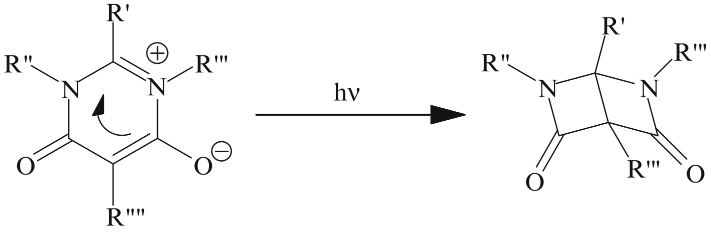
where R is a methoxy or a ring-substituted aniline group attached through the nitrogen or at another position. These pendant groups also undergo reversible conversions into quadricycline units in polymer films when irradiated by ultraviolet light of two different wavelengths. The materials exhibit high photosensitivity as well as a large red-shift in the absorption spectrum upon irradiation.

Sampei et al. [187] reported that polyaddition of 2,5-norbornadiene-2,3-dicarboxylic acid diglycidyl ester to adipoyl chloride gave a polyester containing norbornadiene residues in the polymer backbone and in the pendant groups. When a photochemical rearrangement of norbornadiene residues took place in polymer films, the rate of the photochemical reactions in the polymer backbones was higher than that in the side chains [187].

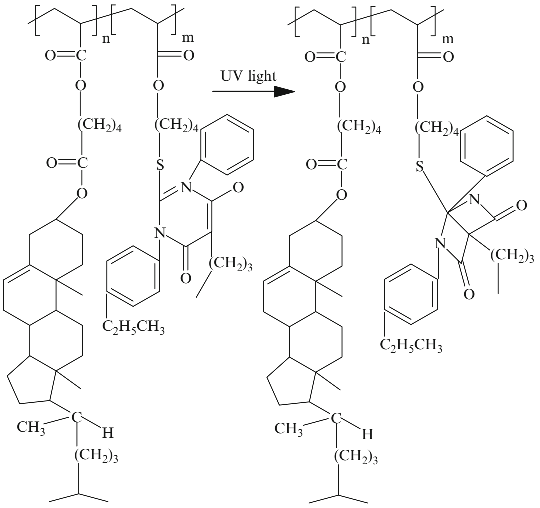
Kawashima et al. [188] reported preparation of donor-acceptor type norbornadiene carboxylic acids compounds with carbamoyl groups, such as dipropylcarbamoyl, methylphenylcarbamoyl, propylcarbamoyl, and phenyl-carbamoyl. Benzyl esters were also prepared. Addition of these groups to polystyrenes formed polymers with pendant donor-acceptor type norbornadiene. Some were formed with 100% substitution. It was found that the polymers containing phenylcarbamoyl groups exhibit especially high photo-reactivity. In addition, the rate of the photochemical reaction in films of these norbornadiene polymers increases efficiently by an addition of 4,4′-bis(diethyl-amino)benzophenone photosensitizer. As a result, all the norbornadiene groups of the polymers isomerize to the quadricycline groups in as little as 20 s. The stored thermal energy of the irradiated polymers was found to be 32–52 kJ/mol.

10.6.1.2 Copolymers of Methacrylates with Cholesteric Monomers

Groups, like 6-oxo-1,6-dihydropyrimidin-3-ium-4-oleates, are light-sensitive and undergo intramolecular photo-cyclization to bis-β-lactams when irradiated with UV light between 320 and 490 nm [189].



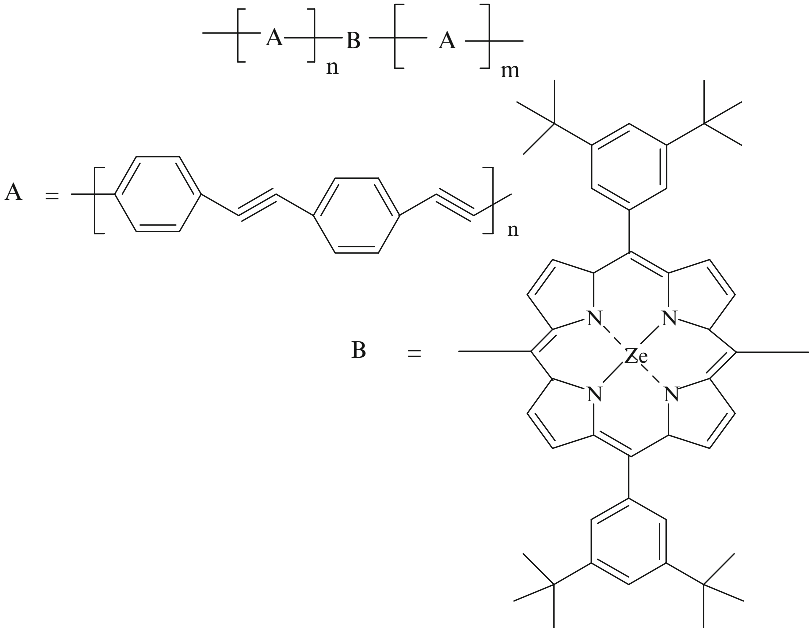
This was utilized to form copolymers of methacrylates with colesteric monomers [190]. An example of such copolymers and the rearrangement is shown below [190]:



It was found that the rate of photo-rearrangement is affected by the length of the alkyl side group in the 5 position of the pyrimidinium oleate and by the embedding of a chromophore, as shown above [190].

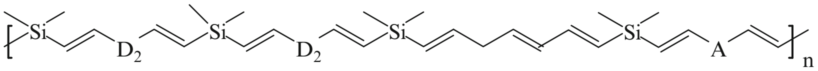
In photosynthesis, antenna pigments harvest energy and transfer it into a reaction center for redox reactions [191]. Different antenna chromophores that surround the reaction center are arranged morphologically in an order of energy gradient [192–194]. Such an arrangement allows the energy to be sequentially transferred and efficiently funneled into reaction centers over small distances in the direction of decreasing band gaps. Considerable research has been carried out on means to develop the sequential multistep energy transfer systems. This was done not just to mimic the natural light-harvesting process [192–194], but also for possible applications and use in optoelectronic and biological systems [195]. It is speculated that a conjugated polymeric backbone, with well-designed interruptions of conjugation by insulating spacers, might allow tuning the emission properties and by providing an alternate model [196].

Based on this concept, Krebs and coworkers [197] reported a synthesis of a light-harvesting material that consists of three structural domains. Two of them are conjugated homopolymers that are linked with a zinc porphyrin:



Sections A and B of the above block copolymer are illustrated above. The polymer has a constant ratio of the zinc porphyrin to the incorporated monomer units, regardless of the molecular weight. The ratio of zinc porphyrin to the polymer blocks can be varied in the material by varying the size of the blocks A. Studies of energy transfer from the polymer to the zinc porphyrin showed that there is actually very little energy transfer when the material is in solution. On the other hand, there is quantitative energy transfer in the solid state. Also, it was observed that the light-harvesting properties of the three-domain structures depend on the chain lengths of the conjugated polymers.

Cheng and Luh reported that they are also trying to develop polymers that would mimic natural photosynthesis with synthetic polymers [198]. They point out that silylene moieties have been used extensively as insulating spacers [198]. In general, when the silylene spacer contains only one silicon atom, no conjugative interactions between the π systems and the silicon moiety are observed [199]. They believe, therefore, that introduction of an energy gradient with three well-designed chromophores into a silylene-spaced polymeric chain may lead to sequential energy transfer. To achieve this goal, they carried out preparations of regioregular silylene-spaced copolymers composed of energy gradients with three different chromophores. One of the polymers prepared in this way can be illustrated as follows:



Their synthesis utilized rhodium-catalyzed hydrosilylation of bis-vinylsilanes and bis-alkynes. The ratio of the three chromophores in the above polymer is 1:2:1, corresponding to D1, D2, and A chromophores, respectively. Cheng and Luh found that upon excitation of the donor chromophore D1, only emission from the acceptor A was observed [199].

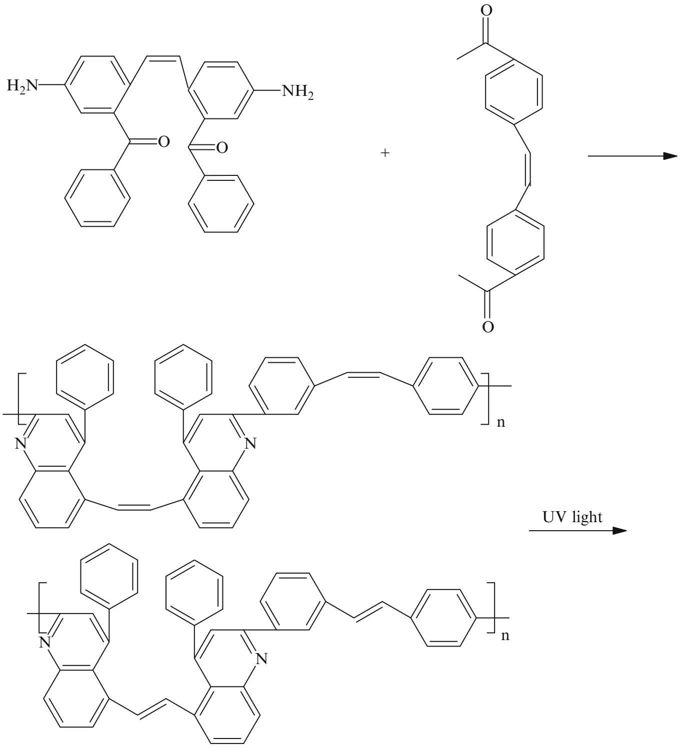
10.6.2 Photo-Isomerization of Polymeric Materials

Among all the photo-rearrangements, a *cis-trans* isomerization reaction is the most useful one. A well-known example is that of *cis*-stilbene to the *trans* isomer. This reaction has been described in many books [200]. The isomerization reaction takes place because many olefins in the excited singlet and triplet states have a perpendicular instead of a planar geometry. This means that in the excited state the *cis-trans* isomerism disappears. Upon return to the ground state, S_0, it is possible for either isomer to form. The return, however, usually takes place to the more stable form. Generally, photo-isomerization of chromophores in dilute solutions is a first-order reaction.

10.6.2.1 Photo-Isomerization of the Olefinic Group

An example of olefinic groups rearrangement is work by Onciu et al. [201] who formed three bis(trimellitimide)s by condensing three aromatic diamines with trimellitic anhydride. This was followed by preparation of two series of photo-reactive copoly(amide-imide)s by direct polycondensation of the bis(trimellitimide)s and 1,4-phenylenediacrilic acid with either 4,4′-diphenylmethanediisocyanate in one case or with 1,6-diisocyanatohexane in another case, respectfully. All of the copoly(amide-imide)s were found to be soluble in polar aprotic solvents and to yield transparent, flexible, and tough films [201]. When the polymers are irradiated in solution, the *p*-phenylenediacryloyl units undergo *trans–cis* photo-isomerization and (2 + 2) photo-cycloadditions [201]. The fully aromatic polyamides also undergo a photo-Fries rearrangement. The photo-Fries reaction, however, is completely suppressed in polymers that contain an aliphatic amide moiety [22]. The same processes are also observed in the polymer films [201].

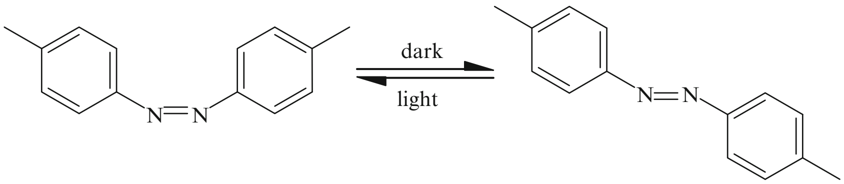
Polymers prepared by condensation of 4,4′-diacetylstiblene as the bis(ketomethylene)monomer with 4,4′-diamino-3,3′-dibenzoylstilbene, a bi(amino ketone), exhibit photo-viscosity effects in dilute solutions due to *cis-trans* isomerization [202]. The preparation of the polymers and the photo-rearrangements can be illustrated as follows:



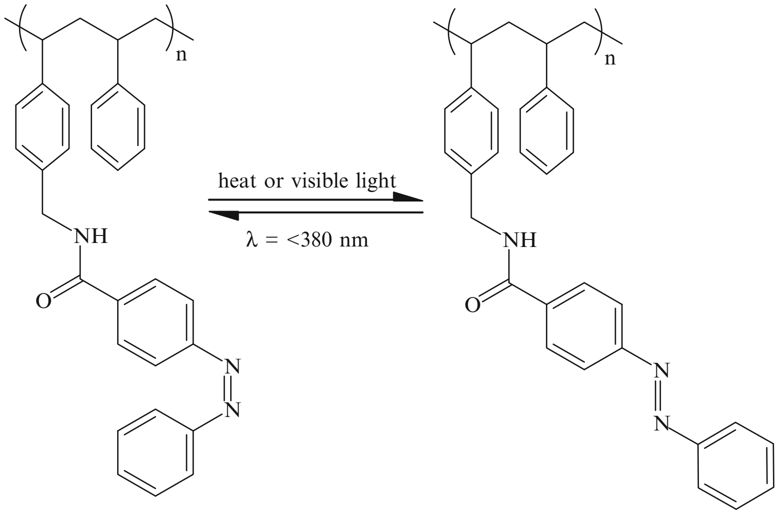
The changes in viscosity can vary from 2 to 23% as a result of irradiation.

10.6.2.2 Photo-Isomerization of the *Azo* Group

Azobenzene is a well-known photo-responsive chromophore, and its photo-induced and thermal geometric isomerizations have been extensively explored [200]. Azobenzene and its derivatives assume both *trans* and *cis* conformations with respect to the *azo* linkage. *Azo* π → π* excitation and *azo* n → π* excitation trigger *trans*-to-*cis* and *cis*-to-*trans* isomerizations [203–205]. The *azo* linkage normally exists in the more stable *trans* form. Also, the *trans* isomer of azobenzene exhibits an intense absorption around 320 nm due to the π → π* transition, while the *cis* isomer shows a weak absorption of the n → π* transition, around 430 nm [206]. Reversible isomerizations between *cis* and *trans* structures are due to these transitions. Photo-isomerization can proceed almost quantitatively [207]. By comparison, the thermal isomerizations from *cis* to *trans* configurations take place due to low activation energy of the *cis*-to-*trans* process. Isomerizations of the *azo* chromophore in compounds are often accompanied by drastic changes in a number of properties such as, for instance, changes in the dipole moments [208]. The isomerization back to the *trans* configuration can be readily carried out either thermally, or by visible light irradiation. Changes in the molecular structure, such as *cis-trans* isomerization in polymers, can induce contraction and expansion of the polymeric chains on both microscopic and macroscopic scale. This was demonstrated on a polymers with *azo* linkages. Exposure from dark to light can result in a contraction of as much as 0.5% [209]:

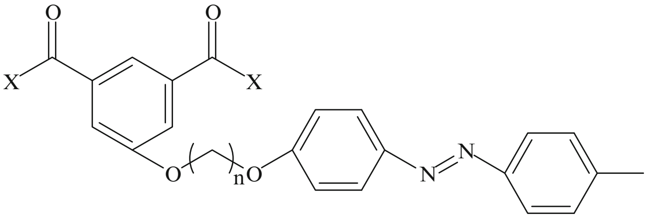


One example is a copolymer of styrene, where azobenzene structures are attached in the comonomer to the benzene portion through amide linkages [210]:



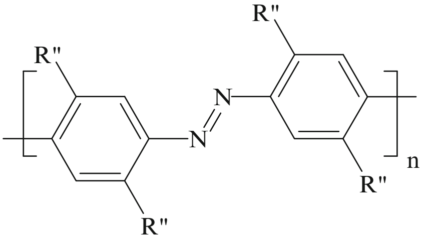
After 10 min of irradiation with ultraviolet light, the photo-stationary state is reached, consisting of 79% of the *cis* isomer. Back isomerization to *trans* of the sample is slow in the dark(less than 10% in 60 min), but is much faster when exposed to visible light [210].

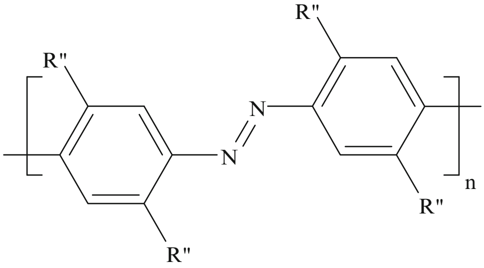
A Japanese patent [211] describes preparation of isophthalic type polyesters that include monomers with pendant *azo* groups:

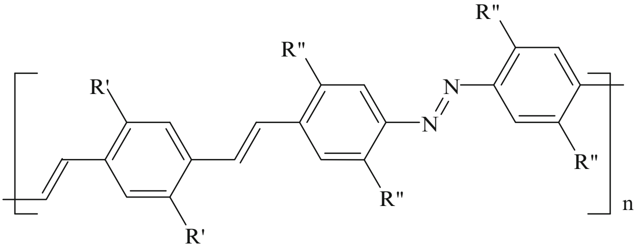


where Y is a hydrogen or a lower alkyl group; $m = 1$–3; $n = 2$–18. Polyesters based on this monomers are claimed to be useful for optical recording media such as holograms recording with low light absorption or without loss and wide range of working wavelengths.

Izumi and coworkers carried out similar preparations of conjugated polymers with azobenzenes in the main chain [212, 213]. Application of various palladium-catalyzed coupling methods such as the Suzuki coupling and the Heck reactions allowed formation of poly(*p*-phenylene)- and poly(phenyl vinylene)-based polymers:







where R′, R″ = H or n-C_6H_{13}.

These isomerization processes are also accompanied by changes in the three-dimensional hydrodynamic volumes of the polymers [213].

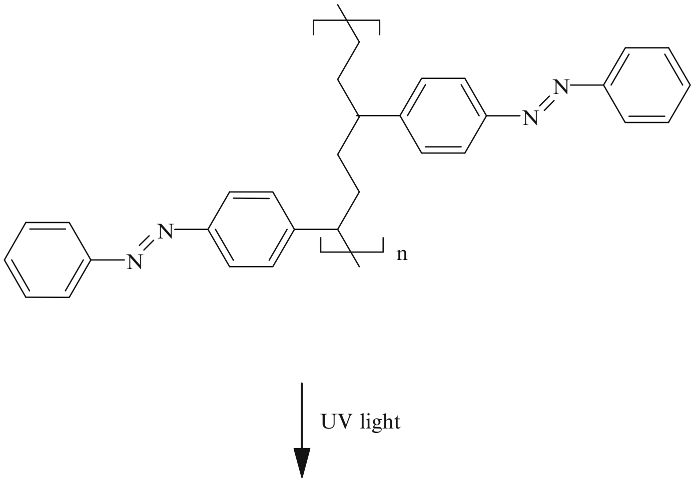
10.6.3 Changes in Viscosity and Solubility of Polymeric Solutions

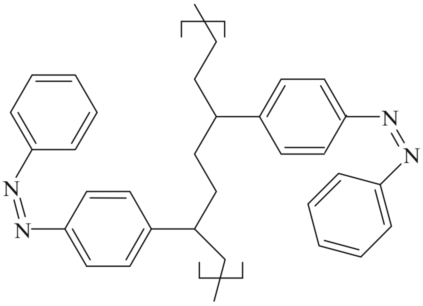
Changes of viscosity in polymeric solutions that are associated with photo-induced conformational changes of the macromolecules were observed by Lovrien [214]. He reported that solutions of a copolymer of methacrylic acid and *N*-(2,2′-dimethoxyazobenzene)acrylamide exhibit an increase in specific viscosity when irradiated with UV light. He also observed a decrease in the viscosity of a poly (methacrylic acid) and chrysophenine solution in water under the influence of UV light [214]. This was followed by various reports of photo-viscosity effects in solutions of azobenzene-based polymers. Matejka and Dusek [215] studied a copolymer of styrene and maleic anhydride with azobenzene in the side chains. UV light irradiation of a solution of this polymer in 1,4-dioxane causes a decrease in specific viscosity between 24 and 30% and in tetrahydrofuran between 1 and 8%. They also observed that this decrease in viscosity is reversible. The magnitude of the effect was found to be related to the quantity of azobenzene linkages present in the polymer.

Hallensleben and Menzel [218] found that irradiation of poly(5-(4-phenylazobenzyl)-L-glutamate) in 1,4-dioxane solution with UV light ($\lambda > 470$ nm) decreases the viscosity by 9%. Here too this change in viscosity is accompanied by a *trans* to *cis* isomerization that was estimated to be 23%. With additional irradiation by 360 nm UV light, the viscosity decreases an additional 9% and the isomerization to *cis* reaches 89%.

Irie et al. [217] synthesized a number of polyamides with azobenzene groups in the backbone. All the polymers exhibit photo-viscosity effects. In solutions in *N*,*N*′-dimethylacetamide, a 60% reduction in specific viscosity can be achieved by UV light irradiation ($410 > \lambda > 350$ nm). The initial viscosity is regained by storage in the dark at room temperature for 30 h.

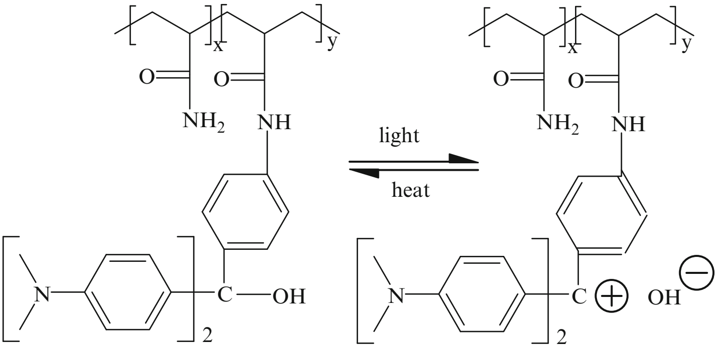
Changes in viscosity of solutions in dimethylsulfoxide of a range of polyureas with azobenzene groups in the polymer backbone were reported [216]. The irradiations were carried out at 35°C with UV light between 410 and 350 nm. It was observed that the intrinsic viscosity is about 40% lower during UV irradiation than in the dark. Also, toluene solutions of polydimethylsiloxane with azobenzene residues were shown to exhibit 20% lower viscosity under UV light irradiation than in the dark [219]. This effect was attributed by them to conformational contraction of the polymer chains due to dipole–dipole interaction between neighboring chromophores [220]. This conformational change might possibly be illustrated as follows:





Also, when copolymers of polystyrene and 4-(methacryloyl-amino)azobenzene containing 2.2–6.5% of the latter are irradiated in a cyclohexane solution with 15 flashes of 347 nm of light. The polymeric chains contract [221]. This occurs at a high rate per second as a consequence of isomerization. At a later stage, several hundred seconds after the flash, there is evidence of polymer aggregation and precipitation [221]. In addition, when azobenzene residues are introduced into the main chain of poly(dimethylsiloxane), reversible solution viscosity changes can be obtained by irradiation with ultraviolet light [221].

Isomerization from *cis* to *trans* and back of *azo* groups, however, is not the only mechanism that can affect photo-viscosity change in polymeric solutions. Thus, reversible solution viscosity changes were also observed [222] in solutions of poly(dimethylacrylamide) with pendant triphenylmethane leucohydroxide in methanol. This can be illustrated as follows:

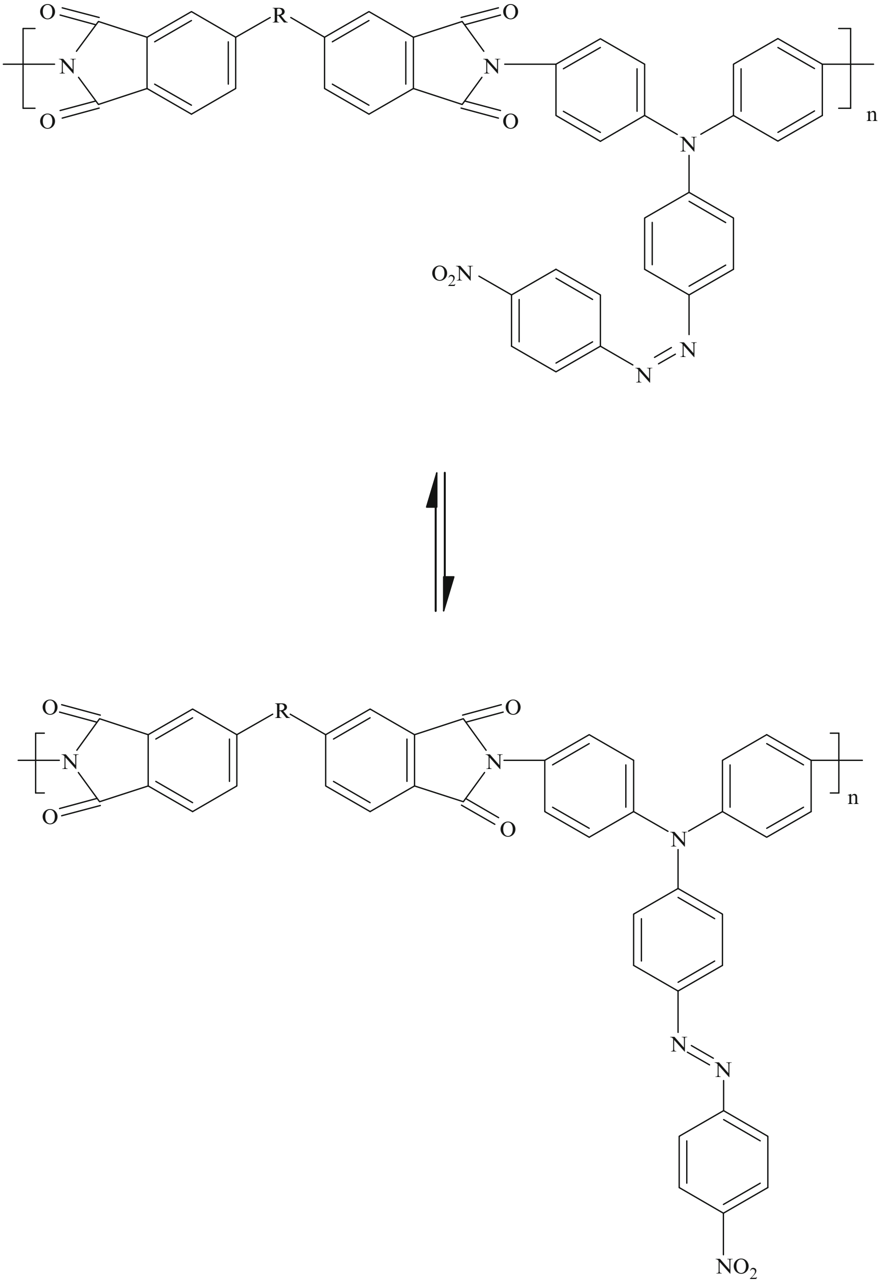


So, as shown, the viscosity changes are due to positive charges that form on the pendant groups.

The solubility of a copolymer of styrene in cyclohexane was found to change reversibly upon ultraviolet light irradiation when the copolymer contains small amounts (~2 mol%) of spirobenzopyran among the pendant groups [223]. This is believed to be due to photo-isomerization of the pendant spirobenzopyran groups to the polar merocyanine form with the resultant decrease in polymer–solvent interaction and subsequent precipitation of the higher molecular weight fractions of the polymer. A copolymer with a high content of spirobenzopyran groups (12.3 mol%) performs as a negative photo-resist with high contrast [223].

10.6.4 Application to Optical Data Storage

Due to possible utilization of photo-induced orientation in polymeric films in optical data storage, this phenomenon and the quadratic nonlinear optical effects were extensively investigated in the last few years. It was reported, for instance, that to study photo-isomerization in a polymeric environment, a series of polymers containing *azo* dyes with large differences in the second order transition temperature were compared [225]. Particular emphasis was placed on the relationship between photo-isomerization, T_g of the polymers, and their molecular structure. As a result, it was shown that light-induced nonpolar orientation in very high T_g polyimides (T_g up to 350°C) can take place even at room temperature. The polymers used in one of these studies can be illustrated as follows [225]:



where R = $(CF_3)_2$–C< in one polymer and –COO–$(CH_2)_2$–COO– in another.

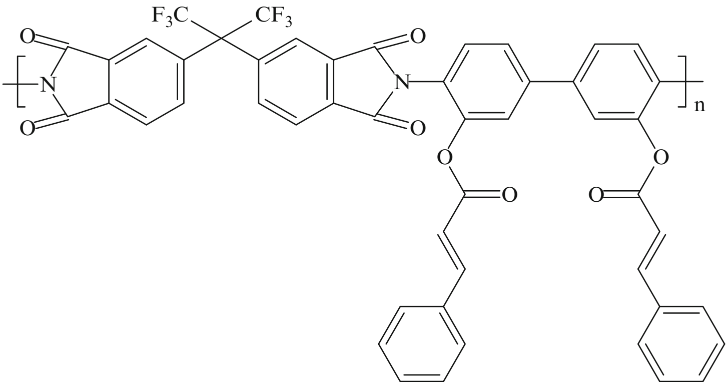
From the behavior of the mean absorbance, it was concluded that all the *azo* chromophores revert to the *trans* form on completion of a thermal back reaction. The observed increase in the dichroic ratio over the first 25 h is believed to be due to the thermal back isomerization and not due to the relaxation of the induced orientation [225]. Heating polymers at 170°C for 1 h fails to erase the green light-induced dichroism in the samples. This dichroism is, however, completely erased on heating the samples above their T_g for 10 min. Irradiation of the films with incident light gives holograms [226].

10.6.5 Liquid Crystalline Alignment

The relationship of glass transitions to mobility and isomerization in confined polymer systems aroused much interest. It was influenced by need for alignment in liquid crystalline flat panel displays, because in these displays films of polyimides are widely used. The surfaces are usually treated to produce uniform alignment of the liquid crystals into suitable "pretilt" angles. The treatments consisted of rubbing process with velvet fabrics. Search for new methods, however, led to development of molecular structures that undergo alignment upon irradiation with linearly polarized UV light [222, 223]. Polymer-stabilized liquid crystals are low-molar-mass liquid crystal. Their bulk alignment or their texture is stabilized by a polymer network. Such polymer network is usually in low concentration [222, 223]. Several types of polarized-light-induced liquid crystalline aligning of molecules were reported in the literature [223].

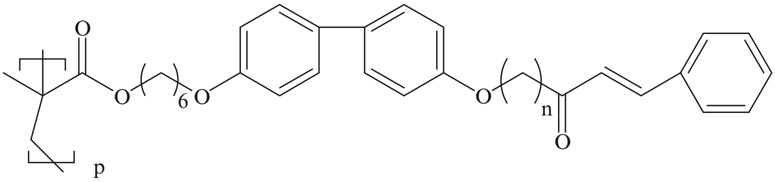
One photo-alignment material is poly(vinyl cinnamate). The polymer and its copolymers were reported to have the ability to align in thin films in the direction perpendicular to the axis of the linearly polarized ultraviolet light. This photo-alignment mechanism has not been fully elucidated at present. A drawback to using poly(vinyl cinnamate) and its copolymers is a low glass transition temperature. As a result, they remain mobile after treatment and chain orientation. Other materials with higher T_g are, therefore, needed. Among the most promising ones are polyimides. They form liquid crystal alignment layers in flat panel displays and possess good optical transparencies, adhesion, heat resistance, and dimensional stability, and are good insulators.

There are various reports in the literature about preparations of soluble photo-reactive polyimides with cinnamate chromophore side groups. Thus, it was reported by Lee et al. [224] that they prepared a photo-reactive polyimide with cinnamate chromophores side groups:



This polyimide is claimed to be thermally stable up to 340°C and has a glass transition temperature of 181°C. Also, it was demonstrated that the cinnamate chromophores, upon irradiation with linearly polarized ultraviolet light, undergo both photo-isomerization and dimerization. In addition, the light exposure induces anisotropic orientation of the polymer main chains and of the cinnamate side groups in the film. The irradiated films align homogeneously the nematic liquid crystal molecules along one direction at an angle of 107° with respect to the polarization. The liquid crystalline alignment was found to be thermally stable up to 200°C.

It was also reported [225] that photo-reactivity of side-chain liquid crystalline polymers can align liquid crystals both in a parallel mode or perpendicularly, depending on the degree of the photoreaction of the polymers. Presumably, this particular polymer can multiphoto-align the liquid crystal pattern without a change of the direction of the linearly polarized UV light. The chemical structure of such an aligning polymer is depicted as follows:

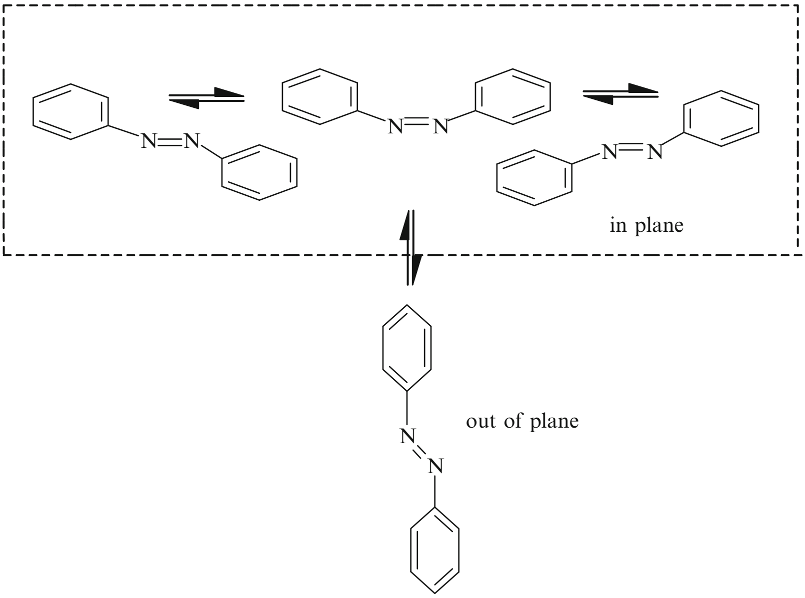


where $n = 2$ or 6.

It was concluded [226], therefore, that the liquid crystals align both parallel and perpendicular to the incident *E* direction on the photocross-linked polymer film by changing the degree of the reacted cinnamoyl group. That can be controlled by irradiation time. A bias-tilt angle between the liquid crystals director and the substrate is also realized by controlling the irradiation angle of the light [226].

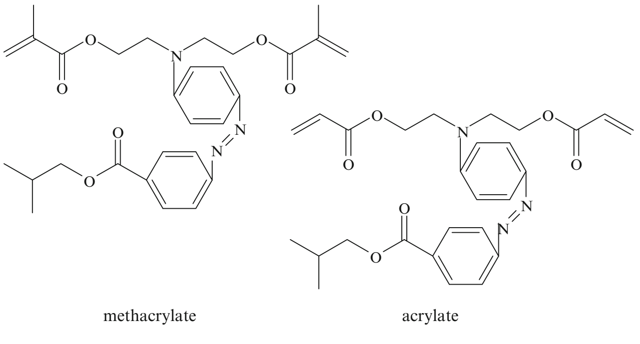
Another approach to liquid crystalline alignment is based on photo-isomerization of *azo* compounds in polymeric materials or as part of the polymer structure [227]. In recent years, investigation of the use of azobenzene-containing polymers for liquid crystalline alignment became quite thorough because of the potential application in holographic storage as well as optical and photonic use [228–230]. The photo-alignment of liquid crystalline polymers containing azobenzene groups has an advantage of local variation of the orientation order due to pixel-wise irradiation. This is a process that is reported to take place via angular-dependent excitation, a series of *cis-trans* photo-isomerization cycles, and rotational diffusion within the steady state of the photoreaction. This results in the photochromic side group becoming oriented perpendicularly to the electric field vector of the incident light and establishing an oblate order in the films.

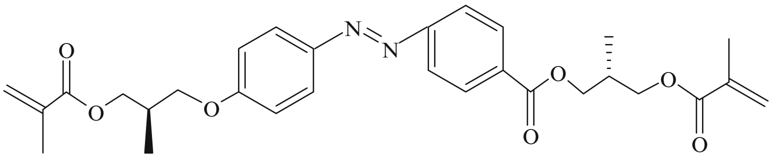
Thus, studies of exposure of films of liquid crystalline polymers with azobenzene side chains to linearly polarized light of 436 nm [231] show successive occurrences of uniaxial in-plane orientations, followed by out-of-plane orientations of azobenzenes [231]. Two kinds of orientation modes were observed. These are possibly extreme cases, when linearly polarized light with the electric vector parallel to the *xz*-plane comes along the *z*-direction. One is the uniaxial in-plane orientation of the azobenzene with a dipole moment parallel to the *x* axis from the *x*- to *y*-direction and the other is out-of-plane (homeotropic) one toward the *z*-direction. Marked dependence of photo-orientation processes on film temperatures was observed. In-plane orientation was generated in the glassy state. Photo-orientation at higher temperatures, slightly below the transition temperature between smectic and nematic phases, gives rise to distinct transformations from in-plane orientation at the early state to successive out-of-plane reorientations [232]. These orientations can be illustrated as follows:



Also, it was reported [233], that irradiation of a liquid crystalline polyester with azobenzene side chains with light of an argon laser (514, 488, or 351 nm) results in orientation of 4-cyano-4′-alkoxyazobenzene side groups. The polyester is characterized by smectic and nematic phases and shows a strong tendency to form J-aggregates. The orientation process is cooperative, whereas the light-induced orientation of the photochromic moiety causes an ordering of the alkylene spacers and even of the main-chain segments into the same direction. It was concluded [226] that the most probable mechanism of this two-step process is the angular-selective transformation of the bulky *trans*-isomers to the rod-like *cis*-isomeric formed by the red light. The aligned *cis*-azobenzene side groups become strongly J-aggregated. Very high values of dichroism of about 0.8 and birefringence of about 0.3 were generated as a result of this combination of the photo-induced orientation process and the thermotropic self-organization, which takes place simultaneously under the irradiation conditions. The process results in a uniaxial prolate order of the film, whereas conventional photo-orientation leads to a biaxial oblate order [93]. Thus, the direction of photo-induced orientation and the type of the three-dimensional orientation order can be controlled by the wavelength of the irradiating linearly polarized light. This can also be done in the same film of a smetic polyester with 4-cyano-4′-alkoxyazobenzene side group [233].

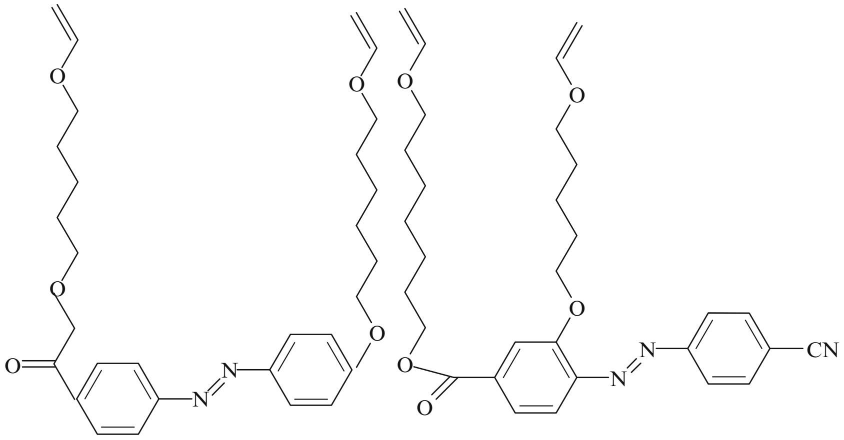
Zhao and coworkers [234, 235] reported that an azobenzene polymer network can also optically align ferroelectric liquid crystals. This was done by dissolving two chiral dimethacrylate and one chiral diacrylate monomers containing azobenzene groups in a commercial ferroelectric liquid crystal host. The monomers were illustrated as follows:

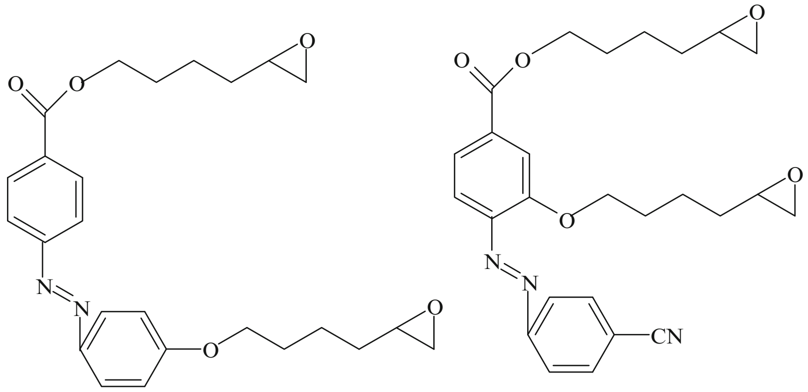




The monomers were then thermally polymerized and simultaneously irradiated with linearly polarized light. Two of the monomers were able to induce bulk alignment of the liquid crystals in direction perpendicular to the polarized light. Monomer #1 was effective in concentrations as low as 1%. It was also concluded from the experimental evidence that the photo-induced bulk alignment of the ferroelectric liquid crystals may take place by a mechanism that is different from one that takes place in achiral azopolymers.

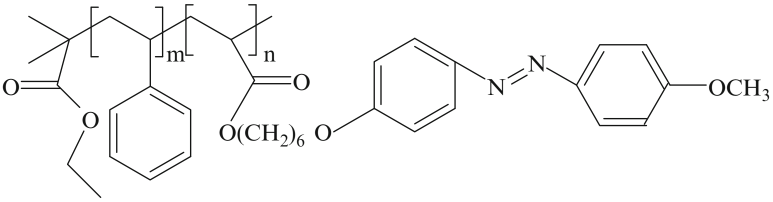
In addition, Zhao and coworkers [236] reported photo-induced alignment of ferroelectric liquid crystals using azobenzene polymer networks of polyethers and polyepoxides. Bulk alignment was achieved by polymerizing several divinyl ethers and diepoxide monomers bearing an azobenzene moiety. Here too, thermal polymerizations were conducted in solution within the ferroelectric liquid crystals, while exposing the reaction mixture to linearly polarized irradiation. The monomers can be shown as follows:





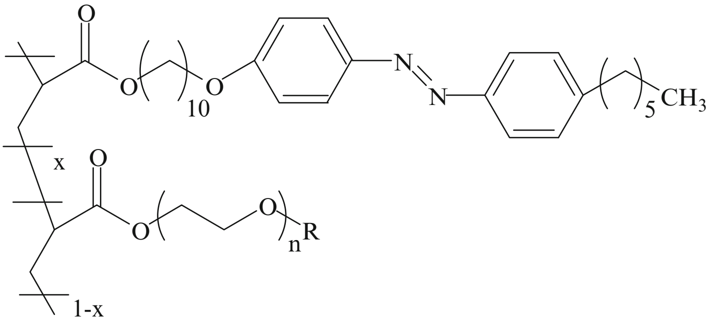
Polymerization of these monomers was achieved by cationic mechanism. The monomers were also found capable of inducing and stabilizing bulk alignment of the liquid crystals. Zhao and coworkers [234–237] concluded, however, that the mechanism of action might be different from the one obtained with chiral azobenzene polymethacrylates. Instead, the results suggest to them that the mechanism might be based on formation of an anisotropic azobenzene polyether or polyepoxide network.

In still another subsequent work, Zhao and coworkers [237] used block copolymers composed of polystyrene and liquid crystalline azobenzene-containing polymethacrylate copolymers as a model system



to investigate the confinement effects on the photo-alignment, photochemical phase transition, and thermochromic behavior of the azobenzene polymer. The study showed [237] that when confined in the microphase-separated domains in the diblock copolymers, the azobenzene polymer behaves differently than it does as a homopolymer free from confinement. The confinement effects are manifested by (1) decreased photo-induced and thermally enhanced orientation of azobenzene mesogenic groups in different aggregation states, (2) slower transformation from a liquid crystalline phase to the isotropic state triggered by the *trans–cis* photo-isomerization and slower recovery of the liquid crystalline phase after the thermally induced *cis-trans* back isomerization, and (3) severely reduced and even suppressed changes in the aggregation states of azobenzene groups on heating, which is at the origin of the thermochromic property. The common cause of these confinement effects is the restriction imposed by the confining geometry on either an order-disorder or a disorder-order reorganization process involving the motion and rearrangement of azobenzene groups [237].

Zettsu and Seki reported [238] preparation of a group of azobenzene-containing polymers that can be used in photo-induced surface relief formations. These are soft liquid crystalline azobenzene-containing copolymers of acrylate with methacrylate monomers bearing oligo(ethylene oxide) chains. The copolymers display a smectic liquid crystal phase at room temperature. After preexposure to ultraviolet light, thin films of the liquid crystalline polymers show highly sensitive photo-induced material transfer to generate the surface relief structures. The typical exposure dose required for full polymer migration is as low as 50 mJ/cm^2.



The inscribed surface relief structures can be rapidly and fully erased either by irradiation with incoherent nonpolarized ultraviolet light or by heating close to the clear point of the soft liquid crystalline polymers. It is also possible to chemically cross-link the polymers with mixed vapors of hydrogen chloride and formaldehyde after surface relief inscription. This results in a drastic improvement of the shape stability, maintaining the structure at high temperatures up to 250°C. After cross-linking, the *trans*-to-*cis* photo-isomerization readily proceeds without any modification of the surface morphology and can, therefore, be applied to the photo-switchable alignment of nematic liquid crystals [238].

10.7 Photo-Conducting Polymers

Unless polymers contain long sequences of double bonds, they are fairly good insulators, particularly in the dark. Nevertheless, a number of common polymers show measurable increase in conductivity, when irradiated with light. When polymeric materials, like poly(vinyl fluoride), poly(vinyl acetate), poly(vinyl alcohol), or poly(*N*-vinyl carbazole), are exposed to light, they develop charged species. The species can migrate under an electric field and thus conduct electricity. When poly(*N*-vinyl carbazole) is doped with photosensitizers or compounds that form charge-transfer complexes, the photosensitivity can be increased and even extended into the visible region of the spectrum. Since discovery in 1957 that poly(*N*-vinyl carbazole) has photoconductive properties, there has been increasing interest in the synthesis and study of this and other polymeric materials with similar properties that allow various photonic applications. Related polymers are presently utilized in photocopiers, laser printers, and electro-photographic printing plates.

Photoconductive polymers can be p-type (hole-transporting), n-type (electron-transporting), or bipolar (capable of transporting both holes and electrons). To date, most photoconductive charge-transporting polymers used commercially are p-type.

Poly(vinyl carbazole) and other vinyl derivatives of polynuclear aromatic polymers, such as poly (2-vinyl carbazole) or poly(vinyl pyrene), have high photoconductive efficiencies. These materials may take up a helical conformation with successive aromatic side chains arranged parallel to each other in a stack. In such an arrangement, the transfer of electrons is facilitated. Also, it is believed that the primary mechanism for poly(vinylcarbazole) charge carrier generation is due to excitation of the carbazole rings to the first excited singlet state. This polymer absorbs ultraviolet light in the 360-nm region and forms an exciton that ionizes in the electric field. The excited state by itself is not a conductive species. The addition of an equivalent amount of an electron acceptor, like 2,4,7-trinitrofluorenone, shifts the absorption of this polymer into the visible region by virtue of formation of charge transfer states. The material becomes conductive at 550 nm. This associated electron-positive hole pair can migrate through the solid polymeric material. Upon dissociation of this pair into charged species, an electron and a positively charged hole, the electron becomes a conductive state. To achieve this, additional energy is required and can be a result of singlet–singlet interaction [239], singlet–triplet interaction [240], singlet–photon interaction [239], triplet–photon interaction [239], and two–photon interaction [240]. Kepler carried out fluorescence quenching studies and concluded that the migration of the exciton is the most probable energy transfer mechanism of poly(vinyl carbazole) [241]. He, furthermore, suggested that the exiton can visit 1,000 monomer units during its lifetime [241]. This is a distance of about 200 Å.

Kang and coworkers [242] also explored steady state and pulsed photo-conductivities in 4–8 μm thick films of *trans*-polyphenylacetylene and also *trans*-polyphenylacetylene films doped with inorganic and organic electron acceptors, particularly iodine and 2,3-dichloro-5,6-dicyano-*p*-modulated by shallow electron traps in the undoped polymer and by trapping the charge-transfer complex in the doped polymer [242]. Guellet [94] states that photo-conductivity σ is equal to the current density J divided by the applied field strength ε, where J is aperture/unit electrode area. This is related to the number of negative-charge carriers (usually electrons) per unit volume, and p is the number or positive charge carriers (or positive holes) per unit [94]

$$\sigma = J/\varepsilon = ne\mu_{\mathrm{n}} + pe\mu_{\mathrm{p}}$$

where e is the charge on the electron, and μ_n and μ_p are the mobilities of the negative and positive carriers, respectively. Photo-conductivity and mobility of the charge carrying species can be determined from a relationship [94]:

$$\mu = d^2/Vt$$

where d is the thickness of the film, V is the applied voltage, and t is the carrier drift time. The photo-effect is evaluated in terms of the effective gain, G. It represents the number of generated carriers reaching the external circuit per unit time, compared with the number of photons absorbed at the same time [94]:

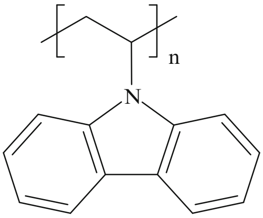
$$G = J_p/eI_0(1 - T)A$$

where J_p is the photocurrent, e is the electric charge, I_0 is the number of incident photons per cm^2/s, T is the optical transmittance of the film, and A is the area of the sample that is being illuminated.

10.7.1 Photoconductive Polymers Based on Carbazole

As stated above, the primary mechanism for charge-carrier generation in poly(vinyl carbazole) appears to be due to the excitation of the carbazole rings to their excited singlet states [112]. While the singlet excited state is not a conductive species, the conductivity is believed to be the result of an associated electron-positive hole pair migrating through the solid polymeric material. Dissociation of the electron pair produces a separate electron and a positive hole in such a way that the electron ends up in the conducting state [94]. This requires acquisition of more energy. One way that can be accomplished is by exciton–surface interaction [243]. Regensburger published an absorption spectrum, fluorescence spectrum, and photocurrent spectrum for a 7.6 μm films of poly(*N*-vinyl carbazole) [244]. The shape of the response of the photoconductor to the wavelength of the light flash is very close to the shape of the absorption spectra. Bauser and Klopffer explain this as a result of interaction of singlet excitons with trapped holes [245].

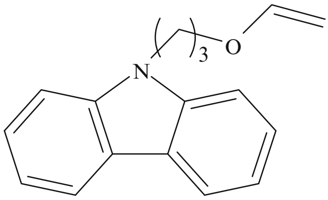
Lyoo used a low-temperature initiator, 2,2′-azobis(2,4-dimethyl-valeronitrile), to polymerize *N*-vinyl carbazole in a heterogeneous solution in a mixture of methyl and *t*-butyl alcohols [247]. The polymer that formed has the M_n molecular weights $>3 \times 10^6$. The author emphasized that this method provides ultrahigh-molecular-weight polymer and conversions greater than 80%.



The optical transparency of poly(vinyl carbazole) films produced by this room temperature process appears to be quite high, although transparency decreases at high conversions. In film form, this material is useful for photoconductors, charge-transfer complexes, and electroluminescent devices. The higher polymer molecular weight typically enhances film mechanical properties [247].

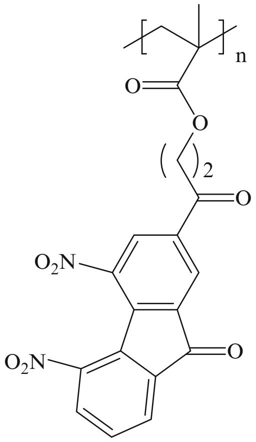
Horhold and Rathe [248] reported that they have prepared poly(9-methylcarbazole-3,6-diyl-1,2dipenylvinylene). The polymer ($M_n = 10{,}000$) was formed by dehalogenating polycondensation of 3,6-bis(α,α-dichlorobenzyl)-10,9-methylcarbazole with chromiun(II) acetate. This polymer was found to be also highly photoconductive. Its dark conductivity increases by doping it with arsenic pentafluoride [248].

Photoconductive polymers and copolymers were also synthesized by Haque et al. [249] from 2-(9-carbazolyl)-1-propenyl vinyl ether:



The polymers and copolymers form by a cationic polymerization mechanism, using boron trifluoride or ethylalumionum dichloride as the catalysts [249].

Charge transfer complexes also form from poly(vinyl carbazole) that acts as the donor, with poly [2-(methacroyloxy)ethyl-4,5,7-trinitro-9-oxo-2-fluorene-carboxylate] that acts as the acceptor [250]:

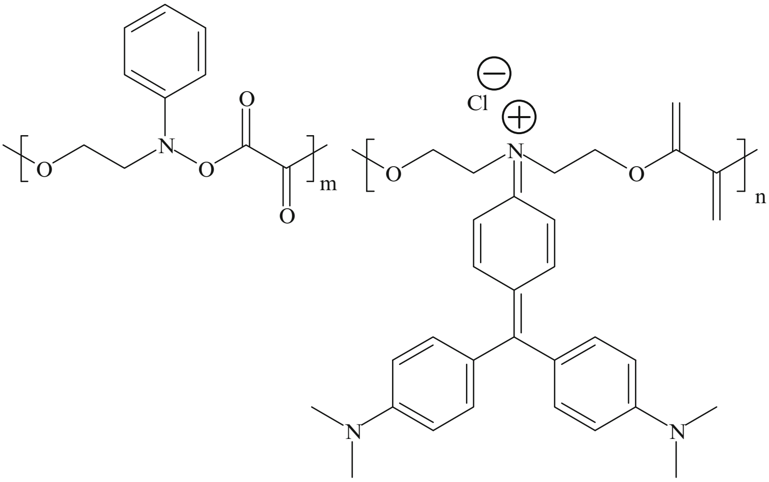


The required mole ratio of components in the complex is 1:1 [250].

Charge transfer complexation occurs in a similar manner in poly(2-carbazolylethyl acrylate) molecularly doped with 2,4,7-trinitrofluorene. Quantum efficiency of the hole propagation of the copolymer with the 0.05–1.0 molar ratio of trinitrofluorene to carbazole chromophores is higher than in the corresponding trinitrofluorene and ethyltrinitrofluorene doped homopolymer of poly(2-carbazolylethyl acrylate) [251].

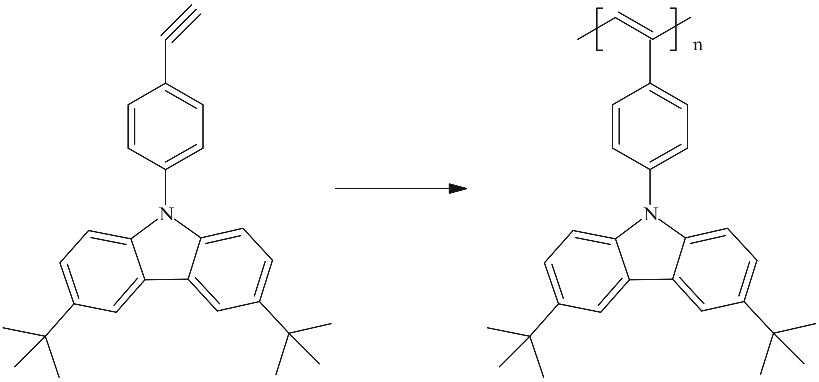
Kim and Webber studied delayed emission spectra of poly(vinyl carbazole) that was doped with dimethylterephthalate and pyrene [252]. On the basis of their results, they concluded that at room temperature dimethylterephthalate does not completely quench the triplet excitation state of poly (vinyl carbazole). They also concluded that phosphorescent states of poly(vinyl carbazole)-dimethylterephthalate are similar, implying a significant charge-transfer character in the former.

In 1985, polymeric triphenylmethane dyes based on condensation polymers such as polyesters and polyurethanes were prepared [252]:



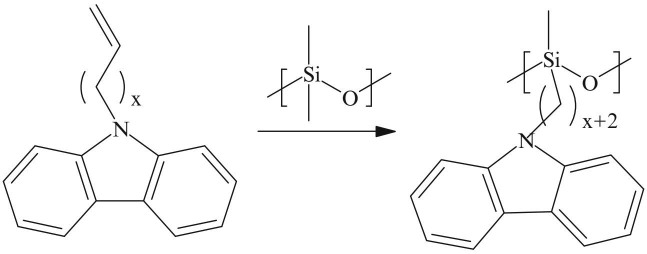
These dyes were then shown to sensitize photo-conductivity of poly(*N*-vinyl carbazole).

Polyacetylene derivatives exhibit unique characteristics such as semiconductivity, high gas permeability, helix inversion, and nonlinear optical properties [253]. Attempts were made, therefore, to incorporate carbazole into polyacetylene in hope of attaining enhance properties [253].

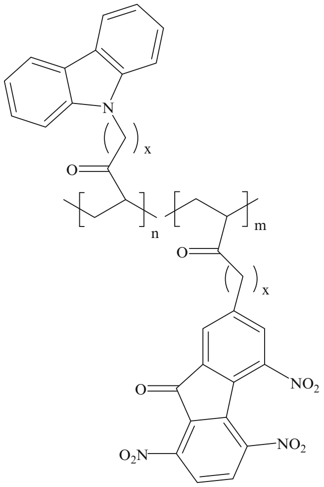


It was found [122] that the current conducted by this polymer during irradiation is 40–50 times higher than it is in the dark. On the other hand, the electron mobility of the di-*t*-butylcarbazolepolyacetylene (shown above) is lower than in poly(vinyl carbazole). This was attributed to the bulkiness of the butyl groups [254].

Siloxanes with pendant carbazole groups were synthesized by Strohriegl [254] by the following technique:

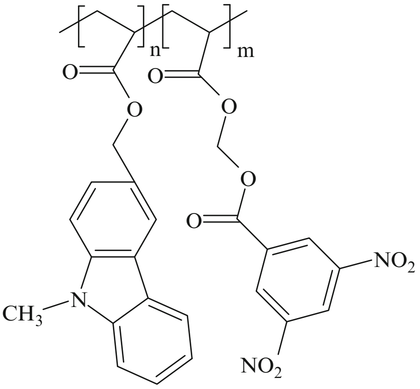


The material, however, did not turn out to be photoconductive. The photo-conductivity of copolymers was also investigated. Copolyacrylates with pendant donor and acceptor chromophores, such as 2-*N*-4,5,7-trinitrofluorenone-2-ethyl acrylate, do exhibit photo-generation properties [254]. These copolymers



can be prepared by free-radical copolymerization of the appropriate monomers. Photo-conductivity in the visible is obtained by charge transfer complexation.

Similar work was done earlier by Natansohn [255], who copolymerized *N*-methyl, 1,3-hydroxymethyl carbazolyl acrylate with acryloyl-3′-hyroxypropyl-3,5-dinitrobenzoate:

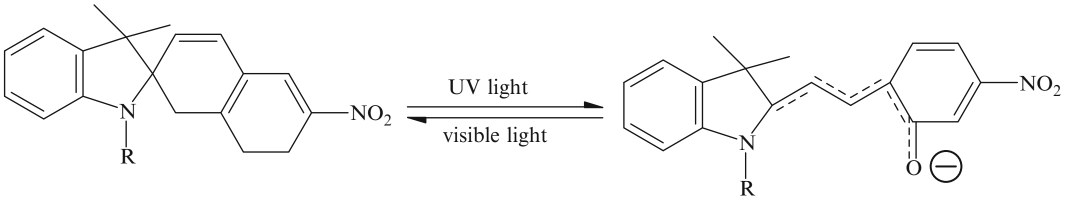


Illumination of the copolymer samples induces a certain degree of ionization accompanied by proton transfer. There is a permanent increase in the quantity of radicals generated by light. Another number of radicals apparently forms during illumination, but disappears in the dark [254].

It was reported [256] that a polymer formed by condensation of *N*-(3-isopentyl)-3,6-diformyl-carbazole and 4-14-bis[(-aminoethyl)aminophenyl-*azo*]nitrobenzene yields a new polyazomethine, carbazole-*azo* polymer. The product is soluble in organic solvents. The polymer possesses carbazole moieties and *azo* type nonlinear optical chromophores in the backbone. It shows high photo-conductivity and nonlinear optical properties.

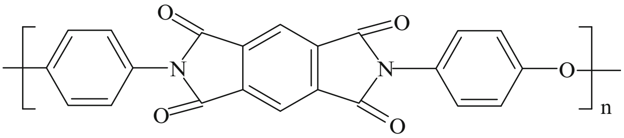
10.7.2 Photo-Conducting Polymers That Are Not Based on Carbazole

When spiropyran is incorporated into plasticized poly(vinyl chloride) membranes and placed between two identical NaCl solutions and irradiated with ultraviolet light for long periods, the potential decreases [257]. This was shown by Ryba and Petranek to be a result of the spiran ring opening up [257]:



When the irradiation is interrupted and the membrane is irradiated with visible light, the potential returns to its original value, because the ring closes back to the spiran structure [125].

The addition of electron donors, like dialkyl aniline, to Kapton polyimide film

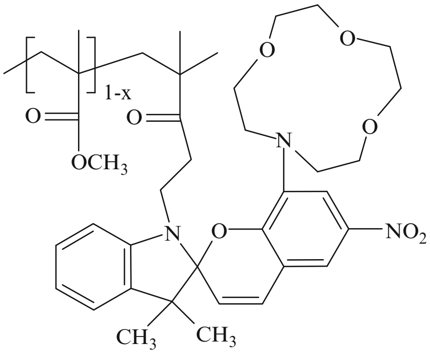


results in an enhancement of photocurrent by as much as five orders of magnitude, compared with the virgin material [258]. Freulich explains the mechanism of enhancement as a result of radiation absorption by the charge-transfer complex formed between the added electron donor and the imide portion of the polymer backbone. Excitations are followed by rapid and complete electron transfer from the donor to pyromelitimide to yield the radical anion of the polymer and the radical cation of the donor [258]. These species undergo rapid back-electron transfer. In other words, the dialkyl aniline donates one of the unpaired electrons in a typical photo-reduction reaction to the carbonyl group. The reaction is reversible and the photo-conduction is by a mechanism of the ion radical returning to the ground state.

Studies of the thermochromic, solvatochromic, and photoconductive properties of 3-, 4-, 6-, and 9-poly[(butoxycarbonylinethyl urethane)-diacetylenes] result from changes from rod (red or blue) to coil (yellow) conformations of the polymer backbone [259]. Photo-excitations of the solutions of these polymers in the rod state result in a large transient photo-conductivity, while only very small conductivity signals are observed in the coil state. The thermochromic shift that occurs in going from the rod state at room temperature to the coil state at 65°C is accompanied by a decrease in the photo-conductivity. The large conductivity signal in the rod state is attributed to the formation of mobile charge carriers possibly via interchain charge transfer within aggregates. The decay of the photo-conductivity is nonexponential and extends to microseconds.

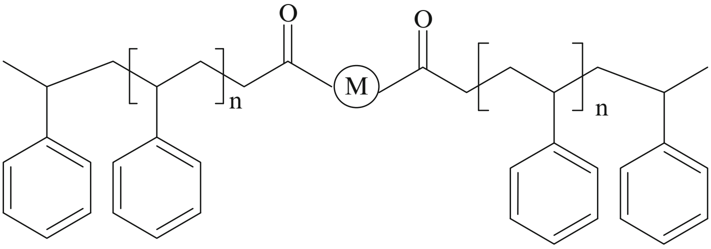
Wong et al. [260] reported that they prepared a soluble rigid-rod organometallic polymer containing electron-donating and electron-withdrawing *trans*-[-Pt-(tibutylphosphine)$_2$-acetylene-R-acetylene-]$_n$ (where R = bithiazol-ediyl) groups. The polymer was formed by cuprous iodide-catalyzed dehydrohalogenation reaction. The electron-donating and electron-withdrawing properties of the thiazole ring confer solubility to the polymer. This polyacetylene is luminescent with a singlet emission peak at 539 nm and photo-conducting. The glass transition temperature of the polymer is 215° and it shows relatively good thermal stability. The π-conjugation of the ligands extends into and through the metal core and the absorption peaks show a significant red-shift of 17–26 nm compared to the bithienyl counterparts due to the presence of the electron-withdrawing imine nitrogen atoms [260].

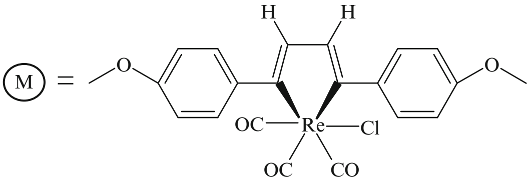
Kimura et al. [259] reported applying organic photochromic compounds to photochemical switching of metal-ion complexation and ionic conduction by combining photochromism with metal-ion binding property of crown ether derivatives. They synthesized vinyl polymers, incorporating a crowned spirobenzopyran moiety at the side chain:



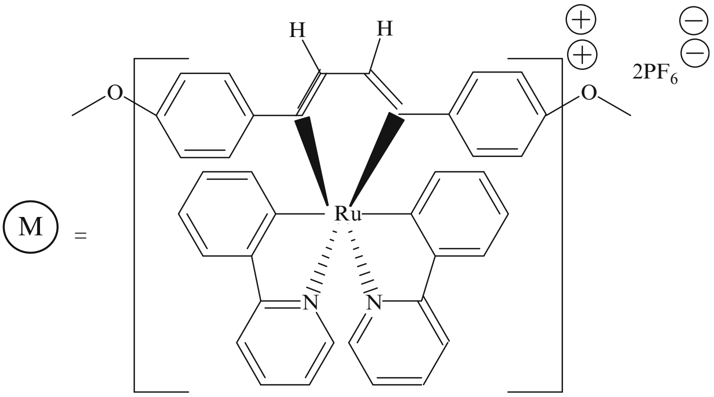
The crowned spiropyran in the electrically neutral form can bind an alkali metal ion with the crown ether moiety. At the same time, the spirobenzopyran portion isomerizes to the corresponding merocyanine form photo-chemically. The zwitterionic merocyanine form of crowned spirobenzopyran moiety brings about a significant change in the metal-ion binding ability. This prompted the authors to apply the compound to photo-responsive ion-conductive materials. They observed that the ion-conductivity was increased by ultraviolet light and decreased by visible light [259].

Chan and coworkers [269] prepared polystyrenes and poly(methyl methacrylate)s that contain metal complex cores:





or



When the polymers are doped with a hole-transporting triphenylamine, an enhancement in photoconductivity in the visible region is observed. This suggests that the metal complexes serve as photosensitizers instead of charge carriers [260]. Chan et al. [260] observed an electric field-dependent charge separation process in these polymers. It is described well by the Onsager's theory of charge germinate recombination. This theory assumes that some fraction of absorbed photons produce bound thermalized electron-hole pairs that either recombine or dissociate under the combined effects of the Coulombic attraction and the electric field. The photo-generation efficiency is given as the product of the quantum yield of thermalized pair formation and the pair dissociation probability:

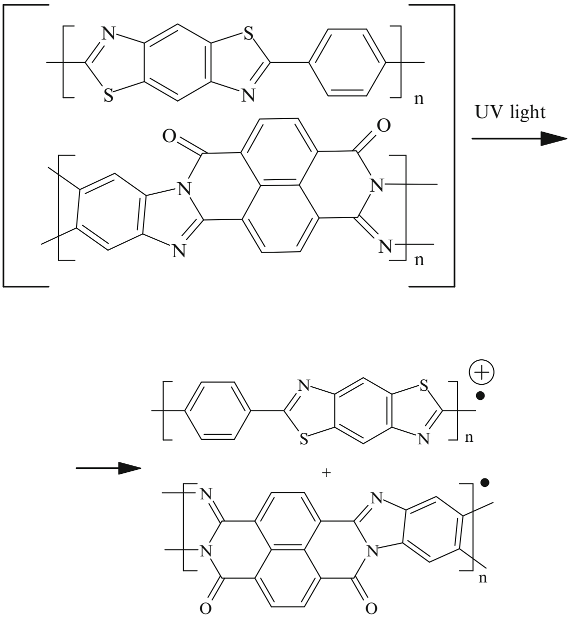
$$\Phi(r_0, E) = \Phi_0 \left[1 - \left(\frac{eEr_0}{kT} \right)^{-1} \sum_{g=0}^{\infty} I_g \left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_r kTr_0} \right) I_g \left(\frac{eEr_0}{kT} \right) \right]$$

where I_g is a recursive formula given by

$$I_{g+1}(x) = I_g(x) - x^{g+1} \exp(-x)/(g+1)$$

where $I_0(x) = 1 - \exp(-x)$, Φ is the primary yield of thermalized bound pairs, r_0 is the initial thermalization separation between the bound charges, ε_r is the relative permeability, and E is the applied electric field strength.

Jenekhe and de Paor [261] reported exciplex formation and photoelectron transfer between several **n-*type*** (***electron accepting***) π-conjugated rigid-rod polymers and donor triarylamine molecules. In particular, they reported an investigation of an **n-*type*** conjugated polymer poly(benzimido azobenzophenanthroline ladder) [132]. No evidence was observed by them of a ground state charge transfer or any strong interactions between the conjugated polymer pairs. Transient absorption spectra of a blend of thin films in the 420–730 nm region were obtained at various time delays following photoexcitation at 532 nm. Dramatically enhanced photo-induced bleaching in the 430–480 nm region was observed. Jenekhe and de Paor propose that they observed enhanced photo-bleaching in the blends and that it is a consequence of photo-induced electron transfer [261]. The electron transfer was illustrated as follows:

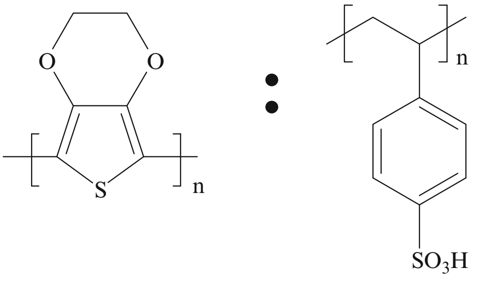


Molecular materials, such as 2-(2-hydroxyphenyl)benzoxazole and 2-(2-hydroxyphenyl)-benzothiazole, which contain intramolecular hydrogen bonds are known to undergo excited state (charge transfer) intramolecular proton transfer upon photo-excitation.

10.8 Polymer-Based Solar Cells

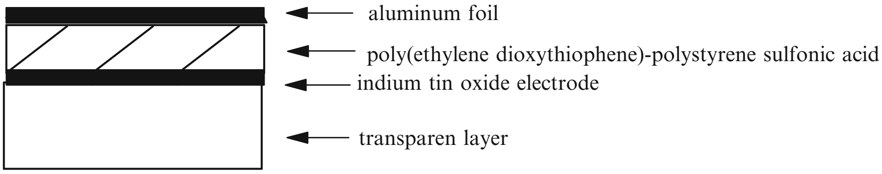
Polymer-based solar cells, also known as organic photovoltaic cells, have been around since the 1990s. But their performance, and their efficiency by end of 2010, to convert light to electricity, after much research, has reached only approximately 8%. This is not good enough to compete with inorganic solar cells, like those based on cadmium teluride, that convert 10–15% of light to electricity. This single digit value of organic solar cells pales even further when compared with some highly specialized, high-priced state-of-the-art inorganic devices with conversion efficiencies topping 40%. The promise of low-cost organic solar cells, however, has encouraged intense research in many laboratories in efforts to improve the efficiency. Such research usually focuses on solution-processable organic polymers that can be converted to semiconductors [262]. The polymers used are regarded as intrinsic wide band gap semiconductors, where the band gaps are above 1.4 eV. This can be compared to insulators, where the band gaps are below 3 eV. Doping of the film forming materials is done to introduce extrinsic charge carriers and convert them into organic semiconductors. Such charge carriers, as explained in Sect. 10.2, can be positive, p-type, or negative, n-type.

Originally, a donor-acceptor bilayer device of two films was used as an n–p junction in solar cells. Thus, they were fabricated as sandwich structures. An example would be one where a transparent substrate is first coated with a conductor, like indium-tin oxide. A conducting polymer like, poly (ethylene dioxythiphene), doped with polystyrene-sulfonic acid, would then be applied from and aqueous solution. The indium-tin oxide acts as an electrode for hole injection or extraction. The polymer is then covered with a conductor, an aluminum foil. The doped polymer can be illustrated as follows:



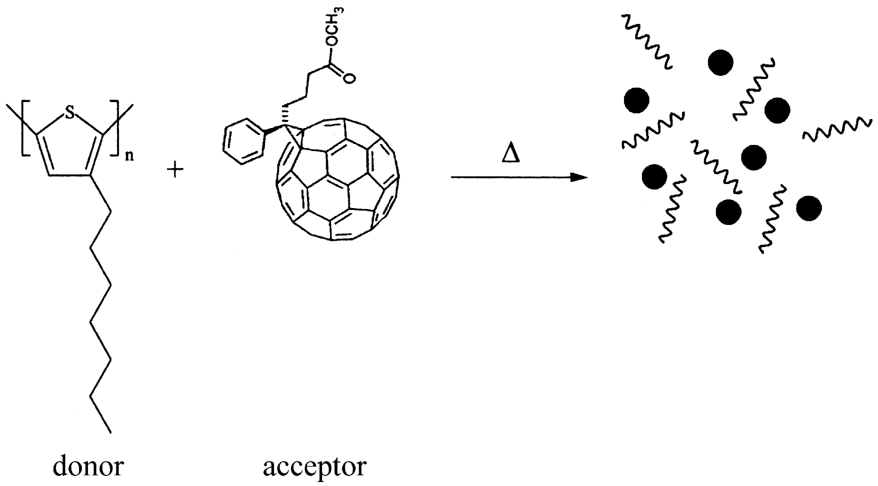
semi conducting polymer doping material

The construction of the above-described solar cell can be illustrated as follows:



The donor material, containing a chromophore, absorbs the light energy and generates excitons. Excitons are high-energy couples where the energetic electrons are bound to positively charged electron vacancies or holes. To produce electric current, the electron-hole pairs must migrate to the interface between the electron donor and electron acceptor materials. Upon reaching the interface, the electron-hole pairs splits into separate mobile charges. The charges then diffuse to their respective electrodes. The electrons are transported by the electron-accepting material to the cathode and the holes by the hole-accepting material (electron donor) to the anode. To put it in other words, the Coulomb-correlated electron-hole pair, the excitons, diffuse to the donor-acceptor interface where exciton dissociation occurs via an electron-transfer process to the n-type layer. With the aid of an internal electric field, the n-type layer then carriers the electrons in the opposite direction. The electric field in turn generates the photocurrent and the photo voltage. Such devices are known as **planar heterojunction** cells. Such an arrangement, however, is not very efficient, because the excitons can decay back to the ground level before they diffuse into to the n-type layer. To overcome the difficulty, the concept of a **bulk heterojunction** was introduced [263]. By blending donor and acceptor materials together an interpenetrating bicontinuous network of junctions, large donor-acceptor interfacial areas can be achieved. This results in an enhanced quantum efficiency of charge separation and in efficient charge collection. Gaudiana [264] likened the morphology of a bulk heterojunction active layer to a sponge. The solid part represents the nano-sized interconnected bits of acceptors. The polymer is represented by the holes that are intimately connected to other holes throughout the sponge and never far from a solid region. Blending the phases on that scale, in effect, distributes small regions of interface throughout the photoactive layer. As a result, excitons need only to diffuse only a short distance before quickly reaching a donor–acceptor interface where they can dissociate into separate charges.

An advancement in efficiency of polymeric solar cells, from 3 to 5%, came in 2009 when it was observed that promising efficient charge transfer materials can be prepared from combinations of poly (alkyl-thiophenes) donors with 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullere acceptors [265]. Mild heating disperses the acceptor molecules among the donor molecules:



This led to exploration of many other combinations of various other polymers with different derivatives of fullerine and with various chromophores. In an attempt to lower highest occupied molecular orbitals (HMO) of the polymer with stronger electron-withdrawing groups, new polymers were developed. The results were summarized in a review [265].

As a result of the research, several research groups reported attaining 5% efficiencies with the combinations of poly(3-hexyl thiophene) with 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullere. Numerous other conducting polymers including copolymers containing fluorene, carbazole, cyclopentadithiophene were investigated.

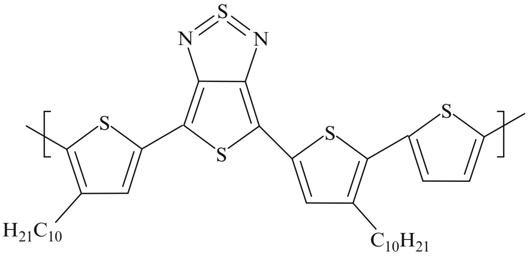
The efficiency of organic solar cells is usually defined as:

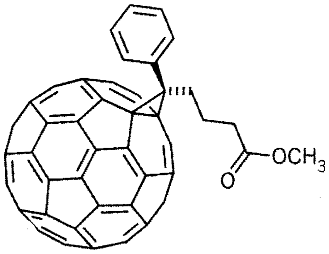
$$\eta = (J_{\mathrm{sc}} V_{\mathrm{oc}} \mathrm{FF})/P_{\mathrm{in}}$$

where P_{in} is the input energy of solar radiation. The output short circuit current density is J_{sc} and V_{oc} is the open circuit voltage. FF is the fill factor. Much of the research effort to date has been based on attempts to increase V_{oc}. This is based on empirical correlation between the magnitude of the open circuit voltage and the difference in energies between HMO of the donor and LUMO of the acceptor. It is expected that by lowering the HMO of the donor, V_{oc} can be increased [266].

To achieve this goal, two research teams headed by Yu and by Yang tested a series of copolymers prepared by reacting a benzodithiophene derivative with various thienothiophenes. The aim was to lower the polymers' HMO by attaching successively stronger electron-withdrawing groups to the polymer backbone. The result was that by replacing an alkoxy group that was adjacent to a carbonyl group with an alkyl chain at the same position, the group lowered the HOMO level by roughly 0.1 eV. They lowered the level by another 0.1 eV by adding a fluorine atom. Solar cells prepared with this polymer were found to be 6.8% efficient [267]. Subsequently, Yu et al. reported slightly improved conversion efficiency of over 7% [268].

It is interesting that at the time of the publication of the review, it was reported in *Chem. and Eng News* [269] that Heeger and Gong developed a broad spectrum donor acceptor combination that can detect photons throughout the whole light spectrum, from the ultra-violet to the infra-red. The combination of the two materials can be illustrated as follows:



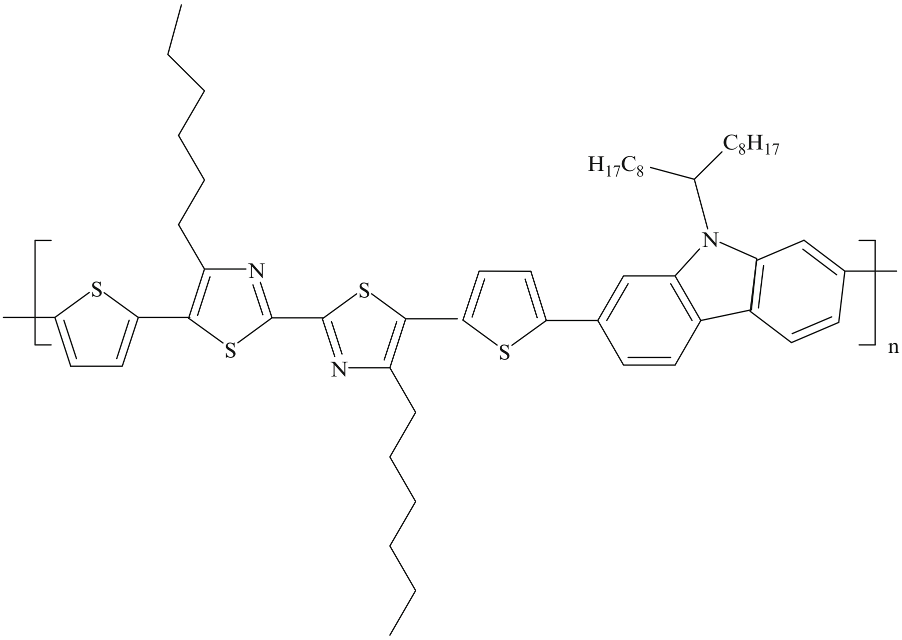


According to a subsequent write up in *Chem. and Eng. News* [270], a private laboratory called "Solamer" claimed, without disclosing details, to have achieved efficiency of 8.13%. They also stated that they hope to achieve efficiency of 10% by end of 2011.

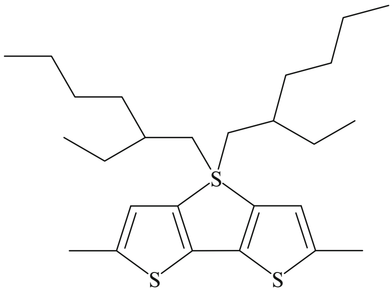
Syntheses of various polymers for solar cells were also reviewed by Cheng et al. [271] where they point out that there is a need to develop better p-type materials that have good film properties and act as very efficient chromophores, with good hole mobility and suitable molecular orbitals levels. They also point out that magnitude of the band gap and the energy positions of the HOMO and LUMO energy levels are the most important characteristics for determining the optical and electrical properties of a given conjugated polymer. These, of course, will in turn greatly influence the ultimate photovoltaic performance and conversion of light energy to electrical energy. The wavelength of the maximum photon flux density of the solar spectrum is located at approximately 700 nm, which corresponds to a low energy of 1.77 eV. The absorption spectrum of a conjugated polymer should cover both the red and near-infra-red ranges to match the greater part of the terrestrial solar spectrum and absorb the maximum photon flux. Thus, it is highly desirable to develop conjugated polymers with broader absorptions through narrowing their optical band gap. At the same time, these materials must efficiently absorb light. The overall high extinction coefficients of the polymers are also of critical importance.

Following are presented some of the published results from recent and current research, to illustrate the bulk of the effort in the field. The examples are chosen at random and there is no implication that these are the best ones published to date.

Li and coworkers [272] reported synthesis and photovoltaic properties of three donor-acceptor copolymers containing bithiazole acceptor. One of them was illustrated as follows:

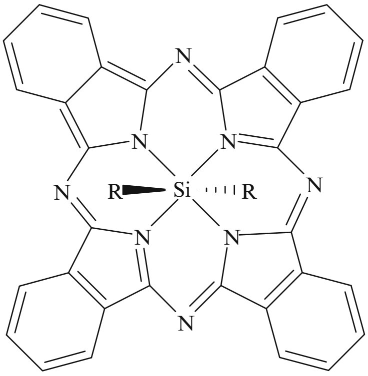


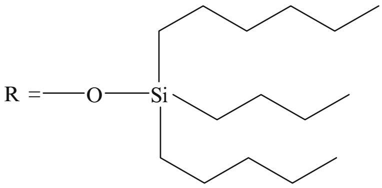
The other two copolymers were similar. The copolymer that yielded the best results had the carbazole replaced with the following molecule:



The results indicate that donor units of carbazole influence the band gaps, electronic energy levels, and photovoltaic levels. The hole mobility was measured at 3.07 × 10^{-4} cm^2/V s.

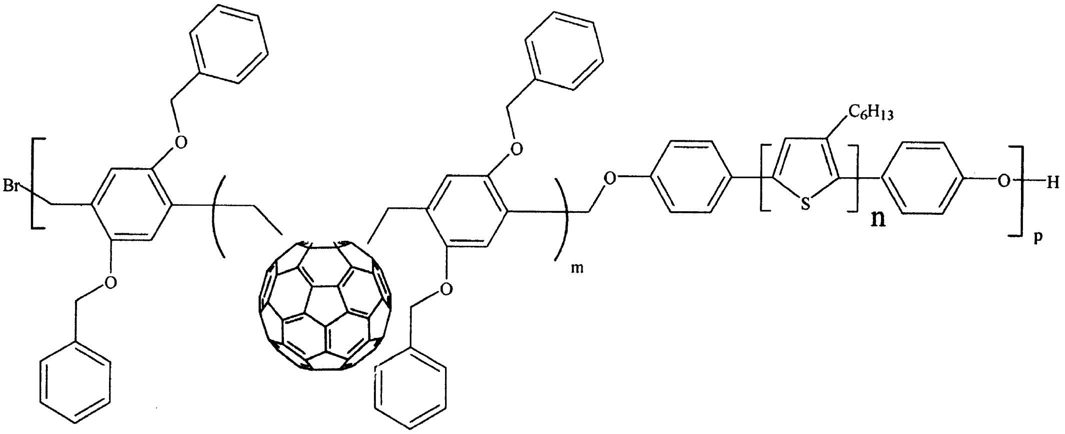
Honda et al. [273] reported injecting a photosensitizer dye into a bulk heterojunction solar cell, based on regioregular poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullere. The dye photosensitizer was illustrated as follows:



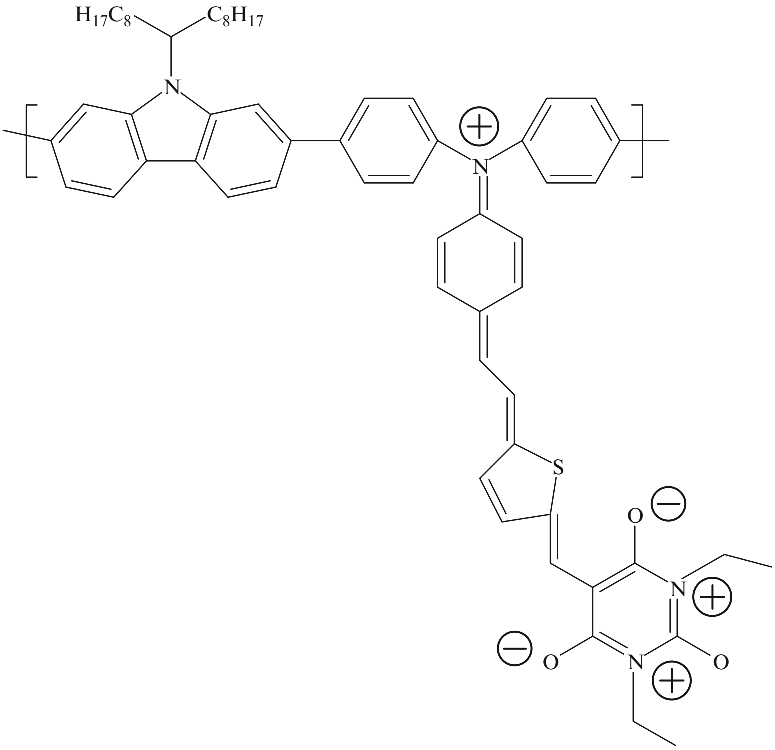


They reported that injection of the dye resulted in an increase in the photocurrent.

Hiorns et al. [274] reported preparation of a block copolymer that incorporated fullerene molecules into the backbone of the polymer. They observed a band gap of 2.3 and 2.2 eV for the block copolymer:

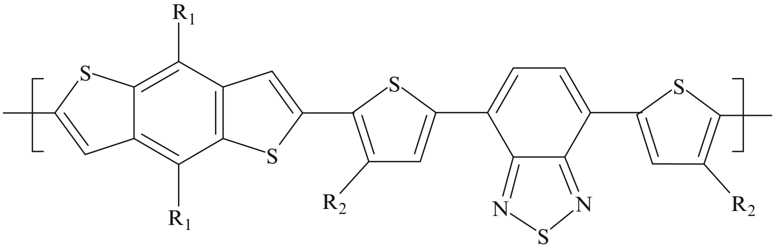


Li and coworkers [275] reported syntheses of four alternating copolymers of carbazole and triphenylamine with conjugated side chain acceptor groups:



The four copolymers that were synthesized contained different acceptor end groups, aldehyde, monocyano, dicyano, and 1,3-diethyl-2-thiobarbituric acid. Through changing the acceptor groups, the electronic properties and energy levels of the copolymers were effectively tuned. Their results indicate that it is an effective approach to tuning the bandgaps in conjugated polymers. The polymers were used as donors in polymer solar cells. They reported, however, conversion efficiency of only 2.76%.

You and coworkers [276] reported syntheses of two low-band gap polymers based on benzo(1,2-*b*:4,5-*b*)dithiophene:

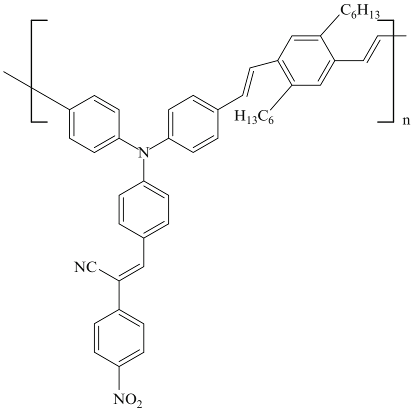


where R$_1$ = 3-butylnonyl and R$_2$ = nonyl and in the send polymer, R$_1$ = 3-hexylundecyl and R$_2$ = hydrogen.

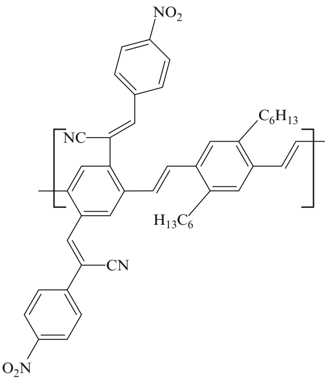
Both polymers were reported to have performed well in preliminary bulk heterojunction solar cells, reaching power conversion efficiency greater than 4%.

Jenekhe, Watson, and coworkers [277] reported synthesizing three new donor-acceptor conjugated polymers incorporating thieno[3,4-*c*]pyrrole-4,6-dione acceptor and dialkoxybithiophene or cyclopentadithiophene donor units. The thieno[3,4-*c*]pyrrole-4,6-dione acceptor containing materials were studied in bulk heterojunction solar cells and organic field-effect transistors. The polymers had optical band gaps of 1.50–1.70 eV. The highly electron-rich character of dialkoxybithiophene in these polymers, however, destabilizes their HMO and significantly affects the photovoltaic efficiency with power conversion efficiencies below 1.5%. On the other hand, cyclopentadithiophene copolymers achieved a better power conversation efficiency greater than 3%.

Sharma and coworkers [278] reported synthesis of two low-band gap copolymers. One consists of alternating dihexyloxyphenylene and α-[4-(diphenylamino)phenyl methylene]-4-nitrobenzene acetonitrile. The other one consists of alternating dihexyloxyphenylene and α,α′-[(1,4-phenylene) dimethylidyne]bis(-4-nitrobenzene acetonitrile):



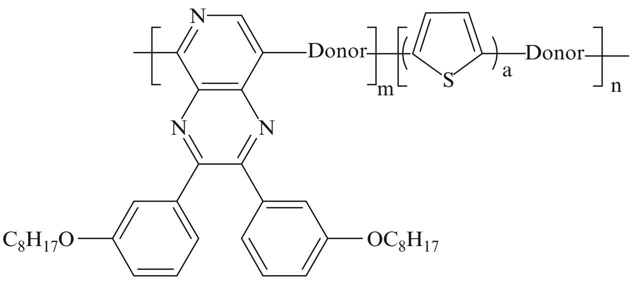
polymer 1

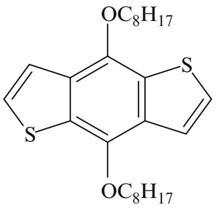


polymer 2

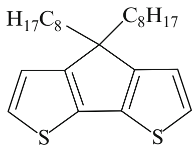
They reported that these copolymers showed broad absorption curves with long-wavelength absorption maximum around 620 nm and optical band of 1.68 and 1.64 eV for both polymers. Both polymers were studied for photovoltaic response in bulk heterojunction solar cells. They observed an overall power conversion efficiency of 3.15 and 2.60% for the cast polymers. Further improvement led up to 4.06 and 3.35% for the devices based on thermally annealed materials.

Wei and coworkers [279] used Stille polycondensation to prepare a series of low-band gap copolymers, by conjugating the electron-accepting pyrido[3,4-*b*]pyrazine moieties with electron rich benzo[1,2-*b*:3,4-*b*]di thiophene or cyclopentadithiophene units. All resulting polymers exhibited excellent thermal stability and sufficient energy offsets for efficient charge transfer and dissociation. The band gaps of the polymers could be tuned in the range 1.46–1.60 eV by using the two different donors, which have different electron-donating abilities. The three-component copolymers, incorporating the thiophene and bithiophene segments, respectively, absorbed broadly, covering the solar spectrum from 350 to 800 nm. The best device performance resulted in power conversion efficiency of 3.15%.The polymeric materials were illustrated as follows:



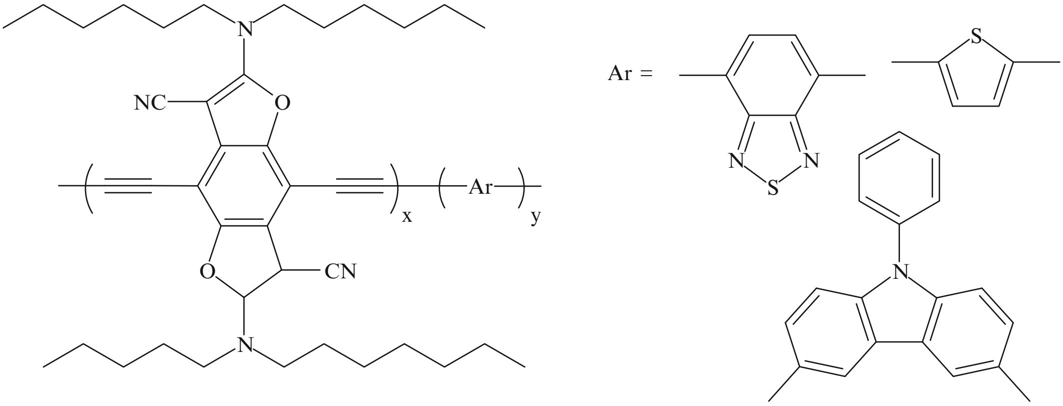


donor



donor

Liu et al. [280] synthesis and evaluation of n-conjugated copolymers were based on a soluble electro active benzo[1,2-*b*:4,5-*b*]difuran chromophore. The comonomer units consisted of thiophene/ benzo [*c*][1,2,5] thiadiazole/9-phenylcarbazole. These copolymers cover broad absorption ranges from 250 to 700 nm with narrow optical band gaps of 1.71–2.01 eV. The band gaps and the molecular electronic energy levels can be tuned by copolymerizing the benzo[1,2-*b*:4,5-*b*]difuran core with different n-conjugated electron-donating or withdrawing units in different ratios.



Bulk heterojunction solar cell devices were fabricated by Liu and coworkers, using the copolymers as the electron donor and ([6,6′]-phenyl-C_{61}-butyric acid methyl ester) as the electron acceptor. The preliminary research has revealed power conversion efficiencies of 0.17–0.59% under AM 1.5 illumination (100 mW/cm^2).

Thompson and coworkers [281] point out that despite the correlation between the absorption and J_{SC}, most polymers used in currently high-performing solar cells have limited absorption breadths and rely largely on band gaps. As a result, there is a heavy reliance on fullerenes (especially on $PC_{61}BM$, 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullere) to absorb photons in the short wavelength range and considerable absorption losses in the longer wavelengths. Although fullerenes absorb in the short wavelength region and are thus complementary to many polymers, they point to the evidence that 60% of excitons formed in the $PC_{61}BM$ phase decay before being harvested and do not contribute to J_{SC} [282]. This research group mixed graphene oxide that acts as a surfactant with fullerenes C_{60} and single-walled carbon nanotubes in water, coated a glass slide with the solution, and heated it to reduce the graphene oxide to graphene. They claimed that chips using this photovoltaic layer were much more efficient at converting light into electricity that the organic devices developed with covalent chemistry.

Simultaneous to doing research on polymeric materials, research is also being carried out on improving the construction of solar cells. One strategy is to stack two light-absorbing materials in a tandem cell to harvest greater fraction of the solar spectrum. By inserting gold nanoparticles between the two layers, Yang Yang and coworkers coupled the two tandem cells and demonstrated a considerable boost inefficiency of light conversion to electricity [283].

Review Questions

Section 10.1

1. How are the support materials utilized? Discuss

Section 10.1.1.1

1. Describe the Merrifield resin.
2. What are the two types of cross-linked polystyrenes that are used for support?

3. What is Tentagel? Describe and illustrate?
4. What is Jenda Gel? Explain and illustrate.
5. Describe the general use of cross-linked styrene derivatives for support.

Sections 10.1.1.2–10.1.4

1. Illustrate an isobutylene-based support material.
2. Describe an acrylic material used for support.
3. Describe a polyether-based support resin.
4. Describe a gel for drug release.

Section 10.1.3

1. Describe immobilized enzymes.
2. Describe nonenzyme immobilized catalysts.
3. Describe immobilized reagents.

Section 10.2

1. Discuss polyacetylene.
2. Discuss polypyrrole.
3. Discuss polythiophene and its derivatives.
4. Discuss polyaniline.
5. Discuss poly(phenyl vinylene).

Sections 10.3–10.6

1. Explain what is meant by a photonic polymer.
2. Discuss the nature of light.
3. Discuss interaction of light with organic molecules.
4. What is the energy transfer process?
5. What is an electron transfer process?
6. Describe the charge transfer process in polymers.
7. Describe the antenna effect in polymers.
8. What is a photosensitizer? Give some examples.
9. Discuss photocross-linking of polymers and give some examples.
10. Describe polymers that are designed to harvest sun's energy.
11. Discuss photo-isomerization of polymeric materials.
12. How is photo-isomerization utilized in liquid crystalline alignment?

Section 10.7

1. Explain photo-conductivity in polymers. Give examples, those that are based on carbazole and those that are not based on carbazole.

Section 10.8

1. Describe a planar heterojunction solar cell.
2. Describe a bulk heterojunction solar cell.
3. What is the equation that defines the efficiency of organic solar cells.

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