Chapter 7
Step-Growth Polymerization and Step-Growth Polymers

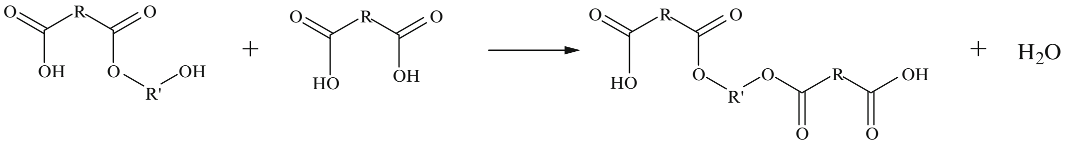
7.1 Mechanism and Kinetics of Step-Growth Polymerization

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*

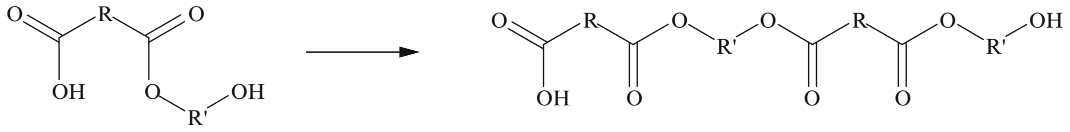
Kinetic considerations are of paramount importance in understanding the mechanism of step-growth polymerization [1]. As stated in Chap. 1, chain-growth polymerizations take place in discreet steps. Each step is a reaction between two functional groups, like, for instance, in a polyesterification reaction, 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:

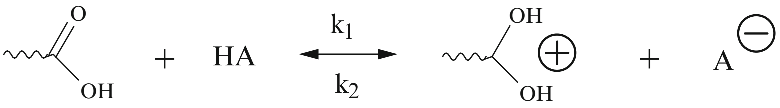


These step condensations continue slowly with the molecular weights of the polymers increasing with each step. In such reactions, the monomeric species disappear early from the reaction mixtures, long before any large molecular weight species develop. In most step-growth polymerizations, on a weight 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].

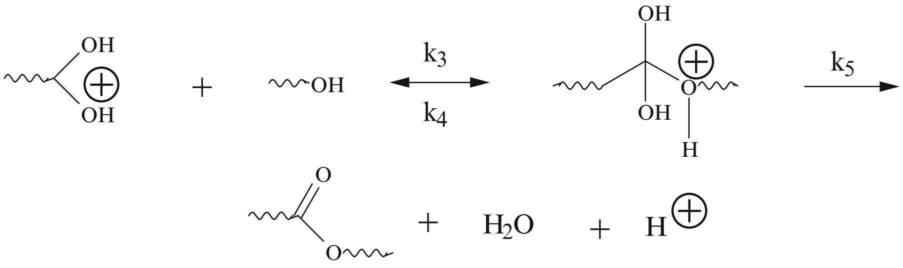
One important characteristic of step-growth polymerizations is that any functional group on any one molecule is capable of reacting with any opposite functional group on any other molecule. Thus, for instance, if it is a reaction of polyesterification, any carboxylic acid group on any one molecule, regardless 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 $[\mathrm{CO_2H}]$, $[\mathrm{OH}]$, 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 $N^{\mathrm{o}}_{\mathrm{A}}$ for A type and $N^{\mathrm{o}}_{\mathrm{B}}$ for B type. These numbers $N^{\mathrm{o}}_{\mathrm{A}}$ and $N^{\mathrm{o}}_{\mathrm{B}}$ 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 $N^{\mathrm{o}}_{\mathrm{B}}$ is slightly larger than $N^{\mathrm{o}}_{\mathrm{A}}$, then we have a *stoichiometric imbalance* in the reaction mixture. This imbalance is designated as r.

$$r=N^{\mathrm{o}}_{\mathrm{A}}/N^{\mathrm{o}}_{\mathrm{B}}$$

(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 $(N^{\mathrm{o}}_{\mathrm{A}}+N^{\mathrm{o}}_{\mathrm{B}})/2$ or $N^{\mathrm{o}}_{\mathrm{A}}(1+(1/r))/2$.

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 $N^{\mathrm{o}}_{\mathrm{A}}(1-p)$. This reaction mixture also contains $N^{\mathrm{o}}_{\mathrm{B}}(1-rp)$ 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 $[N^{\mathrm{o}}_{\mathrm{A}}(1-p)+N^{\mathrm{o}}_{\mathrm{B}}(1-rp)]/2$.

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:

$$\overline{\mathrm{DP}}_n=\frac{N^{\mathrm{o}}_{\mathrm{A}}(1+1/r)/2}{[N^{\mathrm{o}}_{\mathrm{A}}(1-p)+N^{\mathrm{o}}_{\mathrm{B}}(1-rp)]/2}$$

the expression can be reduced (since $r=N^{\mathrm{o}}_{\mathrm{A}}/N^{\mathrm{o}}_{\mathrm{B}}$) 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

$$p = (N_o - N)/N_o$$

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 $N/N_o = 1 - p$. The above expression for N_x can, therefore, be written as:

$$N_x = N_o(1-p)^2 p^{x-1}$$

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:

$$\overline{M}_\mathrm{w} = \sum w_x x M_o$$

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:

$$\overline{M}_\mathrm{w} = \mathrm{M_o}(1-p)^2 \sum x^2 p^{x-1}$$

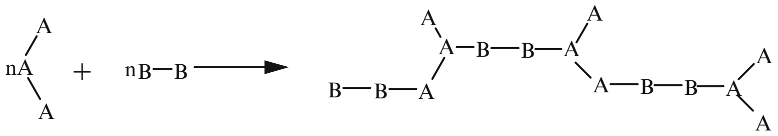
It can be shown that summation, $\sum x^2 p^{x-1} = (1+p)/(1-p)^3$. Based on that, the weight average molecular weight is:

$$\overline{M}_\mathrm{w} = \mathrm{M_o}(1+p)/(1-p)$$

and, the molecular weight distribution is:

$$\overline{M}_w/\overline{M}_n = 1 + p$$

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

$$p = (N_o - N)/N_o$$

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 $2(N_o - N)$. In the modified equation, the number of molecules that were present initially is $N_o f_{ave}$. The equation now becomes:

$$p = \frac{2(N_o - N)}{N_o f_{ave}}$$

N_o/N can be replaced by DP and the above expression becomes:

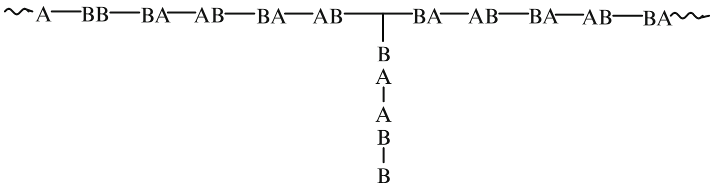
$$\bar{p} = 2/f_{ave} - 2/\mathrm{DP}f_{ave}$$

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:

$$p_c = 2/f_{ave}$$

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:

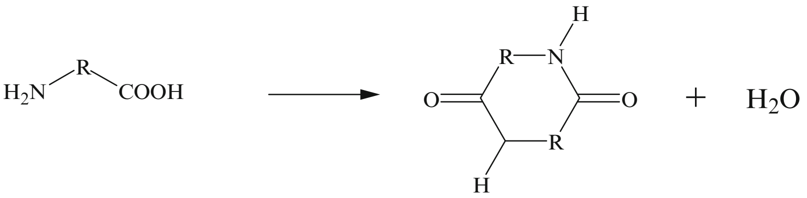


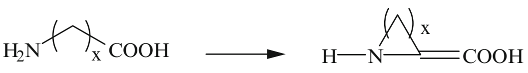
Statistical methods were developed for prediction of gelation [7]. These actually predict gelation at a lower level than does the Carothers equation shown above. As an example, we can use a reaction of three monomers, A, B, and C. We further assume that the functionality of two monomers, f_A and f_B, is equal to two, while that of f_C is greater than two. The critical reaction conversion can then be written as:

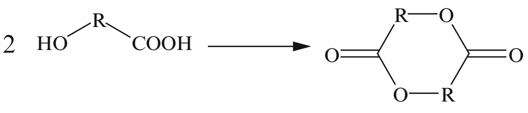
$$p_c = 1/[r + rp(f_C - 2)]^{1/2}$$

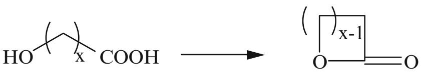
7.1.3 Ring Formation in Step-Growth Polymerizations

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:







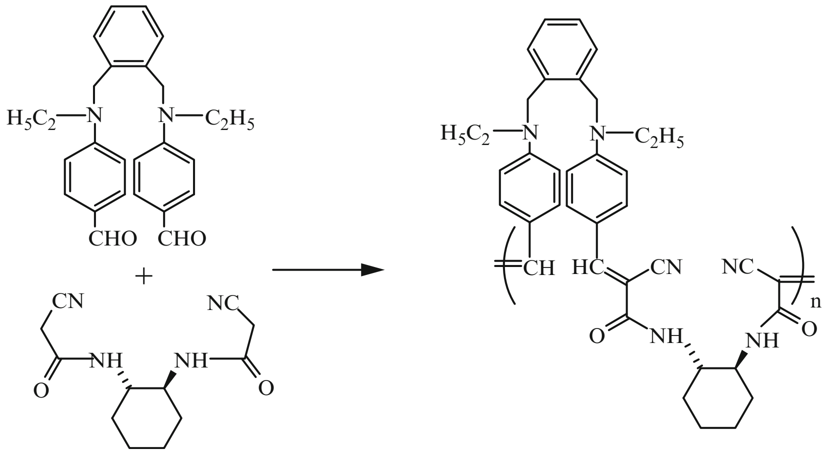


Similarly, dicarboxylic acids can cyclize into anhydrides.

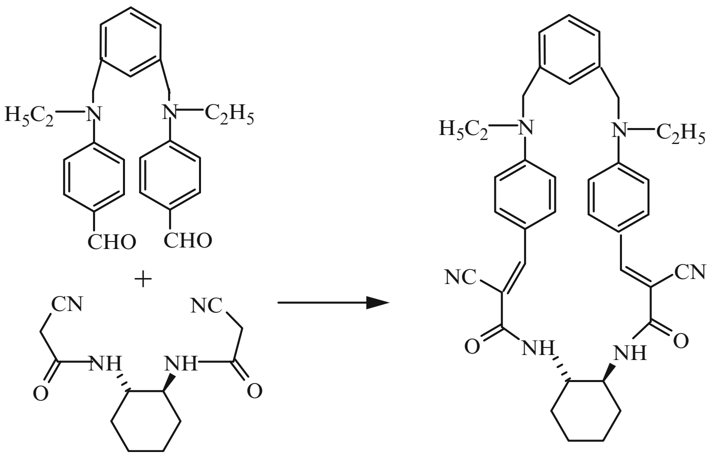
Whether ring formation is likely to take place or not depends upon the size of the ring that can form. If cyclization results in rings with strained bond angles or repulsions due to crowding, the probability of their formation is low. So, small rings, with less than five members, do not form readily. 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:



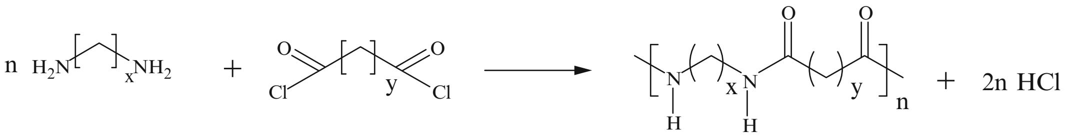
By contrast, the *meta* isomer forms only ring structures instead [242]:



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

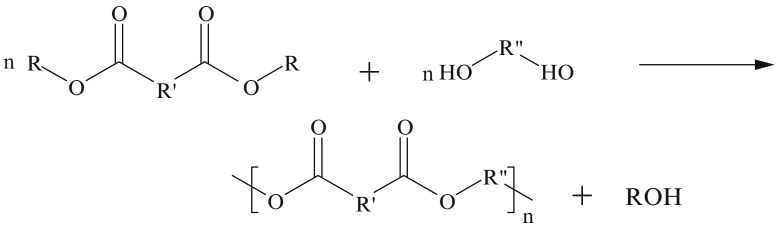
The saturated polyesters that find commercial applications are mostly linear except for some specially prepared branched polymers used in the preparation of polyurethanes. The linear polyesters became commercially important materials early in this century and still find many uses in industry. The earliest 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

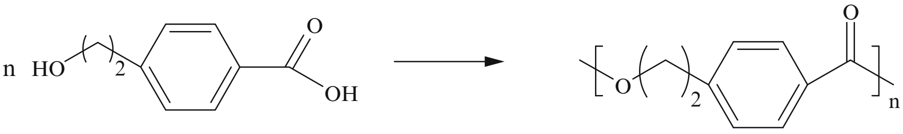
The synthetic methods that are in general use for the preparations of linear polyesters [15] can be summarized as follows:

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]:

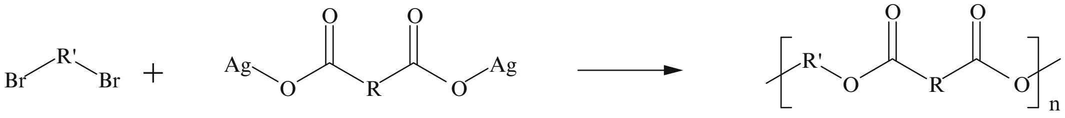


The above transesterification reaction is practical for use with high melting and poorly soluble dicarboxylic acids. In addition, less energy is needed to remove alcohol than water.

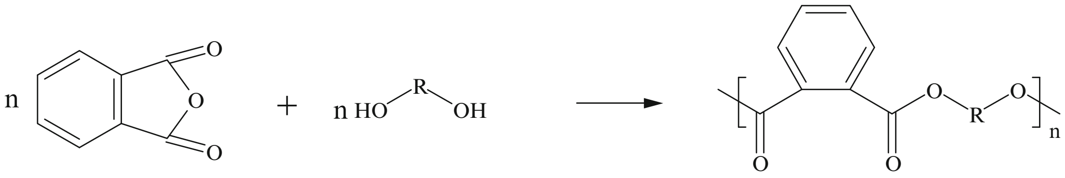
3. Hydroxy acids, like *p*-hydroxyethoxybezoic acid or ω-hydroxydecanoic acid, are capable of self-condensation to form polyesters [10]:



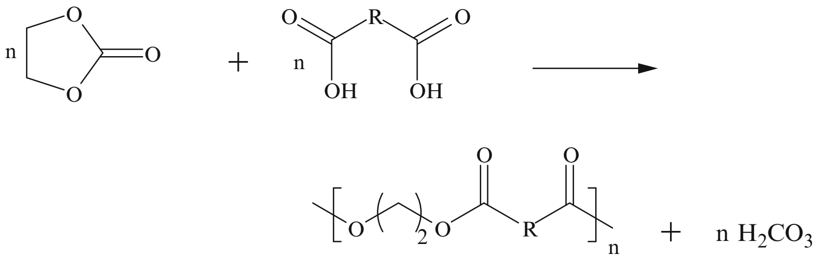
4. Although not practical commercially, polyesters can be prepared in the laboratory by reacting aliphatic dibromides with silver salts of dibasic acids [6]:



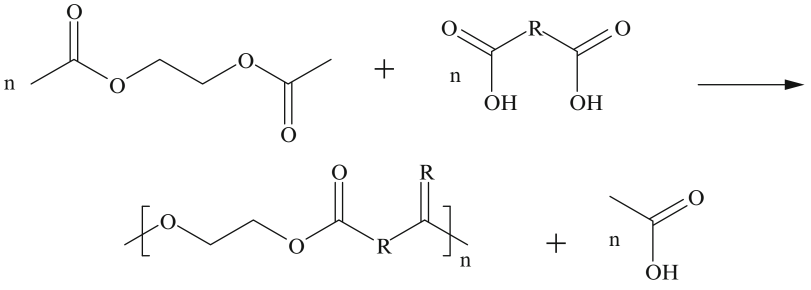
5. Polyesters also form from reactions of dicarboxylic acid anhydrides with glycols [10]:



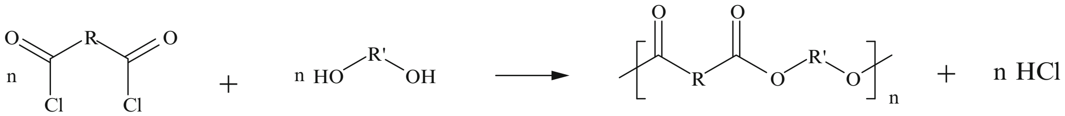
6. Glycol carbonates undergo ester interchange reactions with dibasic acids [11]:



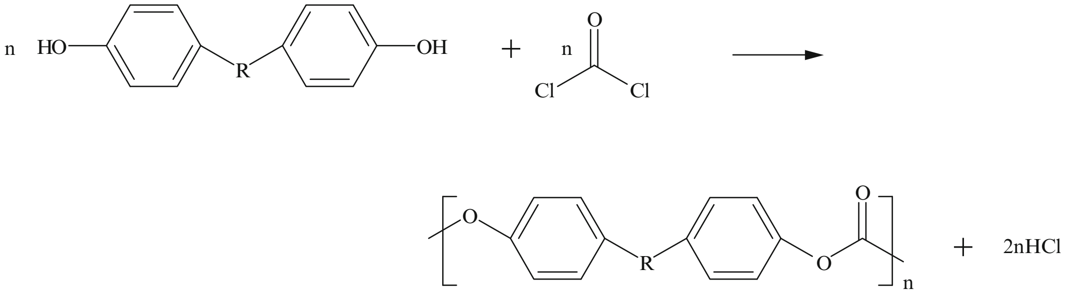
7. Ester interchange reactions between glycol acetates [12, 13] or diphenol diacetates [12] and dicarboxylic acids:



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]:

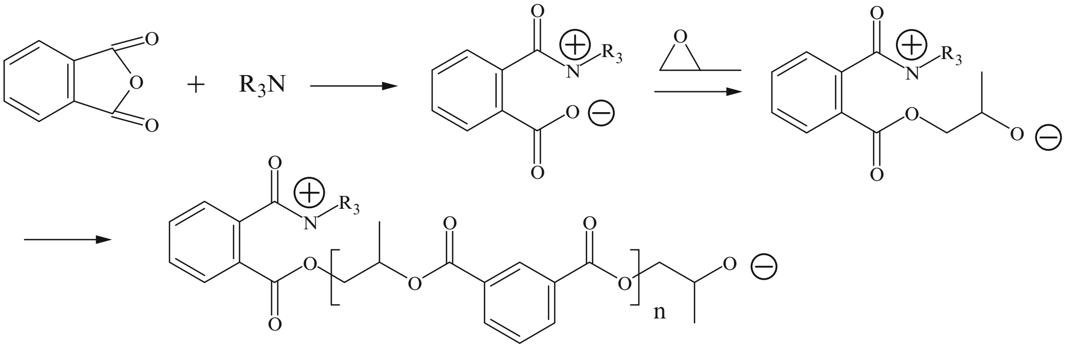


When in place of dicarboxylic acid chlorides phosgene is used, polycarbonates form:

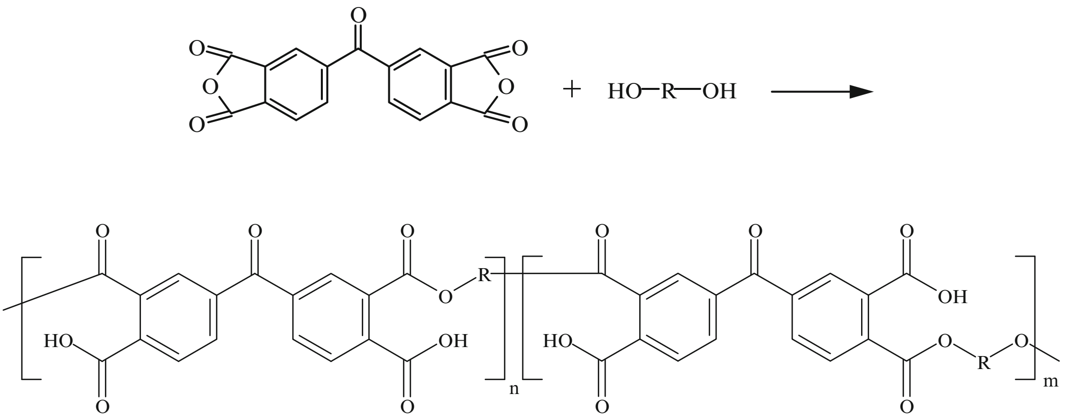


9. Polyesters also form in ring opening polymerizations of lactones. This is discussed in Chap. 5.

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:

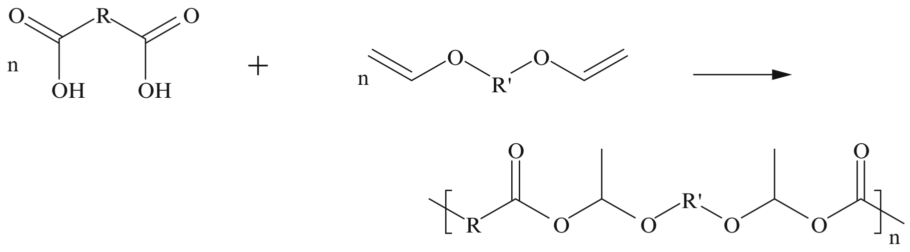


This produces a low molecular weight polyester. A modification is a reaction of a dianhydride with a glycol:

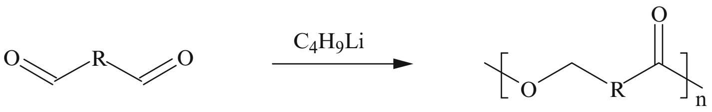


In all esterification reactions, catalysts increase the speed of condensations. Such catalysts are either acids or bases.

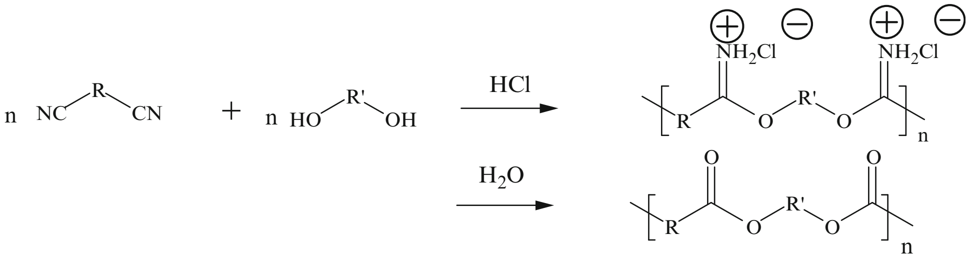
Beyond the above, there are many other polyester syntheses that can be found in the literature, but are not in common use. For instance, polyesters form from additions of carboxylic acids to divinyl ethers [29]:



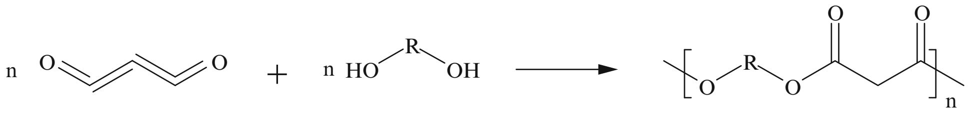
Polyesters also form by the Tischenko reaction from dialdehydes [26, 27]. The intramolecular hydride transfer reaction is typically catalyzed by bases:



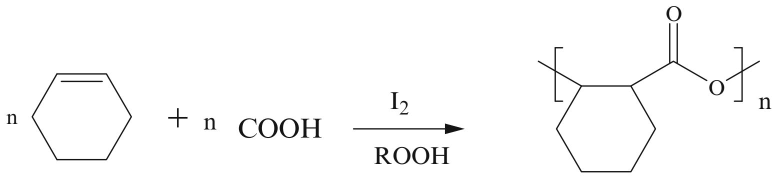
Another reported procedure consists of condensations of nitriles with glycols. The resultant poly (iminoether hydroxide)s hydrolyze to polyesters [32].



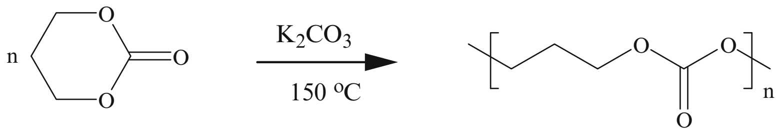
Carbon suboxide condenses with glycols to form polyesters [26]:



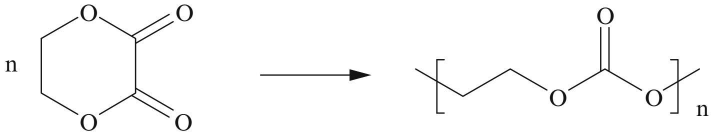
Also, an alternating free-radical addition copolymerization of cyclohexene and formic acid, perhaps via charge transfer, donor–acceptor complexes, yields polyesters [30]:



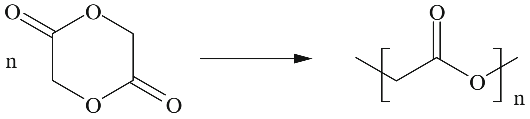
Cyclic carbonates, oxalates, and glycolates polymerize by ring opening polymerizations to yield polyesters. An example is a conversion of a cyclic carbonate into a low molecular weight polymer (about 4,000) [39, 40]:



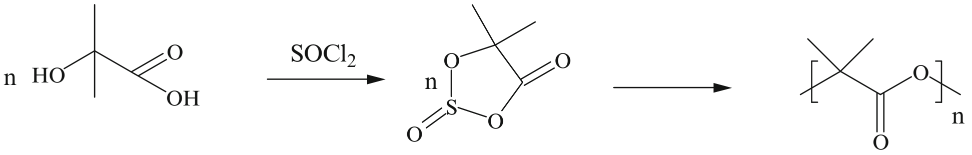
Another example is a ring opening polymerization of an oxalate [39]. Again, only low molecular weight polymers result:



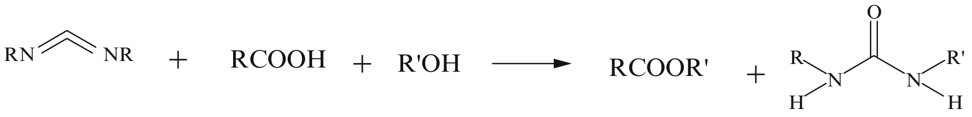
Lactides, on the other hand, when subjected to ring opening polymerization with Lewis acids yield high molecular weight polymers [41]:



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:

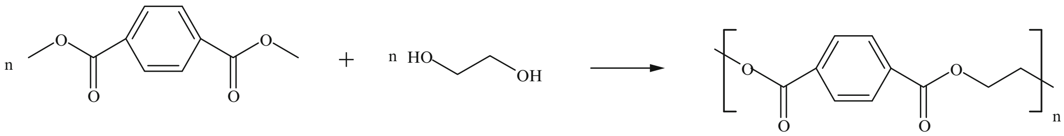


The reaction is useful in preparations of isoregic ordered chains with translational polar symmetry. It can also be applied in polymerizations of functional or chiral monomers.

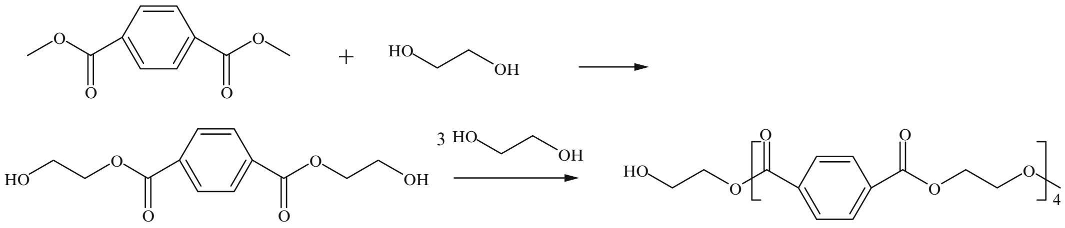
7.2.1.2 Commercial Linear Saturated Polyesters

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.

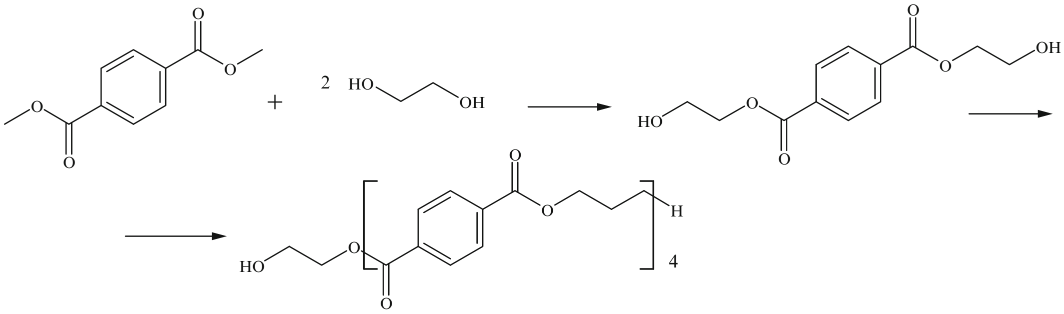
Among the high molecular weight aliphatic-aromatic polyesters, the highest commercial volume material is poly(ethylene terephthalate). Most of it is prepared from dimethylene terephthalate and ethylene glycol by a transesterification reaction:



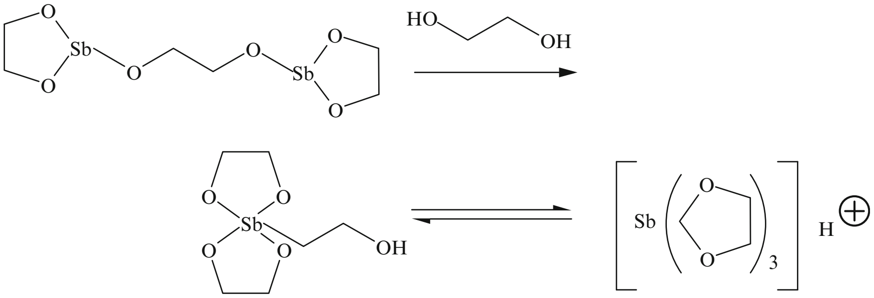
Often the reaction is carried out in two steps. An excess of two moles of ethylene glycol is used and the first stage of the reaction is carried out at 150–210°C to form bis(2-hydroxyethyl)terephthalate, a small amount of an oligomer, and methanol, which is removed:



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:



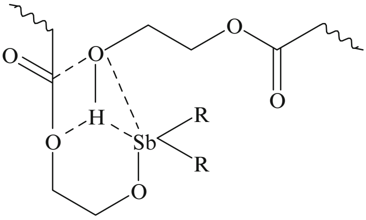
In the process, ethanol forms and is removed. Various metal oxide or acetate catalysts are employed in the first stage. These are antimony, barium, calcium, cobalt, lead, manganese, titanium, or zinc oxides or acetates. Carbonates, alcoholates, and alkanoates can also be used. Based on disclosures in 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]:

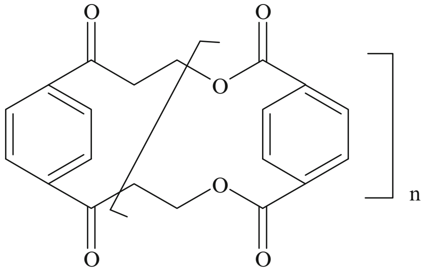
$$5 = 3>2>1 \gg 0$$

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:

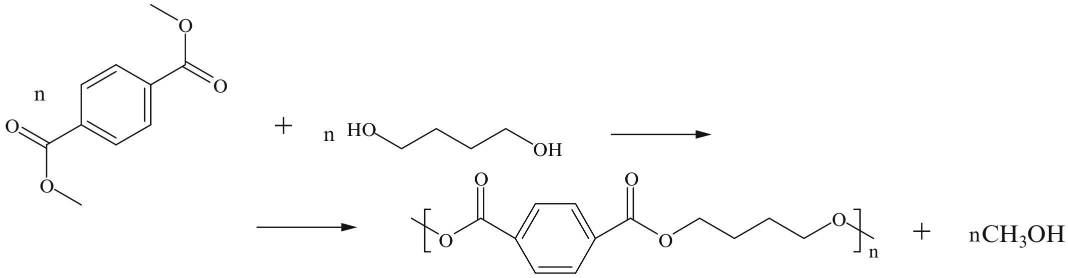


The most important side reaction, however, is formation of diethylene glycol. It becomes included in the polymer as a di(oxyethylene)oxy link. Commercial polymerizations are carried out until molecular weights of about 20,000 are reached, for use in fibers, and higher ones, for use in injection moldings 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).

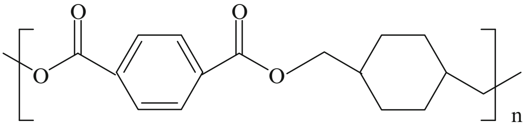
Another commercially important high molecular weight polyester is poly(butylene terephthalate), also called poly(tetramethylene terephthalate). The polymer is prepared by a catalyzed ester interchange of dimethyl terephthalate and 1,4-butane diol:



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.

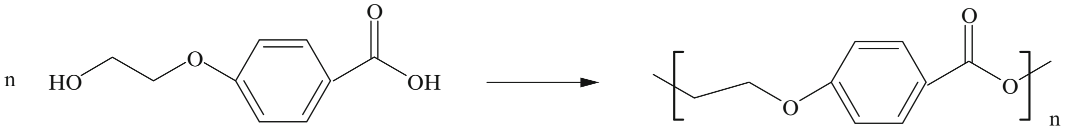
Prolonged heating of the reaction mixture at excessive temperatures results in formation of large proportions of tetrahydrofuran. This is objectionable because it affects the properties of the product. It also results in lower molecular weight polyesters.

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.

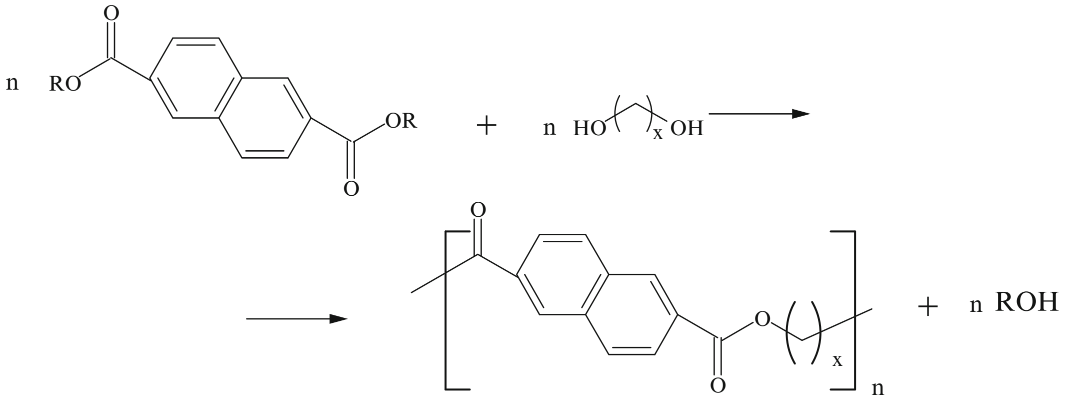
A polyester is being manufactured in Japan from a methyl ester of *p*-2-hydroxyethoxybenzoic acid by transesterification:



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.

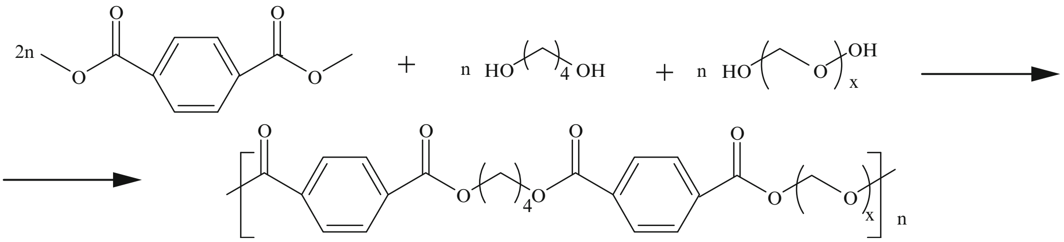


where $x = 2{,}4$

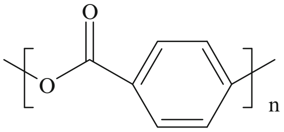
7.2.1.3 Copolyesters

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.

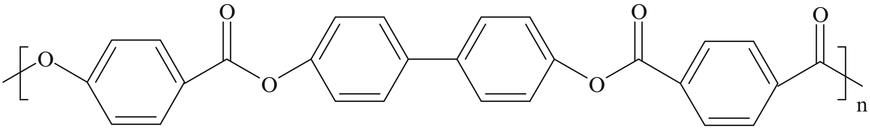
In addition, there are thermoplastic polyester elastomers. These are produced by equilibrium melt transesterification of dimethyl terephthalate, 1,4-butanediol, and a poly(tetramethylene ether) glycol (molecular weight about 1,000). Because equilibrium conditions exist in the melt, the products are random 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:

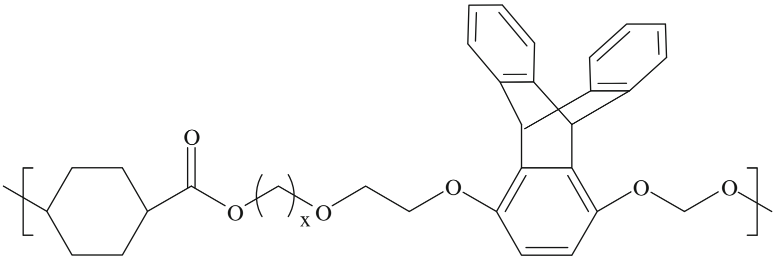


Another one is a copolyester prepared from *p*-hydroxybenzoic acid, *p*,*p*′-biphenol, and terephthalic or isophthalic acids:



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:

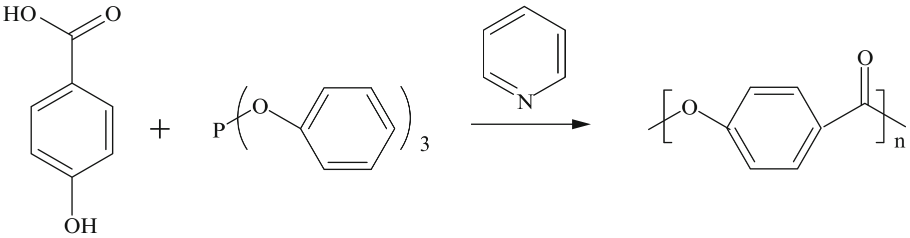


where $x = 2,4$, or 6.

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.

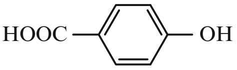
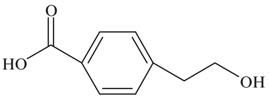
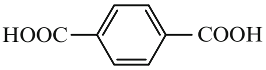
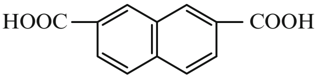
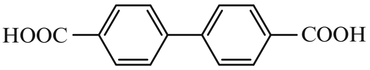
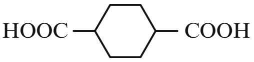
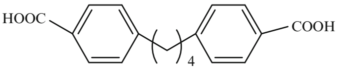
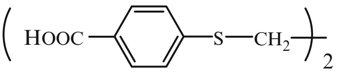
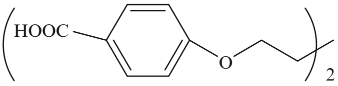
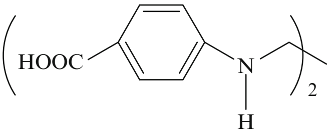
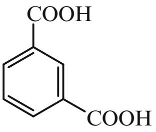
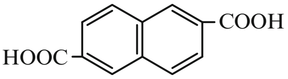
The properties of various polyesters were summarized by Wilfong [15]. Table 7.1 presents T_m and T_g values of some polyesters based on information from Wilfong and other sources in the literature.

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]:



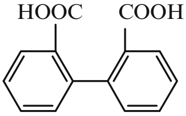
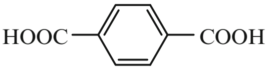
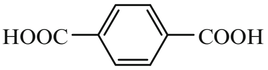
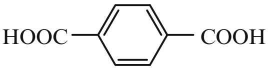
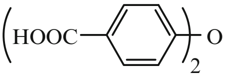
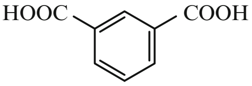
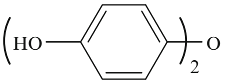
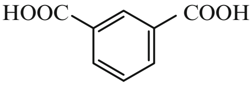
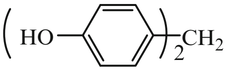
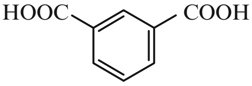
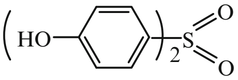
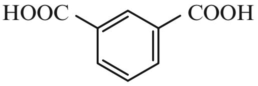
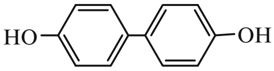
Hexachlorotriphosphatriazine can also be used to attain direct polycondensations of hydroxybenzoic acid [43].

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

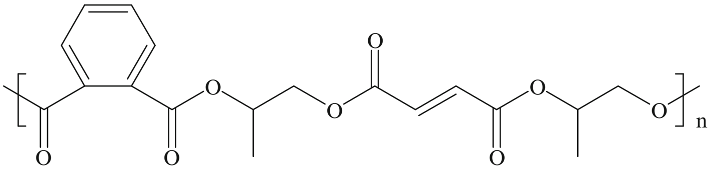
The materials in this group are linear copolyesters. One of the dicarboxylic acids is an aliphatic unsaturated diacid. The unsaturation is introduced into the polymer backbone for the purpose of subsequent cross-linking. Unsaturated polyester technology was developed for use in glass fiber laminates, 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.

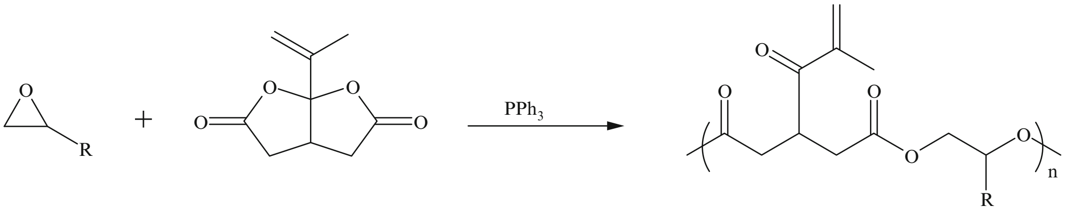
The saturated dicarboxylic acids act as modifiers. While aliphatic dicarboxylic acids can be used, the most common one is *ortho* phthalic acid (added to the reaction mixture as an anhydride). The acid improves compatibility with styrene that is polymerized in the presence of the polyester to form hard, 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:



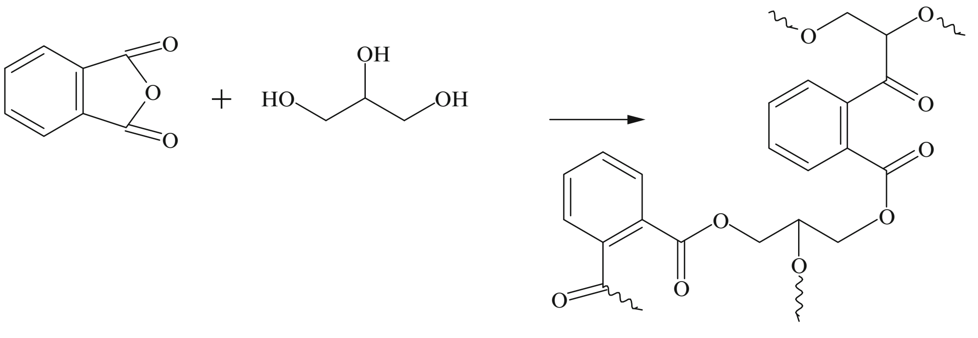
It is interesting that unsaturated polyesters can actually be prepared by anionic alternating copolymerization of an epoxide and bicyclic bis(γ-butyrolactone) bearing an isopropenyl group [34]. The reaction was illustrated as follows:



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***:



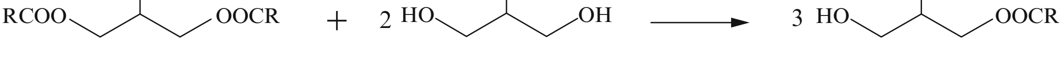
The products from above polyesterifications are brittle materials. They are, therefore, modified with oils, either drying or nondrying. Such oil-modified resins bear the names of ***alkyds***. While glycerol is widely used, other polyhydroxy compounds (polyols) are also utilized. These may be trimethylolpropane, 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.

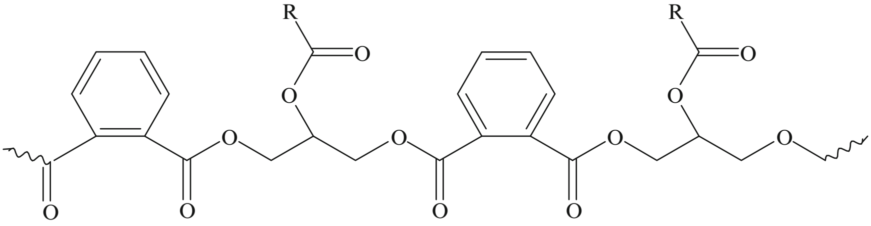
There are two main methods for preparation of alkyd resins. In the first one, called ***fatty acid process***, a free fatty acid is coesterified directly with the dibasic acid and the polyol at 200–240°C. The reaction may be carried out without a solvent by first heating in an inert atmosphere. At the 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.

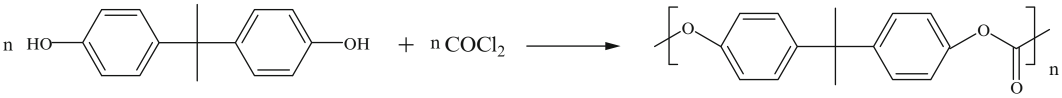
The conditions under which the reaction is carried out and the rate at which the temperature is raised during the condensation affect the molecular weight distribution of the final product. In addition, the monoglyceride content of the original reaction mixture determines the microgel content of the 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.

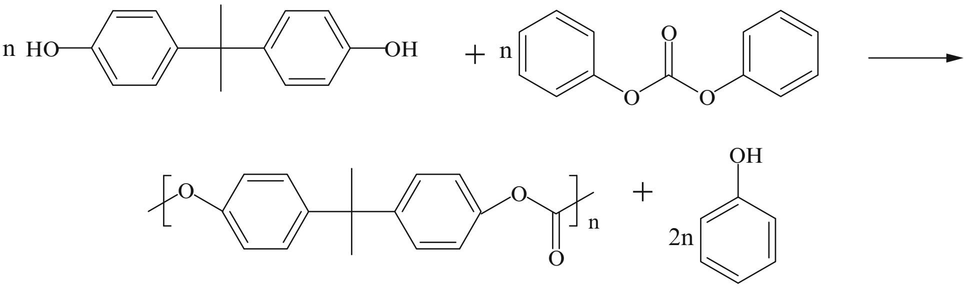
There are two main methods for preparing polycarbonates, one is by a direct reaction of phosgene with the diphenol and the other one by an ester interchange. The direct phosgenation is a form of a Schotten–Baumann reaction that is carried out in the presence of a base:



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.

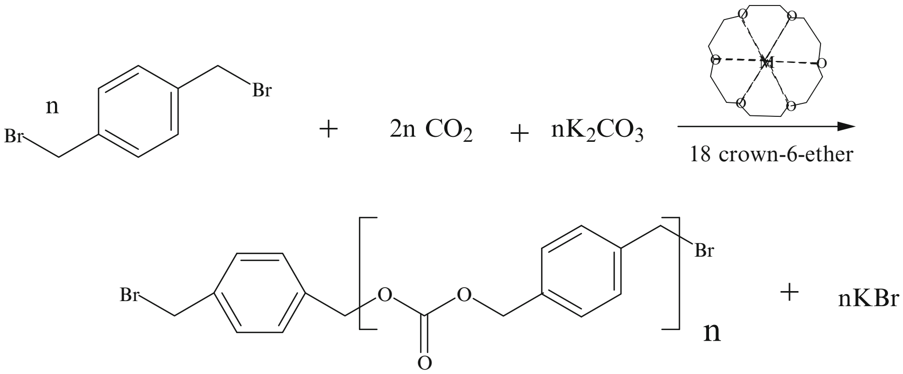
An interfacial polymerization procedure is also employed in direct phosgenation. A caustic solution of the diphenol is dispersed in an organic chlorinated solvent containing small quantities of a tertiary amine. Phosgene is bubbled through the reaction mixture at 25°C. When the reaction is complete, 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:

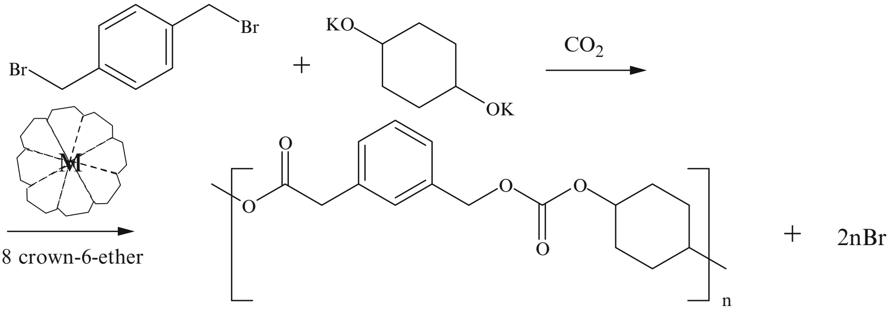


To obtain high molecular weights by this method, almost complete removal of the phenol is required. The reaction is carried out with typical basic catalysts, like lithium hydride, zinc oxide, or antimony oxide under an inert atmosphere. Initial reaction temperature is 150°C. It is raised over 1 h period 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:

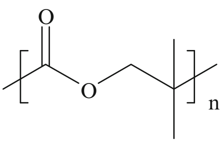
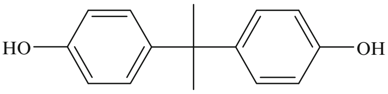
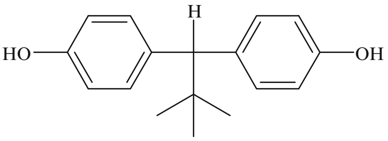
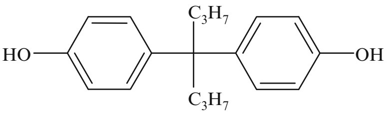
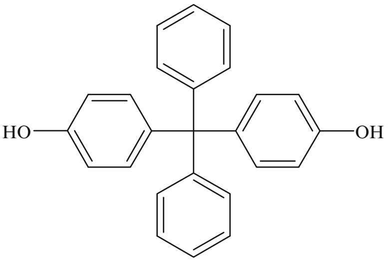
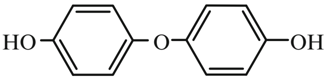
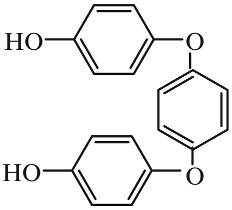
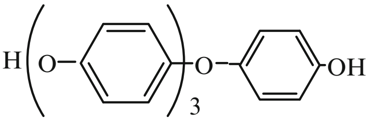
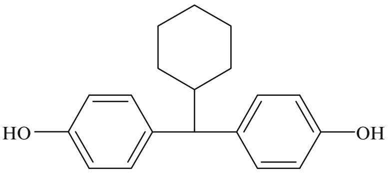
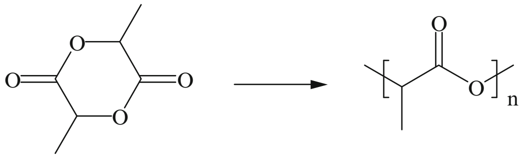


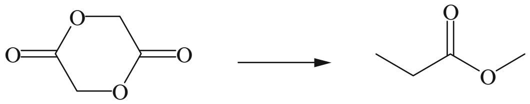
Table 7.2 Melting points of some polycarbonates

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:





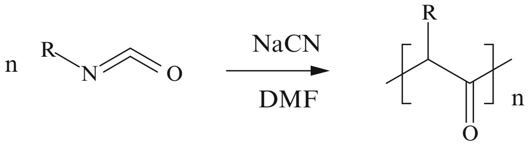
7.3 Polyamides

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.

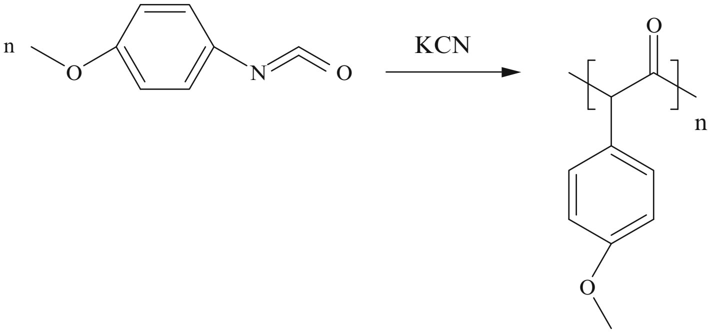
7.3.1 Nylons

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:



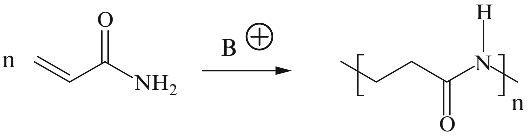
Potassium and sodium cyanide catalyze the reaction. It can be carried out between −20 and −100°C. An example is the following preparation [47]:



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.

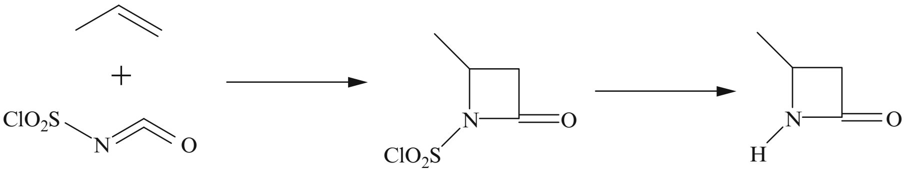
Polymerization of *N*-carboxy-α-amino acid anhydrides results in formations of ***Nylon 2***. This reaction is also discussed in Chap. 5. These polymers are mainly of interest to protein chemists in model studies of naturally occurring poly(α-amino acids).

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]:

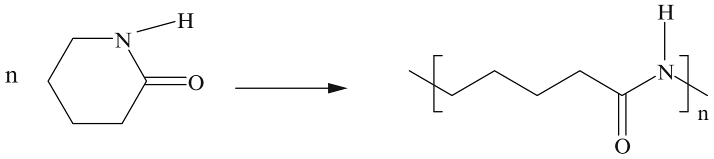


The above shown β-butyrolactam polymerizes readily by anionic mechanism, yielding a very high molecular weight polymer. This lactam preparation reaction is quite general. It can be carried out on propene, 1-butene, 1-hexene, and styrene [50]. Although substituted lactams are harder to polymerize [53], 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.

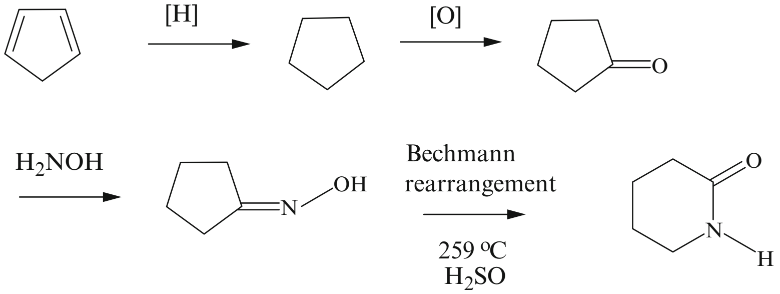
Nylon 4 or polypyrrolidone is an attractive polymer for use in fibers. The original syntheses of nylon 4 from 2-pyrrolidone were carried out by alkaline catalyzed ring opening polymerizations promoted by *N*-acylpyrrolidone [49]. The products from these reactions melt between 260 and 265°C.

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]:

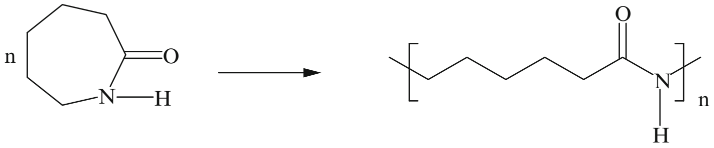


One route to valerolactam is from cyclopentadiene:



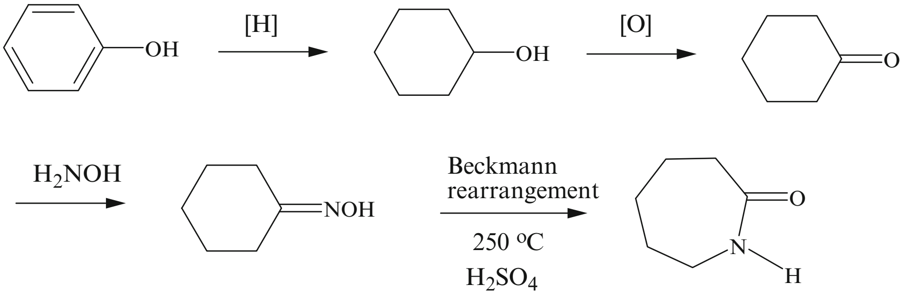
Valerolactam can also be polymerized with the aid of coordination catalysts to a high molecular weight polymer using alkali metal-$Al(C_2H_5)_3$ catalysts or alkali metal alkyl-$Al(C_2H_5)_3$ catalysts [55]. The polymerizations require **relatively long times**.

Nylon 6 is obtained via ring opening polymerization of caprolactam:

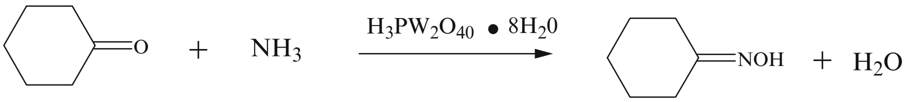


This polymer developed over the years into an important commercial material. As a result, many preparatory routes were developed for the starting material and the polymerization reaction was studied thoroughly.

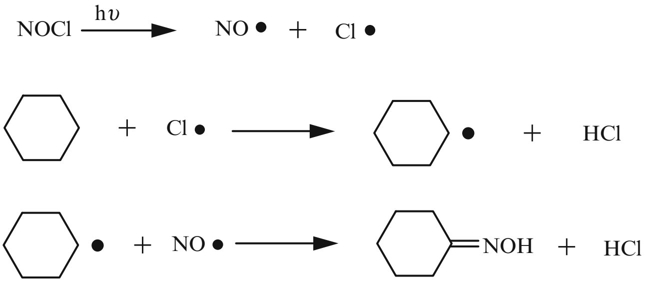
The most common starting materials for preparations of caprolactam are phenol, cyclohexane, and toluene. Some caprolactam is also made from aniline. In these synthetic processes, the key material is cyclohexanone oxime. The route based on phenol can be shown as follows:



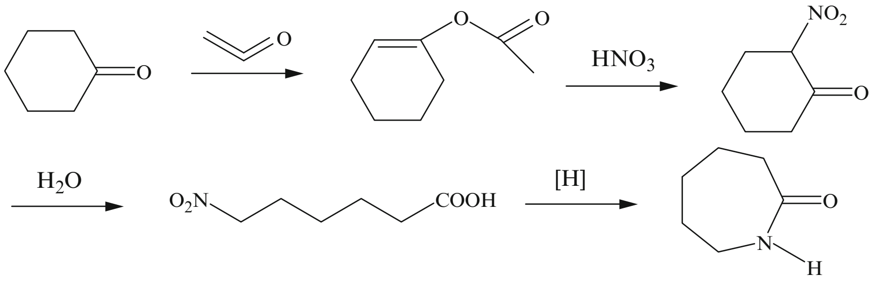
A by-product of the above reaction is ammonium sulfate. To avoid the necessity of disposing of ammonium sulfate, many caprolactam producers sought other routes to the oxime. One approach is to form it directly by reacting cyclohexanone with ammonia and hydrogen peroxide in the presence of tungstic acid catalyst [56]:



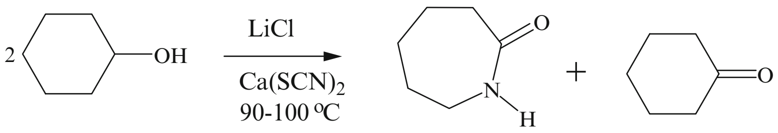
The reaction is conducted in water and the product oxime is extracted with an organic solvent. Another process is based on photo-nitrosyl chlorination. Here cyclohexane is converted in one step to cyclohexanone oxime hydrochloride [57]:



Another process uses ketene to form cyclohexene acetate [58]:

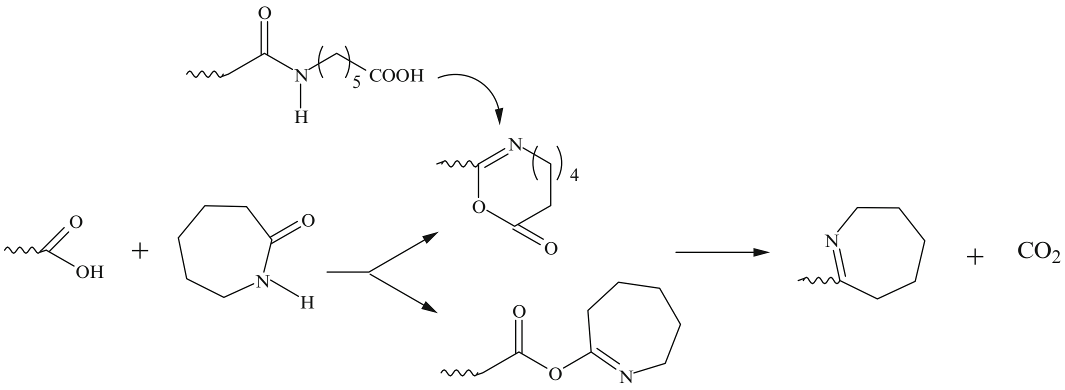


Among some more recent developments is a one-step synthesis of caprolactam from cyclohexanol [59]:

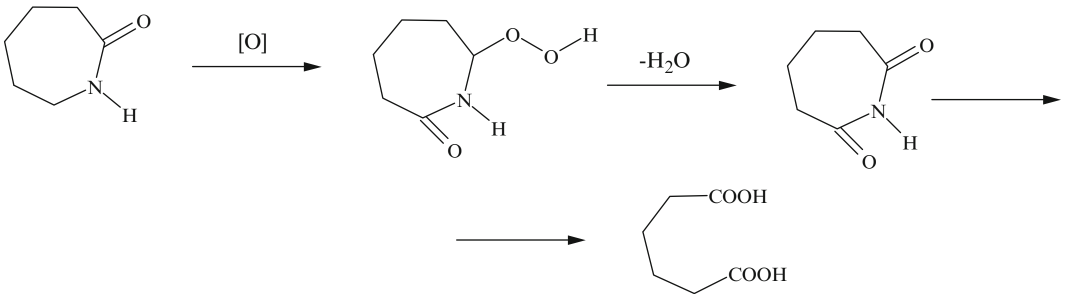


There are other processes for caprolactam syntheses as well; however, a thorough discussion of this subject belongs in books dedicated to the subject.

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.

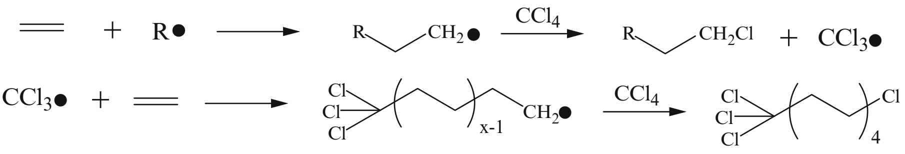
Nylon 7 and *nylon 9* are part of a process developed in Russia to form polyamides for use in fibers. The process starts with telomerization of ethylene [66]. A free-radical polymerization of ethylene is conducted in the presence of chlorine compounds that act as chain-transferring agents. The reaction is

Table 7.3 Compositions of telomers

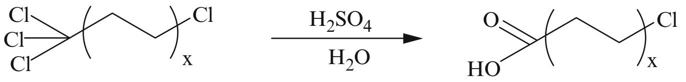
X	Fraction (%)
1	5
2	44
3	28
4	15
>4	8

From Nesmeyanov and Reundlina [66], by permission of Tetrahedral Letters, Elsevier Science, Ltd

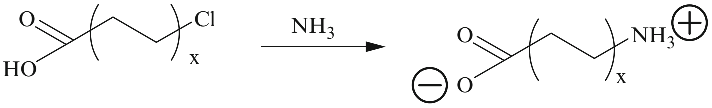
carried out at 120–200°C temperature and 400–600 atmospheres pressure. The preferred chain-transferring agents for this reaction are CCl_4 and $COCl_2$ [66]:



The resultant chloro alkanes are then hydrolyzed with sulfuric acid:

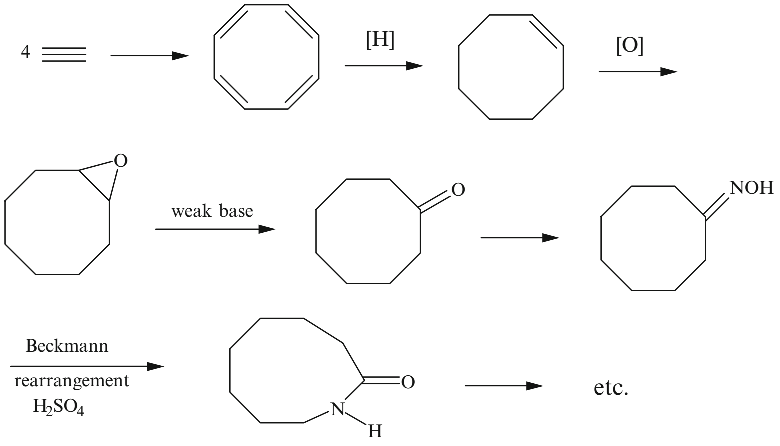


After hydrolyses, the products are treated with ammonia:

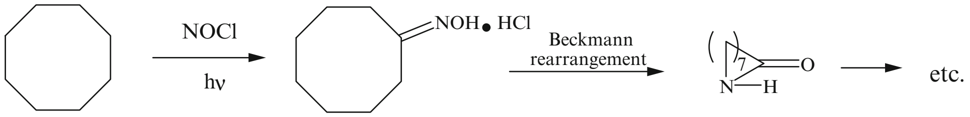


The amino acid is condensed to a lactam and subsequently polymerized. Table 7.3 shows the composition of the telomers in the above free-radical polymerization [66]. As seen from the table, the economics of producing nylon 7 by this process is not as favorable as one may wish. An advantage, however, to producing nylon 7 is that the polymer contains little monomer and can be spun without washing or extraction, as is required with nylon 6.

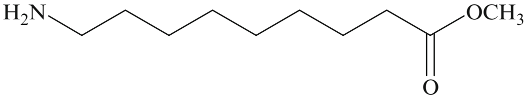
An early synthesis of *nylon 8* used cyclooctatetraene that was formed from acetylene and then converted to ***nylon 8*** as follows:



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:

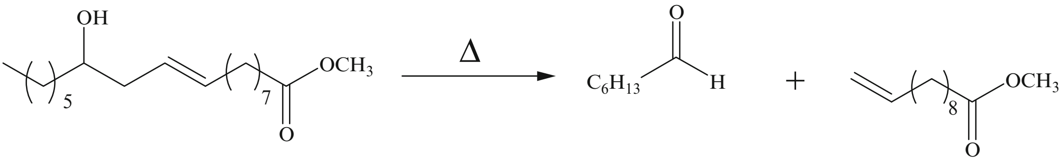


Nylon 9 or poly(ω-pelargonamide) is produced in Russia together with nylon 7, poly (aminoenanthic acid) as described above. In the U.S., Kohlhase et al. [67] developed a route to nylon 9 via ozonolysis of unsaturated fatty acids like those that can be obtained from soybean oil. The glycerol fatty acid 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:

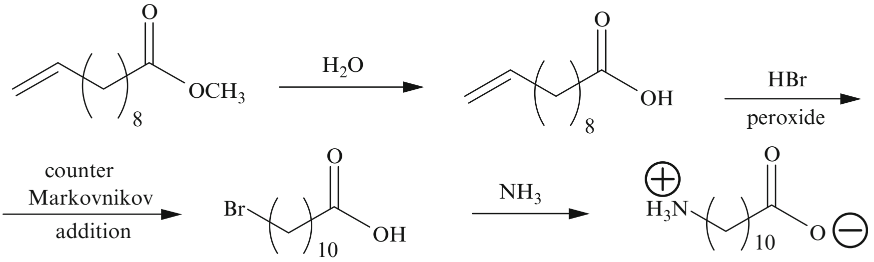


After hydrolysis and purification, the free amino acid is converted to high molecular weight polymers [68]. To date, nylon 9 has not been commercialized in the U.S., though the polymer has a high melting point of 209°C and is more flexible than nylon 6. It is also lower in water absorption.

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.

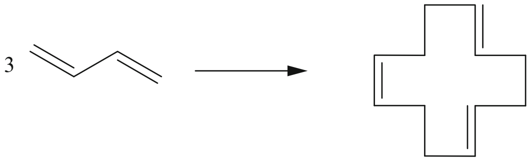
Nylon 12 is produced in U.S., Japan, and Europe with the original development coming from Europe. All current manufacturing processes of this polyamide, formed by ring opening polymerization of lauryl lactam, are based on cyclododecatriene. This ring compound can be obtained by

Table 7.4 Approximate melting points of polyamides

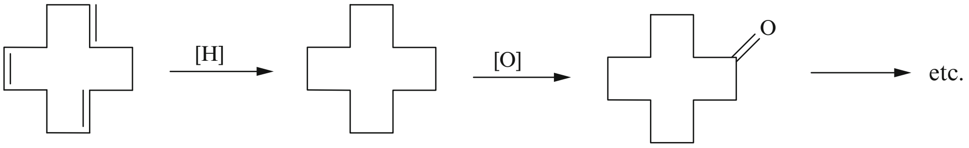
Nylon	Repeat unit	MP (°C)
3	$-(CH_2)_2-CO-NH-$	320–330
4	$-(CH_2)_3-CO-NH-$	260–265
5	$-(CH_2)_4-CO-NH-$	260
6	$-(CH_2)_5-CO-NH-$	215–220
7	$-(CH_2)_6-CO-NH-$	225–230
8	$-(CH_2)_7-CO-NH-$	195
9	$-(CH_2)_8-CO-NH-$	197–200
10	$-(CH_2)_9-CO-NH-$	173
11	$-(CH_2)_{10}-CO-NH-$	185–187
12	$-(CH_2)_{11}-CO-NH-$	180
13	$-(CH_2)_{12}-CO-NH-$	173

From various literature sources

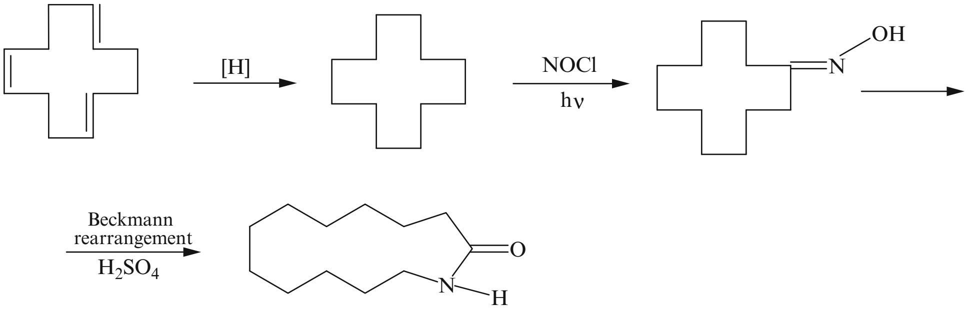
trimerization of butadiene using Ziegler–Natta type catalysts. One patent reports using polyalkyltitanate and dialkylaluminum monochloride [69]:



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:

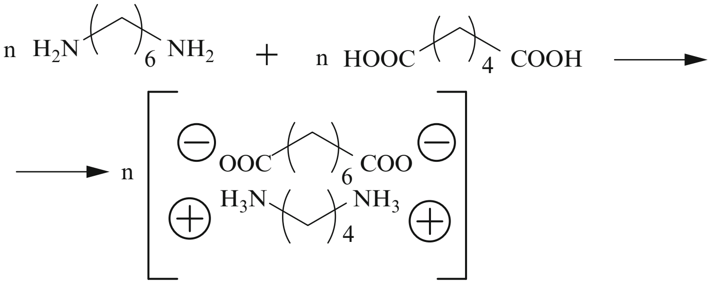


There are still other processes, but they lack industrial importance. Nylon 12, like nylon 11, exhibits low moisture absorbency, good dimensional stability, and good flexibility at low temperatures.

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:

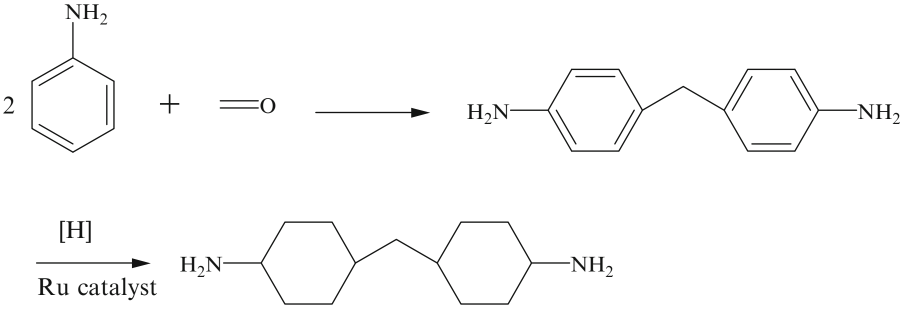
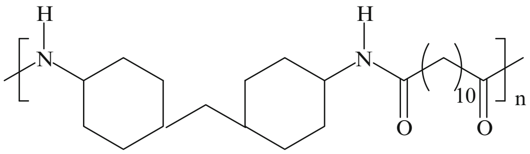


Table 7.5 Melting points of nylons

Nylon	Repeat unit	Melting point (°C)	
		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

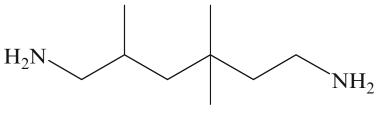
From ref [70] and other literature sources

The diamine is then condensed with dodecanedioic acid, which is obtained from cyclododecatriene. The structure of this polyamide is as follows:

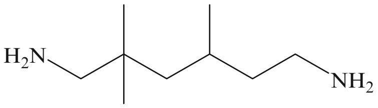


The polymer has a T_m of 280–290°C and a T_g of 120°C. It exhibits lower moisture pick up than do nylons 6 and 6,6, increased hardness and tensile strength, though lower impact strength. The bulk of this polymer is used in fiber production. The fibers, with a trade name of “Quiana,” are claimed to exhibit high luster and a silk like feel.

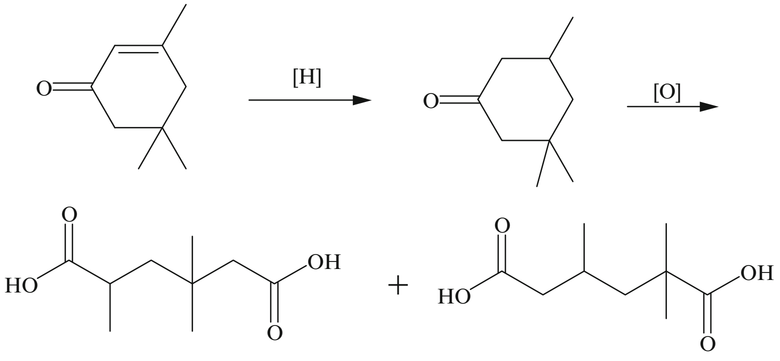
A number of ***copolyamides*** are manufactured commercially to suit various needs. One of them is a polyamide formed by condensation of trimethylhexamethylene diamine with terephthalic acid. The diamine is a mixture of 2,4,4 and 2,2,4 isomers:



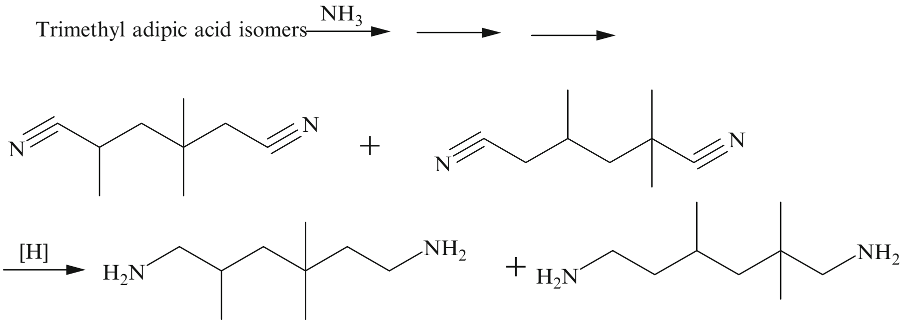
and



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.

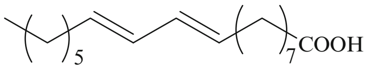
Many commercial nylon copolymers are also formed by melt mixing different nylons. Amide interchange reactions occur at melt conditions. At first block copolymers form, but prolonged heating and stirring results in formation of random copolymers. Nylon copolymers are also best prepared directly from mixed 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

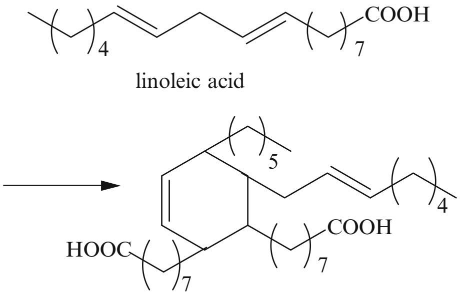
In any one series of melting points of polyamides, polymers that contain even numbers of methylene groups between amide linkages fall on a higher curve than those that contain odd ones do [72]. This is due to the crystalline arrangement of the polymeric chains [72, 73]. A zigzag planar configuration 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:

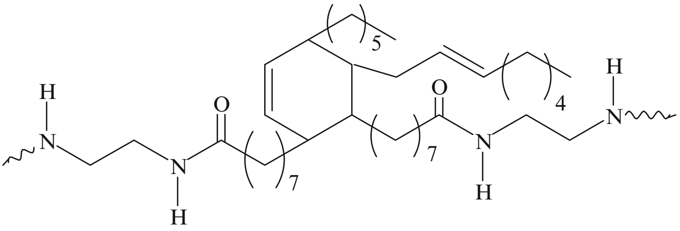


isomerized linoleic acid



linoleic acid

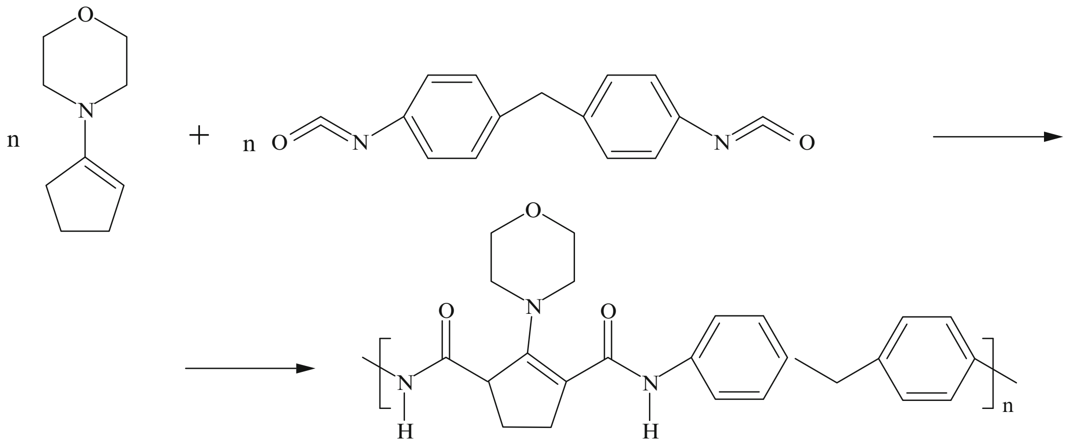
The polyamide from the above shown dimer acid condensed with a diamine, like ethylene diamine, can be illustrated as follows:



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.

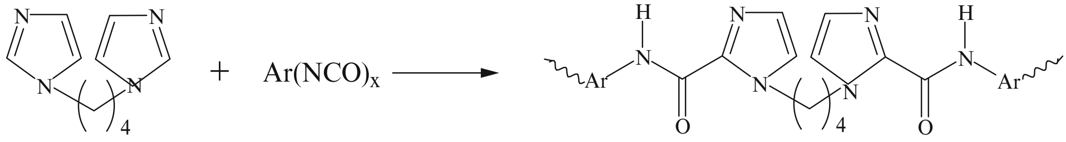
7.3.3 Special Reactions for Formation of Polyamides

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]:

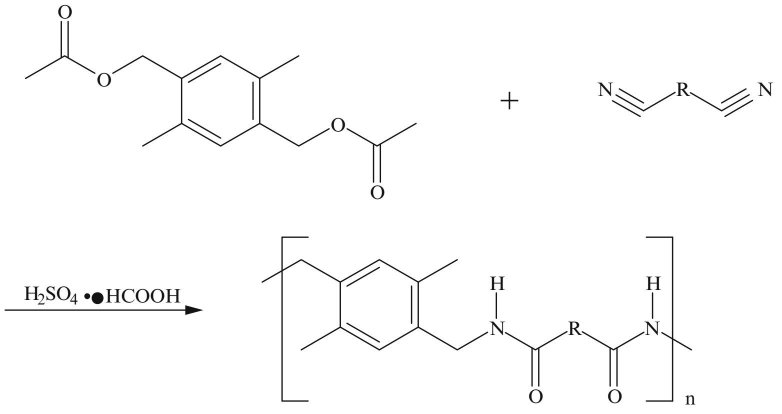


The molecular weights of the polymers decrease when the ring sizes of the ketone components increase. Excess diisocyanate yields branched and cross-linked polymers. The enamine units in the polymers can be hydrolyzed with formic acid to the corresponding ketones [77].

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]:



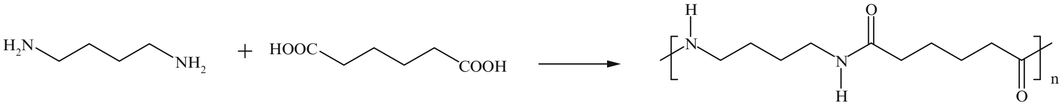
Another route to polyamides is via the Ritter reaction [78]:



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.

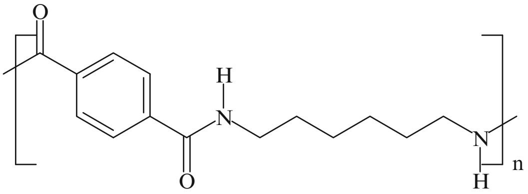
Direct polycondensation of a diamine with dicarboxylic acid was carried out in supercritical carbon dioxide in preparation of nylon 4,6 [84].



This nylon was reported to melt at 210°C.

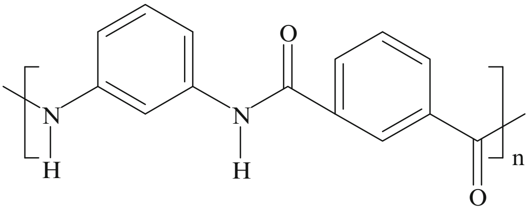
7.3.4 Aromatic Polyamides

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:

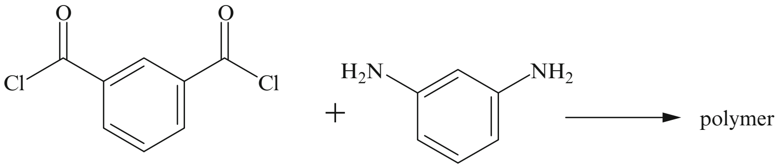


The polymer has good heat stability and the strength is unaffected by heating up to 185°C for 5 h. The polyamide melts at 370°C. When hexamethylene diamine is replaced with tetramethylene diamine, the melting point rises to 430°C. The condensation product from isophthalic acid and tetramethylene diamine 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):

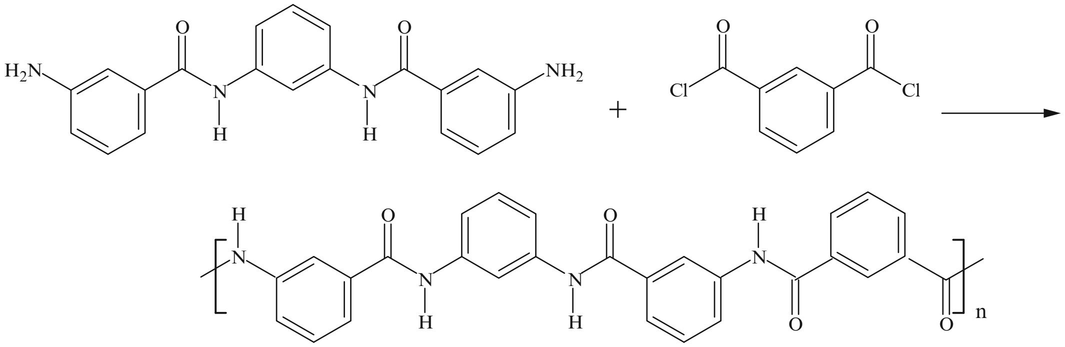


The polymer can be prepared in dimethylacetamide from isophthaloyl chloride and *m*-phenylene diamine in the presence of an acid scavenger at room temperature:



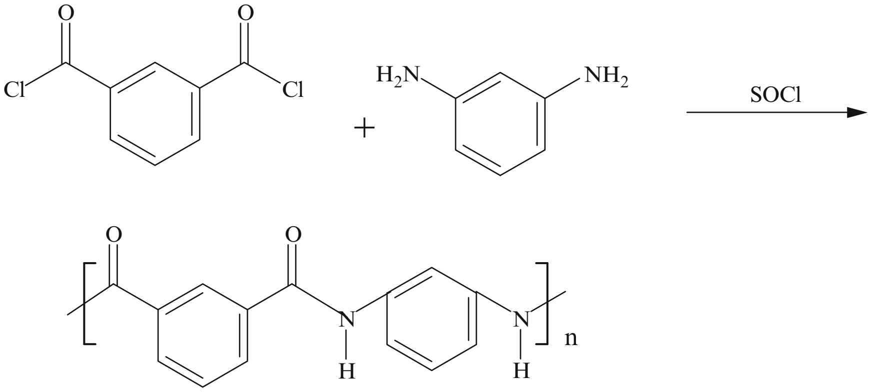
Because the polymer is soluble in dimethylacetamide containing 5% LiCl, fibers can be spun directly from solution. This polyamide melts at 371°C with degradation. It is fire-resistant. The fibers are sold under a trade name of Nomex.

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:

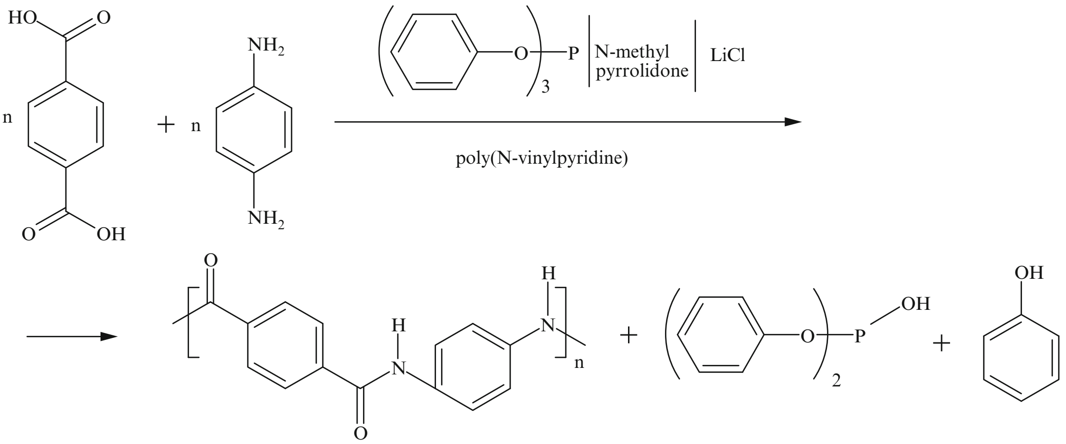


The above condensation, carried out with terephthaloyl chloride, yields a polymer that melts at 450°C. Preparations of many other wholly aromatic polyamides from aromatic diacid chlorides and aromatic diamines were reported in the literature [79, 80]. In addition, several polymers are manufactured from both fully and partially substituted (*para*) structures. They carry the trade name of HT4.

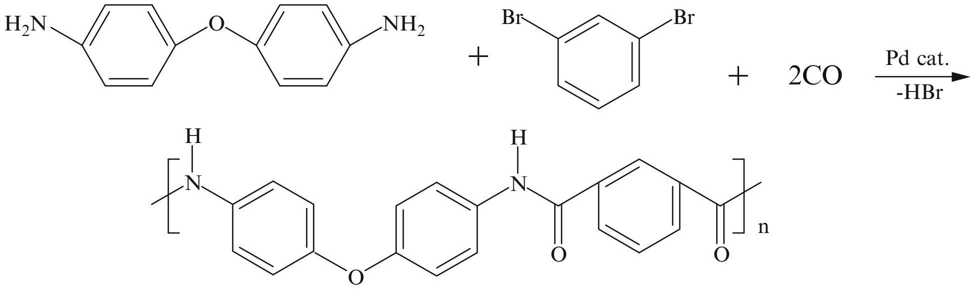
As described in the previous section, direct polycondensation of various nylon salts is possible under mild conditions in the presence of polyphosphates and organic bases [84]. This reaction, useful in forming aromatic polyamides, takes place also in the presence of thionyl chloride [84]:



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]:



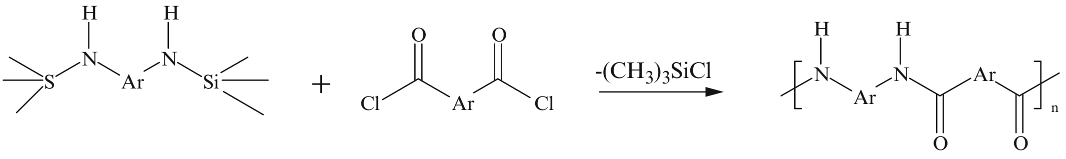
The Heck reaction was extended to carbonylation of aromatic dibromides with aromatic diamines in the presence of carbon monoxide [112]. High molecular weight aromatic polyamides form with the help of palladium catalysis:



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.

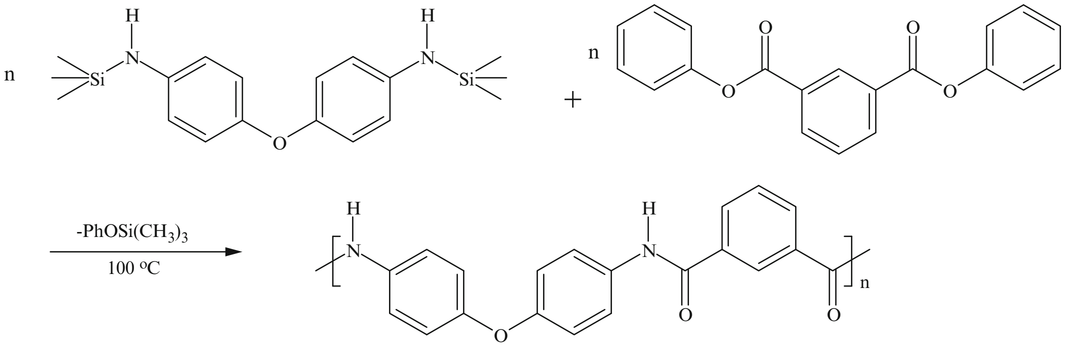
Palladium is a relatively high-priced catalyst and it would be preferable if a lower-priced nickel catalyst could be used instead. All attempts, however, to form polymers by nickel-catalyzed carbonylation polycondensations of aromatic diamines with aromatic dibromides failed to yield high molecular weight 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:



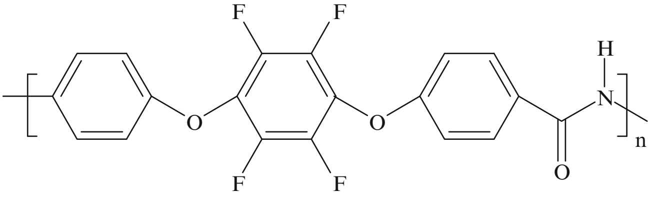
Preparations of poly-*p*-phenyleneterephthalamide by polycondensations with *N*-silylated diamine proceed more rapidly than with the parent diamine [113]. In addition, the products have higher molecular weights than similar commercial materials made from the parent diamine and sold under the trade name of Kevlar.

Silylated diamines can also condense with diphenyl esters of aromatic dicarboxylic acids [114]:

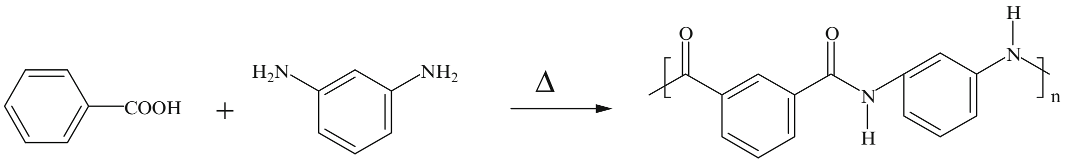


The product, above shown aromatic polyamide, was reported to be of sufficiently high molecular weight and to be a useful material [113].

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]:



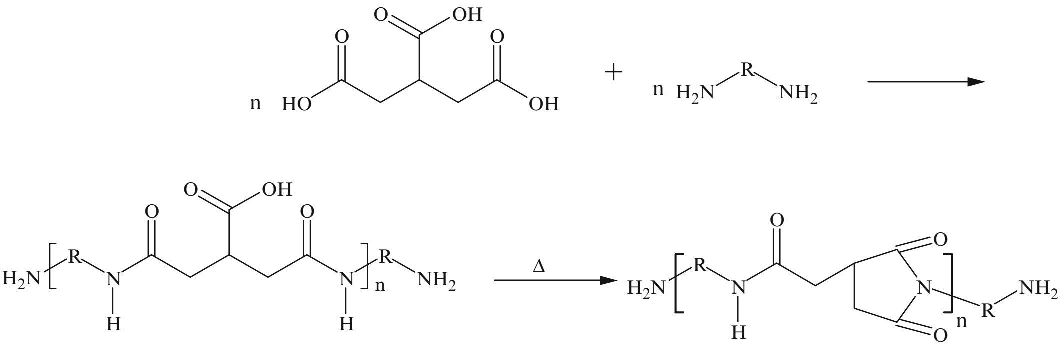
Mitsuru et al. [113] reported a direct synthesis of Nomex, an aromatic polyamide, mentioned above, by a solid state polycondensation:



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.

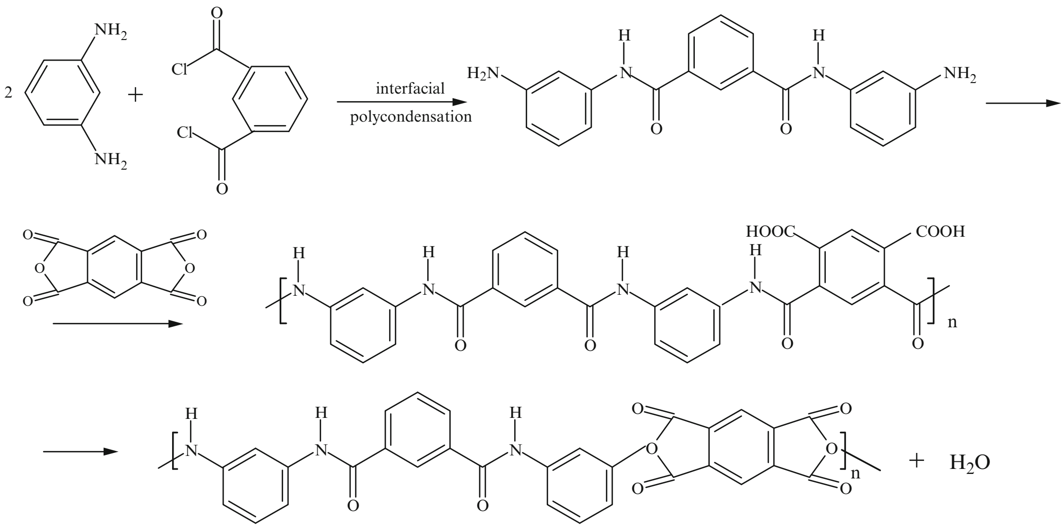
7.4 Aromatic Polyamide-Imides and Aromatic Polyester-Imides

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]:



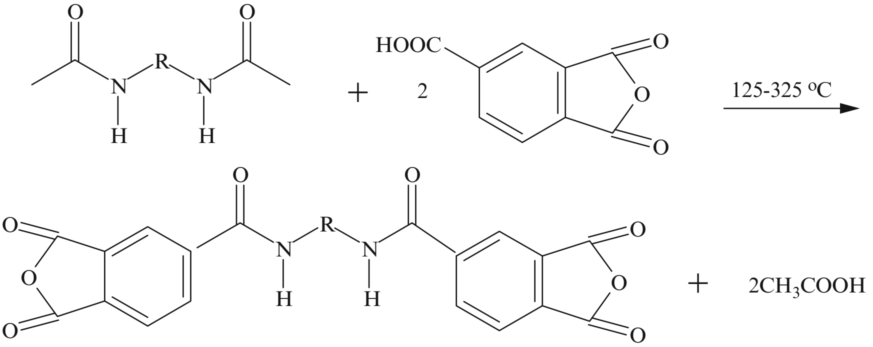
The aliphatic polyamide-imides prepared to date don't have desirable properties. When aromatic diacids are employed, however, the products exhibit good heat stability and toughness. This led to a development of a number of useful materials.

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:

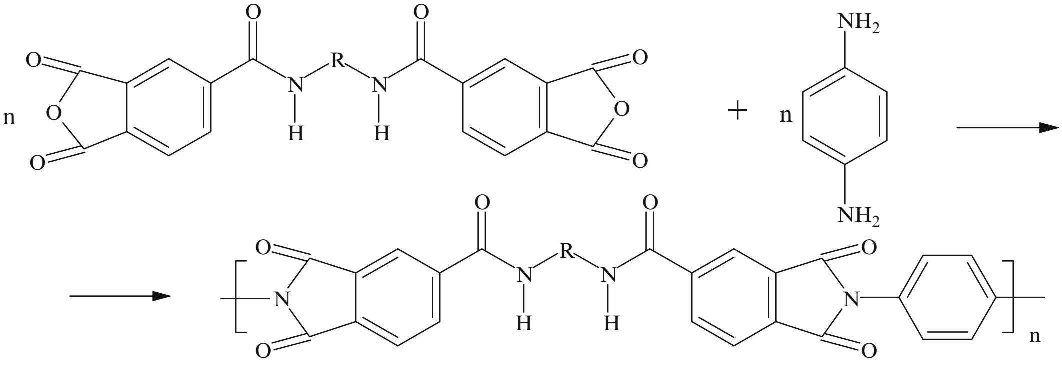


In the second method, a dianhydride is prereacted with an excess of a diamine. The product is then reacted with a diacid chloride by interfacial polymerization technique.

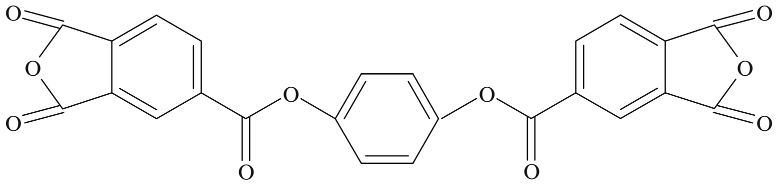
In the third method, an anhydride, like, for instance, trimellitic anhydride, is condensed with a diamine to form a preliminary condensate. An acetylated diamine can be used in this initial condensation [85]:



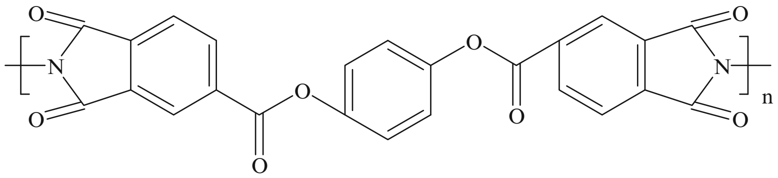
This is followed by a reaction with the same or a different diamine:



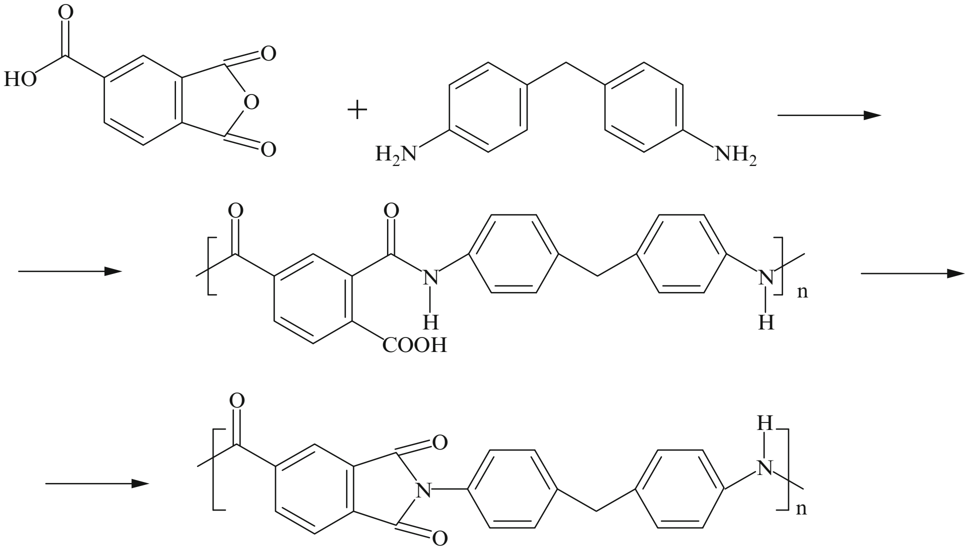
The same techniques are applied to preparations of polyester-imides. A diester can be formed first from trimellitic anhydride:



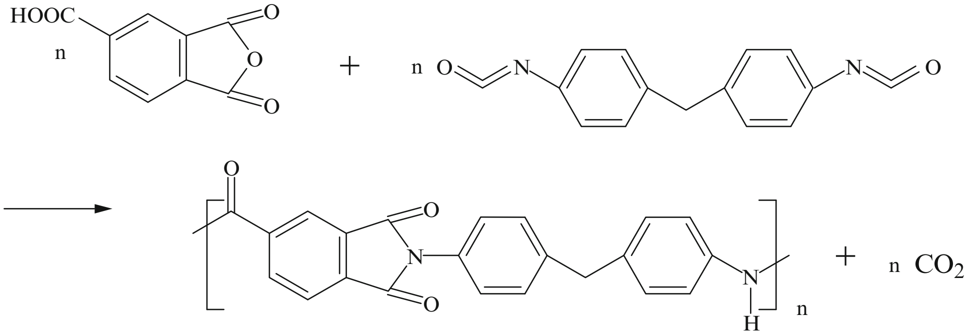
The product is then condensed with a diamine to form a polyester-imide:



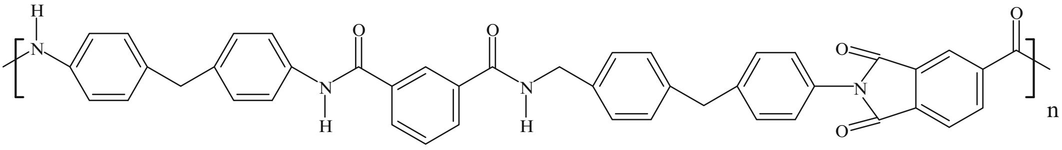
Several polyamide-imides are available commercially. Two are based on trimellitic anhydride and methylene dianiline. They are, however, prepared by two different processes. In the first one, the polymer is formed from the anhydride and a diamine:



In the second one, trimellitic anhydride is reacted with a diisocyanate:



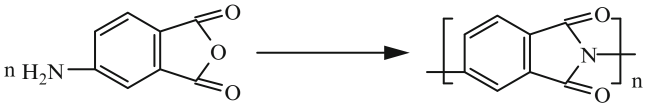
Another polyamide-imide is formed through a reaction of trimellitic anhydride, isophthalic acid, and diisocyanate. It has the following structure:



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].

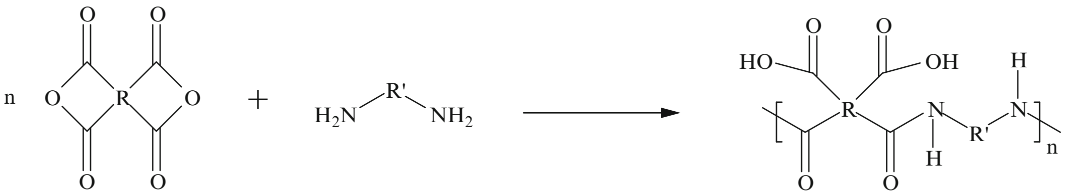
7.5 Polyimides

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:

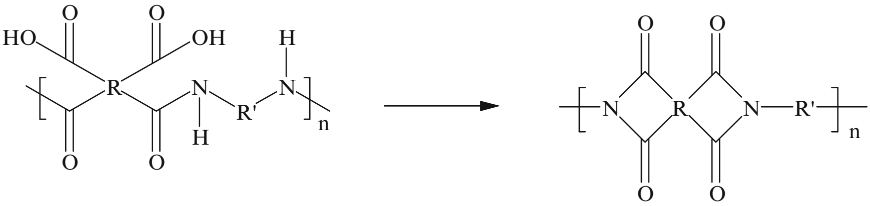


Formation of polymers, however, was at the time considered undesirable, so the material was not pursued [87]. It was learned since that an imide link is more thermally stable than an amide one and that polyimides can be very useful materials. Many polyimides were developed since. Aromatic structures 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:

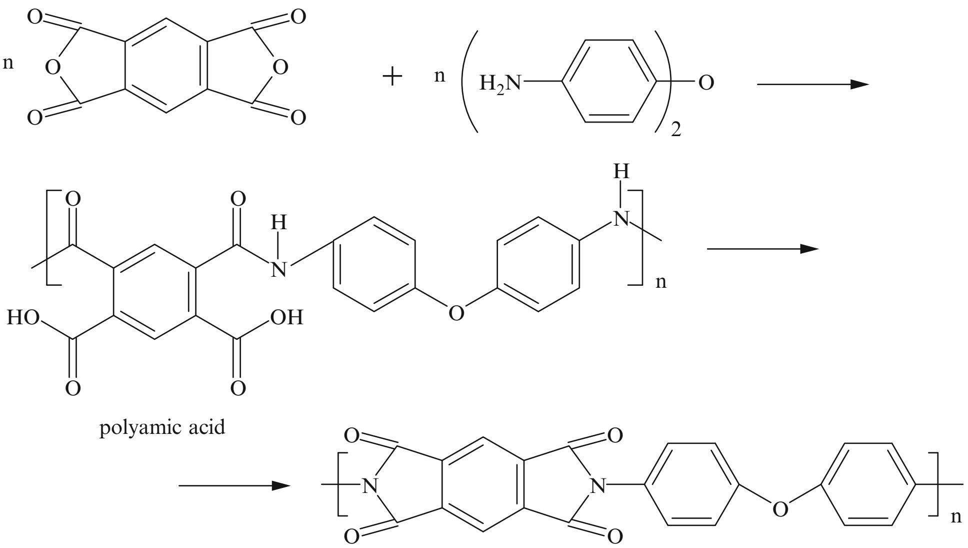


The polyamic acids are usually prepared in solution. Suitable solvents are *N*,*N*-dimethylformamide, dimethyl sulfoxide, and *n*-methyl-2-pyrrolidone. The reactions require anhydrous conditions at relatively low temperatures, like 50°C (or lower). Some, however, need high temperatures, as high as 175°C [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].

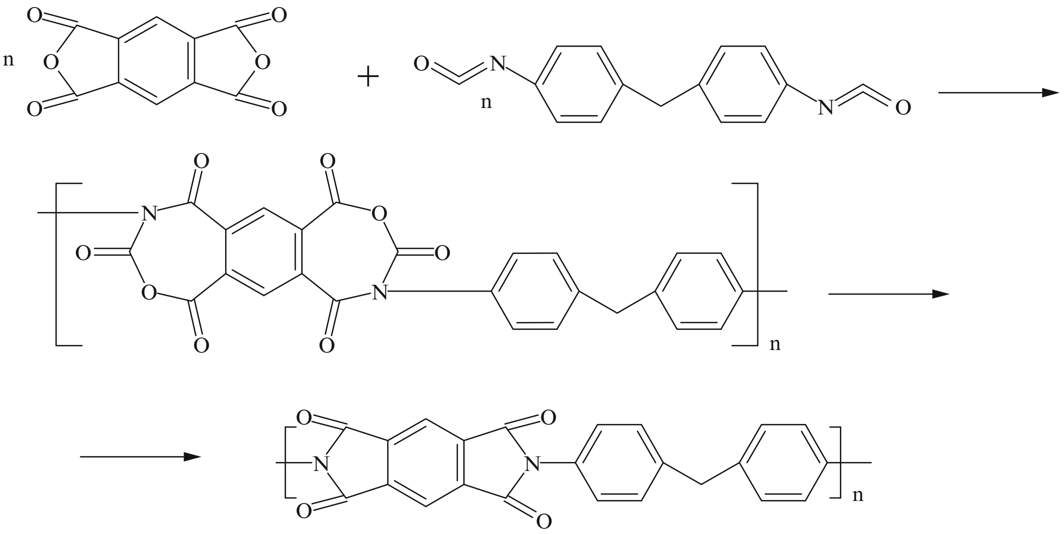
Lozano et al. reported on an improved method for forming high molecular weight polyimides [88]. They used in situ sililation of the diamines to carry out the reaction. Trimethylchlorosilane is added to the diamine solution prior to the addition of the electrophilic monomer.

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:

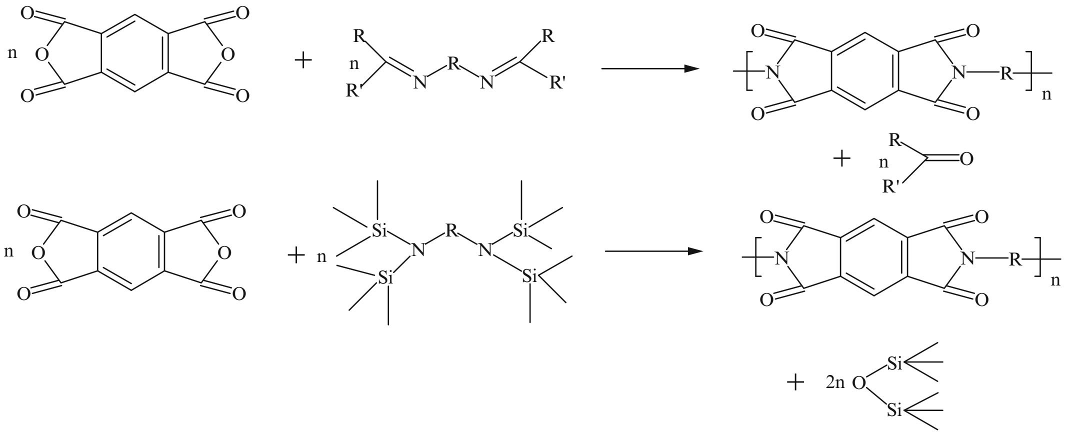


The above shown polymer melts above 600°C and is heat stable up to 500°C in an inert atmosphere. It is sold under the trade name of Kapton. A different polyether-imide sells under the trade name of Ultem.

Another route to polyimides is through reactions of diisocyanates with dianhydrides [89, 90]:

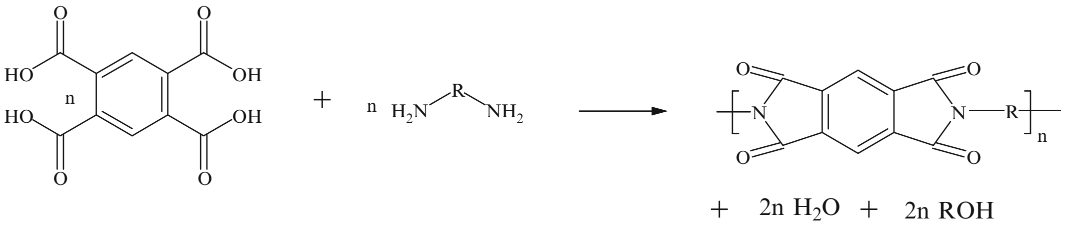


The reaction is kept between 120 and 200°C [91]. In place of isocyanates, it is also possible to use aldimines or ketimines, as well as silylated diamines.

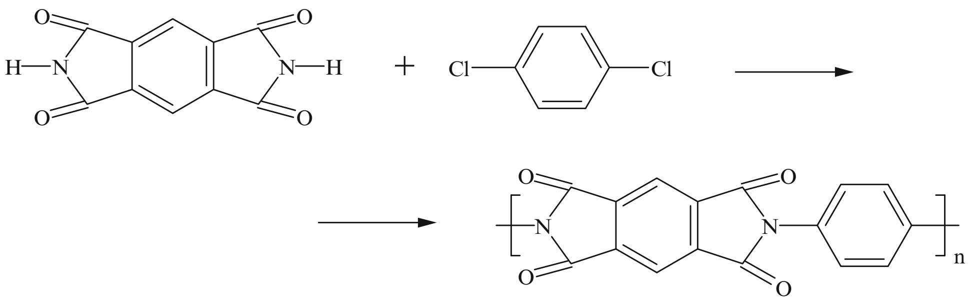


When silylated diamines are used, trimethylsilyl esters of polyamic acids are formed first and then desilylated with methanol. Due to increased solubility of silylated aromatic amines, the initial condensations and formations of polyamic acid trimethylsilyl esters can be done in various solvents, yielding 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].

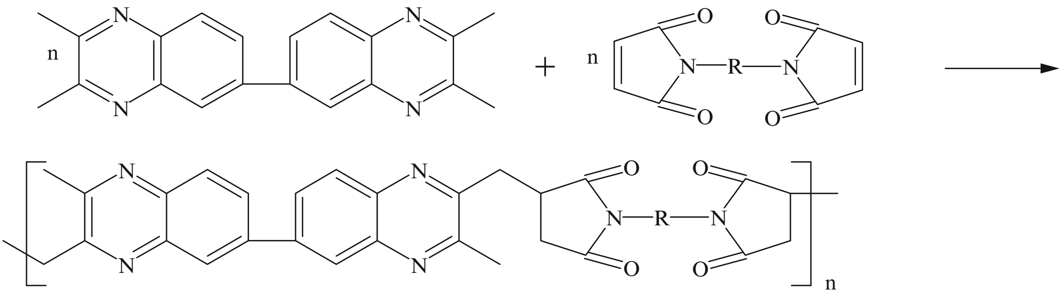
The films of the silylated precursors of polyamic acid convert directly by heat treatment to yellow, transparent, and tough films of aromatic polyimides with the elimination of trimethylsilanol [91]. Other preparations of polyimides include the use of di-half esters of tetracarboxylic acids [92]:



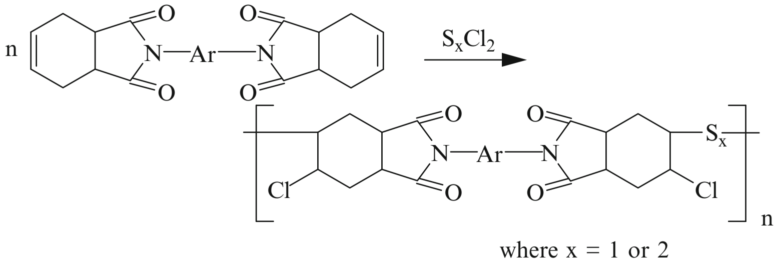
Polyimides can also be prepared by reactions of diimides with dihalides [93]:



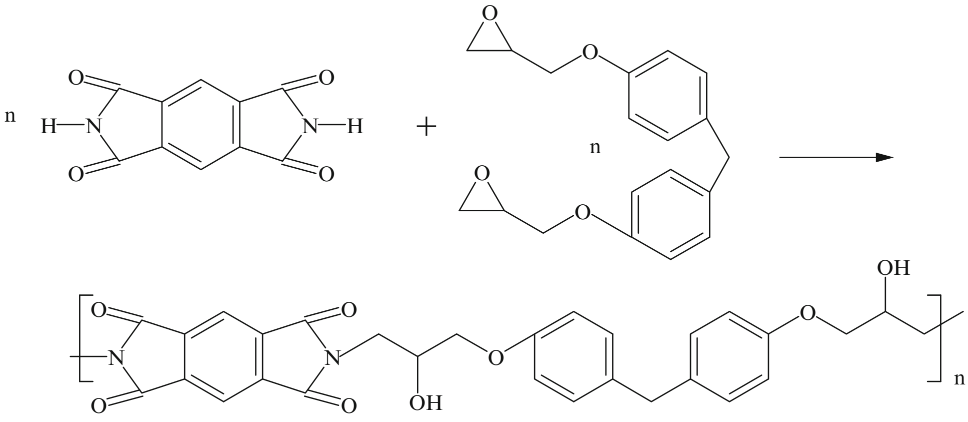
Reactions of bis maleimides with compounds containing active hydrogens can also lead to formations of polyimides [94]:



Also, unsaturated diimides can be reacted with sulfur halides to form polyimides [95]:

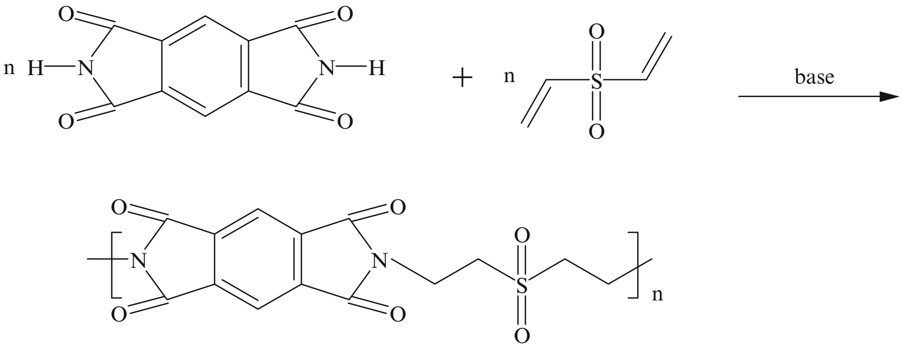


Diepoxides can add to pyromelitimide in the presence of a base to form polyimides with pendant hydroxyl groups [96]:

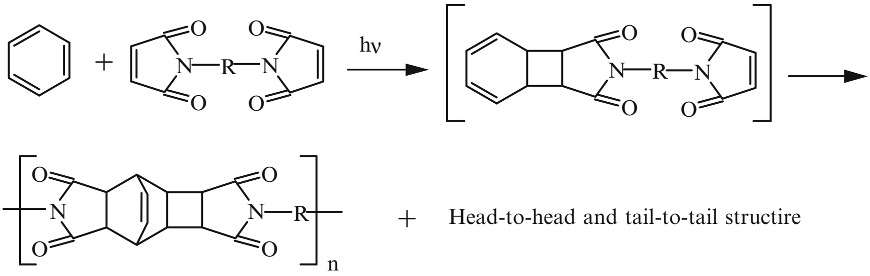


Tertiary amines and quaternary ammonium halides catalyze this reaction. Acetylation of the pendant hydroxyl groups of the product yields polymers that are soluble in solvents like dioxane and dimethylformamide.

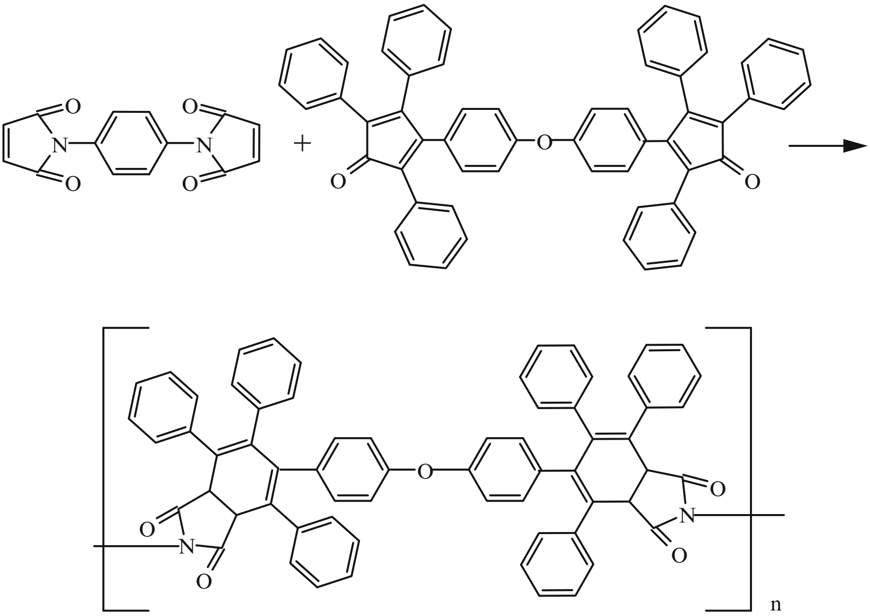
Pyromelitimide can also add to double bonds to form polyimides [97]:



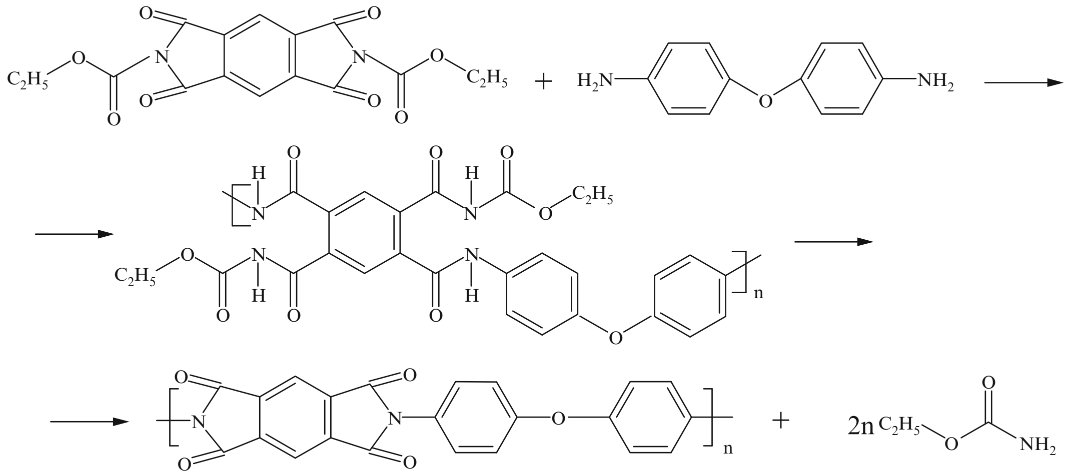
Polyimides also form by photo additions of aliphatic or aromatic bis maleimides to benzene [98]. The reactions involve 2 + 2 cycloadditions that yield homoannular diene intermediates. Diels–Alder additions follow and result in formations of the polymers:



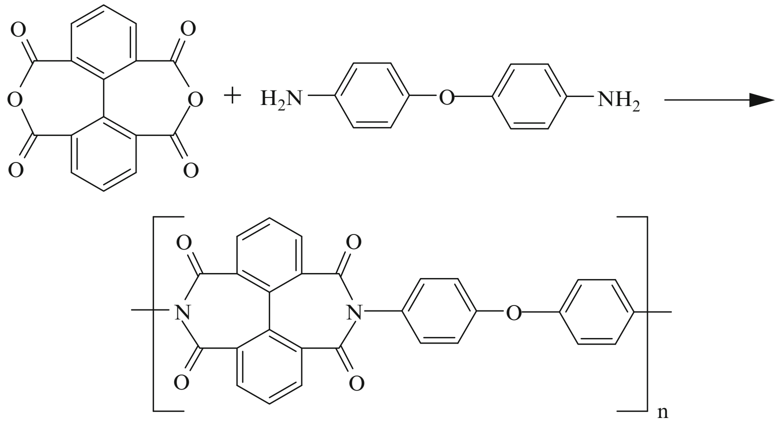
Diels–Alder reactions yield other polyimides, as, for instance, the following [99]:



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:

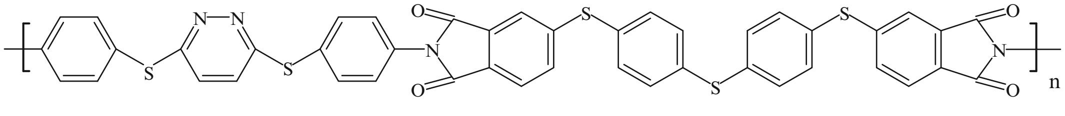


As in the previous cases, the polyamic acid forms first in solution at approximately 40°C. It is converted to the polyimide by heating in acetic anhydride at reflux for 18 h.

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.



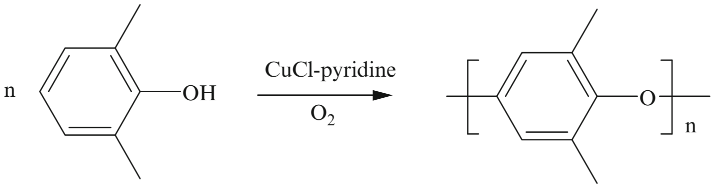
The polymer has a high refractive index, high transparency, and is aimed at optical devices.

7.6 Polyethers

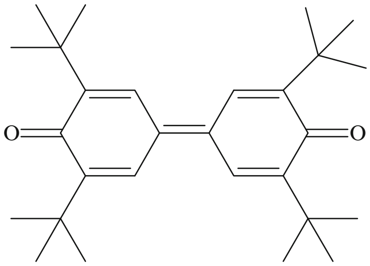
Polyethers that form by chain-growth polymerizations of carbonyl compounds and by ring opening polymerizations of cyclic ethers and acetals are discussed in Chap. 6. In this section are discussed poly(phenylene oxide)s and phenoxy resins.

7.6.1 *Poly(phenylene oxide)s*

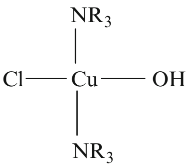
These polymers are known for good thermal stability and good mechanical properties. Commercially, these aromatic polyethers are prepared by oxidative coupling of phenols [102]. To obtain linear polymers and achieve high molecular weights, 2 and 6 positions of the phenol must be protected by substituents. 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:

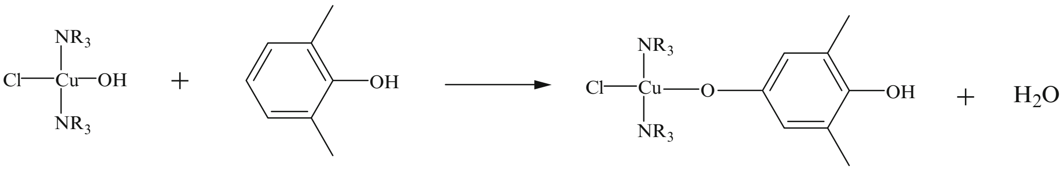


The active catalyst is believed to be a basic cupric salt that forms through oxidation of cuprous chloride followed by complexation with two molecules of the amine [102]:

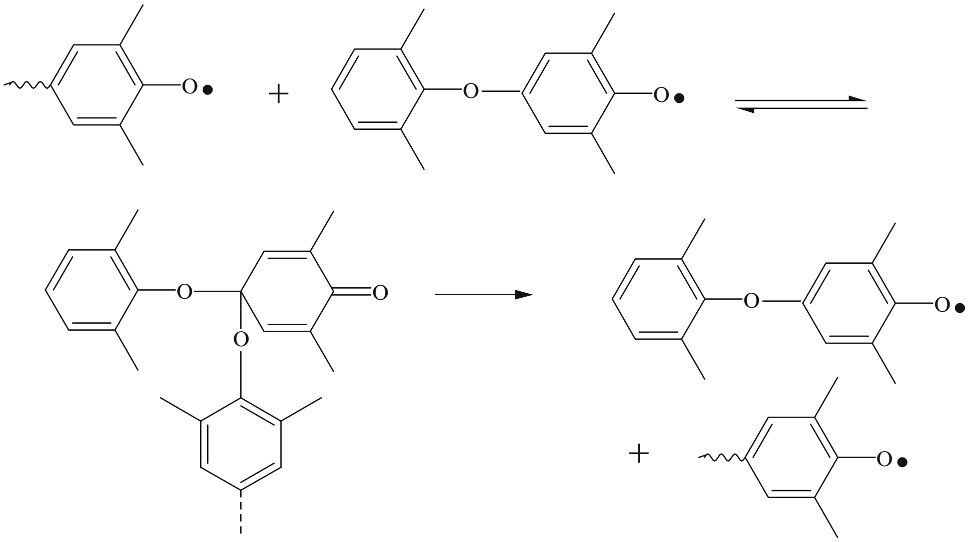


$$\mathrm{Cl{-}\underset{\underset{NR_3}{|}}{\overset{\overset{NR_3}{|}}{Cu}}{-}OH}$$

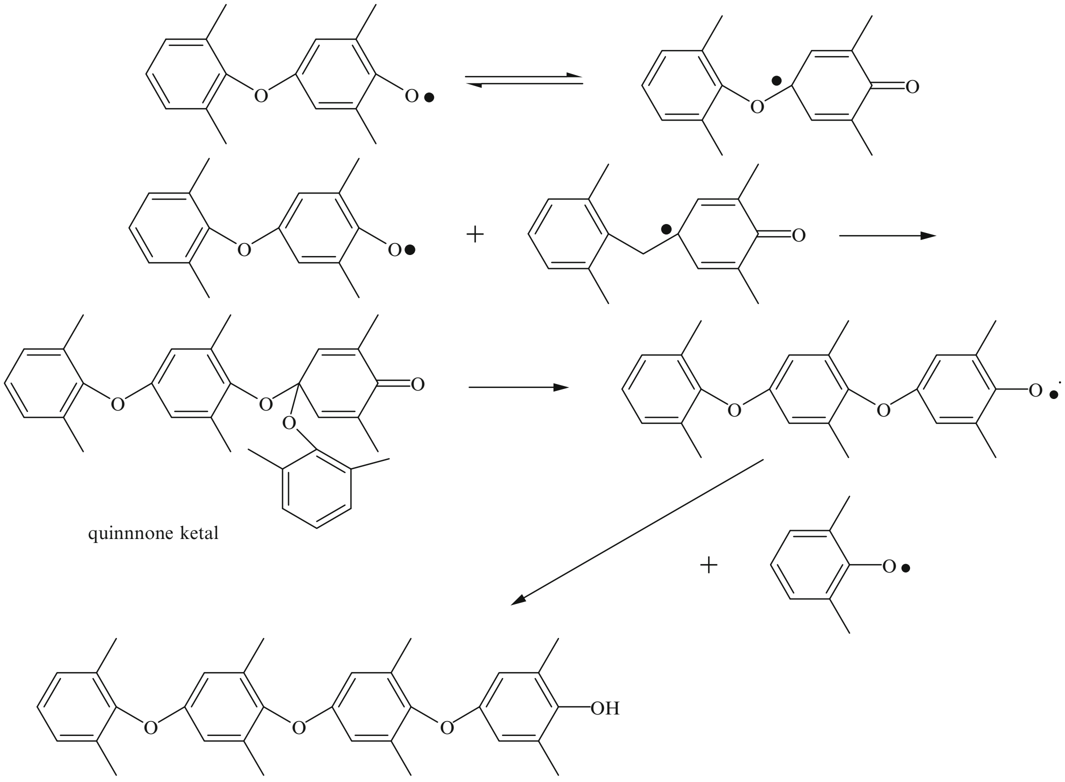
This is a step-growth polymerization involving phenoxy radicals. The polymer formation can be illustrated as follows:



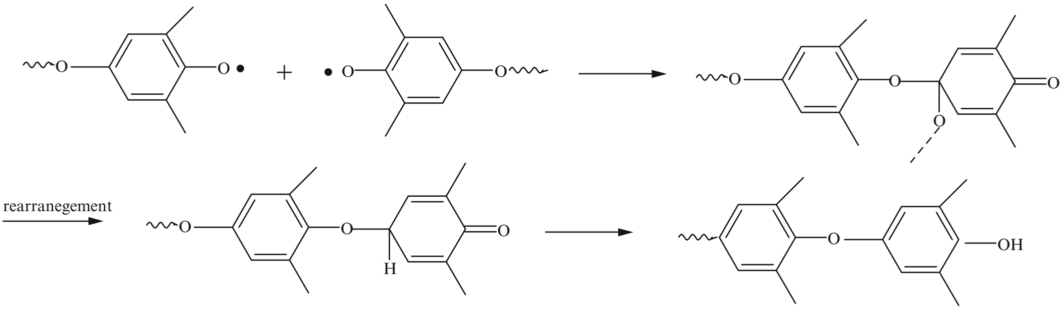
Dissociation leads to aryloxy radicals or to two new radicals that couple. Quinone ketals are formed initially. They dissociate to yield the original aryloxy radicals and then couple [102]:



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:

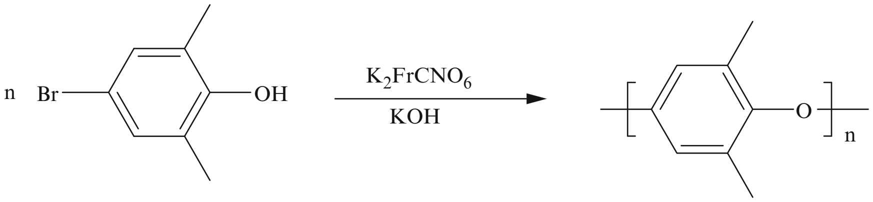


The quinone rearranges to a phenol through enolization. The product is identical to one that is obtained by direct head to tail coupling of two aryloxy radicals [102].

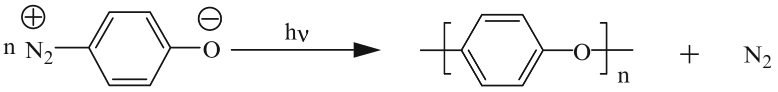
It is important to realize that both processes, redistribution and rearrangement reactions, can occur within the same polymer molecule. At any point during the rearrangement, there may be dissociation into aryloxy radicals. Also, redistribution does not have to occur by transfer of only a single unit. 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:



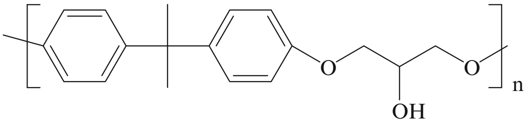
Poly(phenylene oxide)s also form through photodecomposition of benzene-1,4-diazooxides [102]:



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.

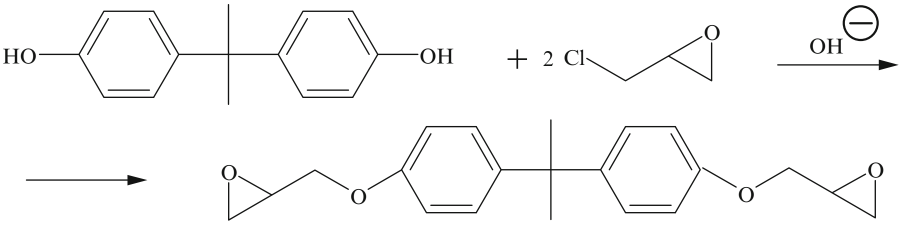
7.6.2 Phenoxy Polymers

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:

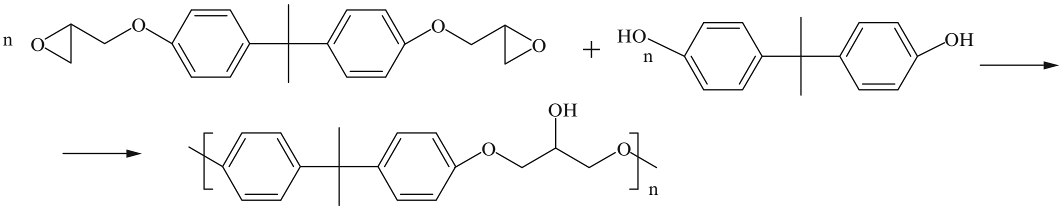


The polymer forms through caustic catalyzed condensations of diphenols with epichlorohydrin. Any diphenol or combination of diphenols can undergo this reaction. In commercial practice, however, mainly 4,4-isopropylidinediphenol, commonly called Bisphenol A, is used.

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:



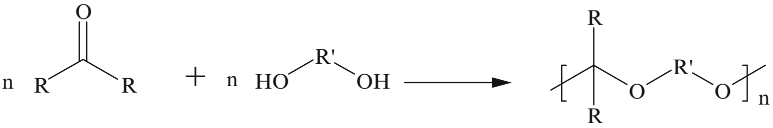
In the second step, equimolar quantities of the diepoxide are reacted with the diphenol:



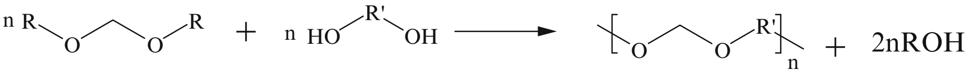
Both reactions are conducted in solution, where methyl ethyl ketone is the choice solvent. The commercial resins range in molecular weights from 15,000 to 200,000.

7.7 Polyacetals and Polyketals

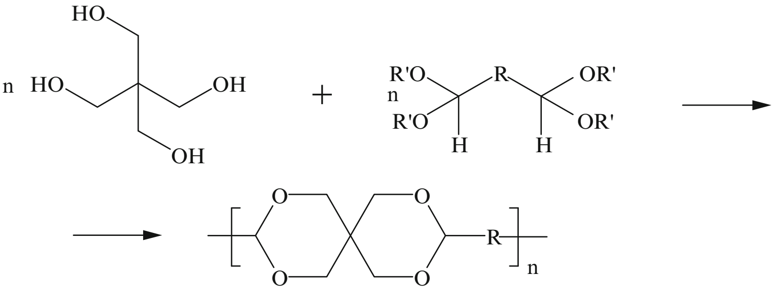
Polyacetals and polyketals are polyethers that form (1) through condensations of glycols with carbonyl compounds, (2) by exchange reactions of acetals or ketals, and (3) by additions of diols to dialkenes [109]:



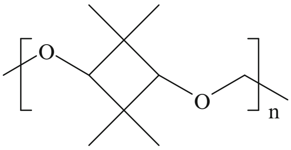
An acid-catalyzed exchange reaction of glycols and acetals yields polyacetals as follows:



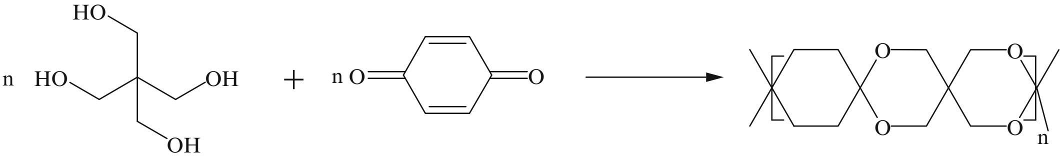
These reactions often lead to cyclic acetals that interfere with the formation of high molecular weight products. Useful polyacetals, however, can be formed from pentaerythritol and acetals of dialdehydes:



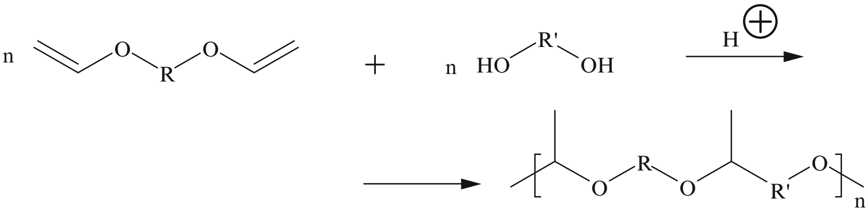
Acetals generally exhibit poor resistance to hydrolytic attack. Some, however, are much more resistant than others, depending upon the glycol. The following formal was reported to exhibit good hydrolytic stability under both acidic and basic conditions [109]:



Pentaerythritol yields spiro polymers by this reaction. The products offer superior thermal resistance [114]:



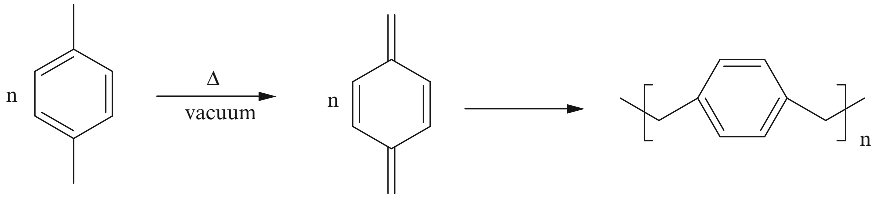
The addition of diols to dialkenes can be illustrated on addition of a glycol to a divinyl ether:



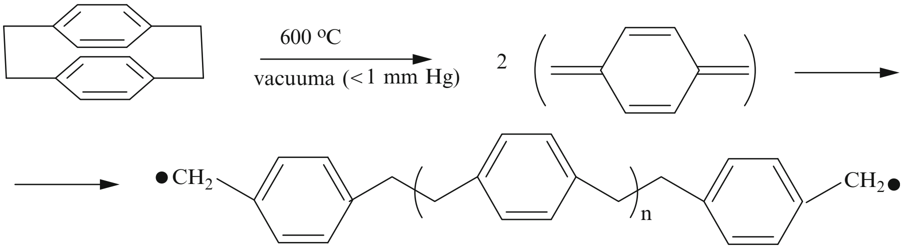
Commercially, large volume acetals are only produced by polymerizations of formaldehyde and by ring opening polymerizations of trioxane. These reactions are discussed in chapters three and four. Two such materials are manufactured in this country. One is a homopolymer of formaldehyde, polyoxymethylene. 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]:



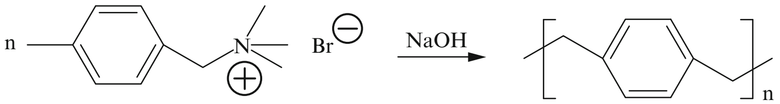
The process was improved by using di-*p*-xylylene as an intermediate [106]. This dimer converts to a polymer under milder conditions quantitatively. Both methylene bridges cleave to form *p*-xylylene, which is a reactive intermediate:



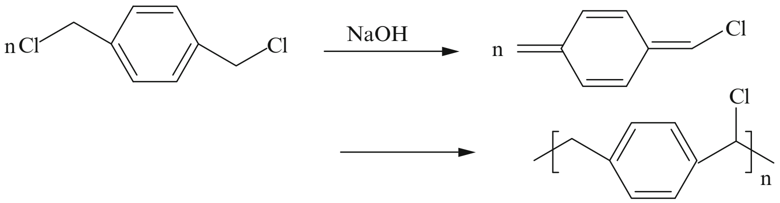
The molecular weights of these polymers were estimated to be as high as 500,000. The total process is sometimes called *transport polymerization*. Poly(*p*-xylylene) films are produced commercially. T_m of this polymer, which is crystalline, is 400°C and it carries the trade name of Perylene. Films of 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].

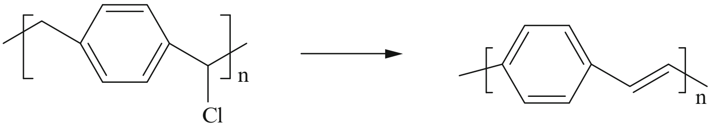
Poly(*p*-xylylene)s can also be prepared by other reactions. Among them is the condensation of trimethyl(*p*-methylbenzyl) ammonium halide in the presence of a base [47]:



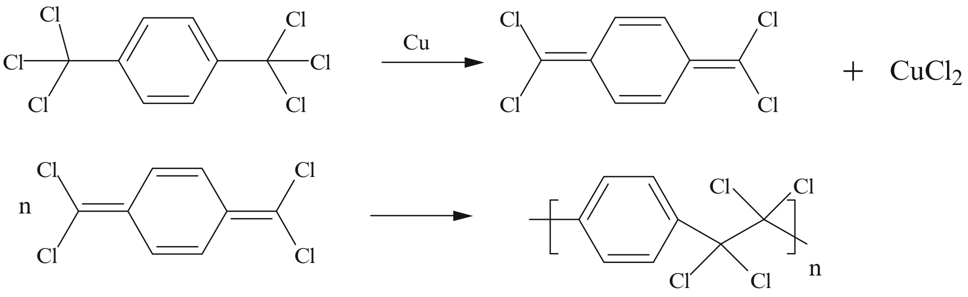
A route to a halogen-substituted polymer is through a reaction of di halo-*p*-xylylenes with caustic. It results in 1,6 elimination of HCl and formation of a chlorine-substituted poly(*p*-xylylene) [47]:



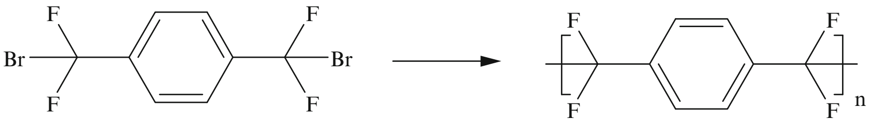
With excess caustic, however, all chlorine is removed and presumably an all-conjugated poly (phenylene vinylene) polymer forms [47]:



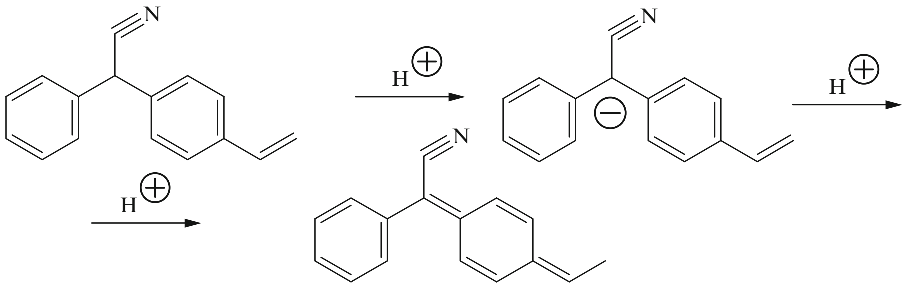
p-Bis(trichloromethyl) benzene can be pyrolyzed over copper gauze at 300–600°C temperatures to form α,α,α′,α′-tetrabromo-*p*-xylylene. This monomer polymerizes at temperatures just below 140°C [107]:



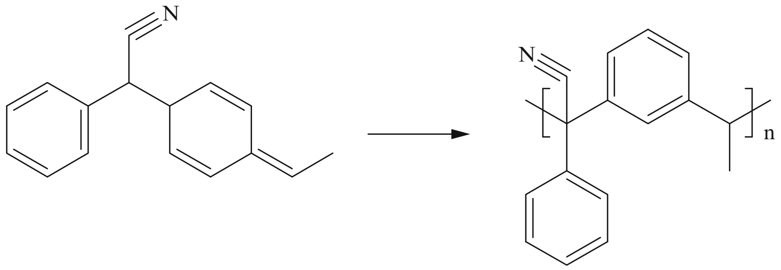
p-Xylylene polymers also form electrolytically [88] in dioxane-water solution with mercury or lead cathodes and carbon rod anodes. During the reaction, a quinone dimethide intermediate probably forms [88]. Many substituted polymers also form by this reaction [88]. Following is an example of one of them:



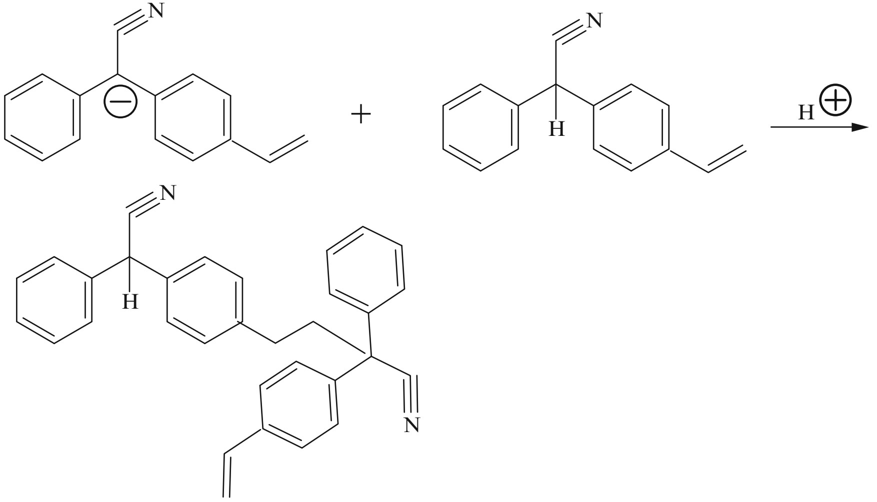
Another interesting synthesis is through an equilibration reaction of suitably substituted styrenes to *p*-xylylenes that spontaneously polymerize to linear polymers [108]. A suitable substituent can be a *p*-cyanophenylmethyl group. Such compounds undergo complete ionization and rearrange in the presence of a strong base:



The *p*-xylylene intermediate then polymerizes:



There are, however, competing side reactions, such as dimerization [108]:

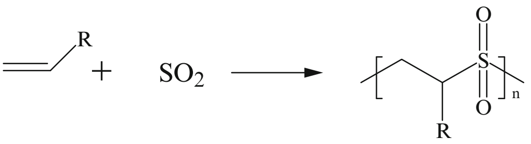


7.9 Sulfur-Containing Polymers

Industrially important sulfur-containing polymers are polysulfones and polysulfides. The materials differ considerably in properties and in use.

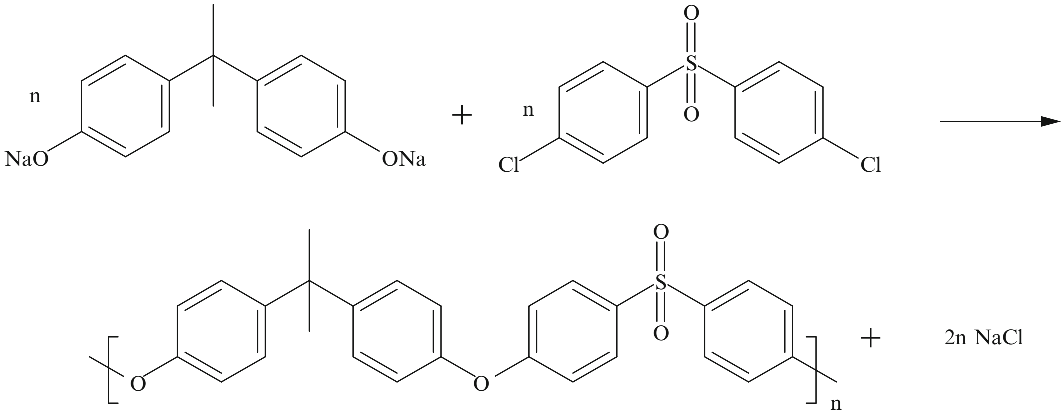
7.9.1 Polysulfones

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:



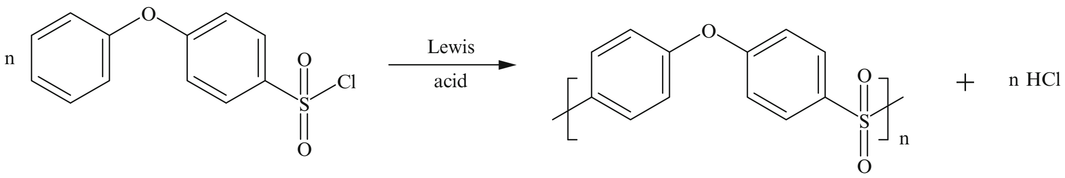
Aliphatic sulfones, however, lack good thermal stability and are not commercially important. Aromatic sulfones, on the other hand, have many desirable physical properties. They are clear, rigid, tough materials, with a high T_g. Several aromatic sulfones are prepared commercially.

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]:

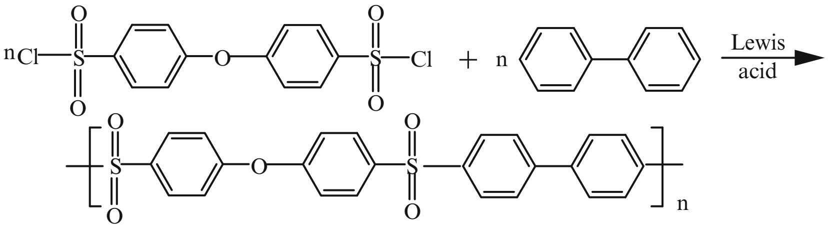


The condensation takes place at 160°C in an inert atmosphere and in some suitable solvents, like chlorobenzene. Commercially, polymers are available in molecular weight ranges from 20,000 to 40,000. Much higher molecular weight materials, however, form readily.

Aromatic polysulfones also form by the Friedel–Craft reaction [111], as for instance:

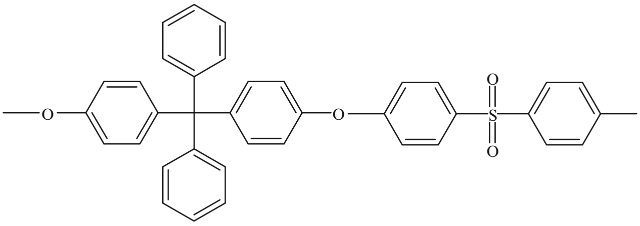
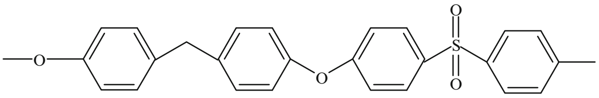
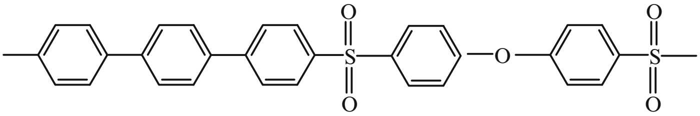
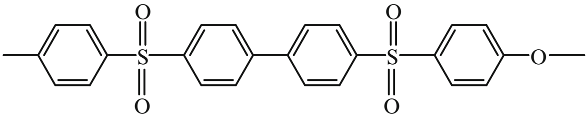
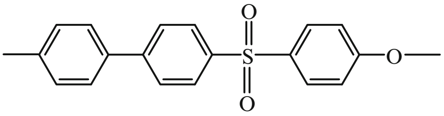
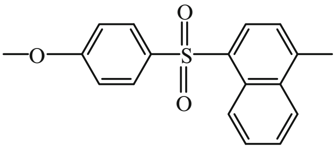


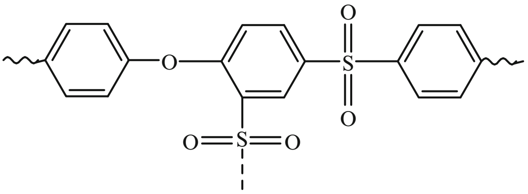
or



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]

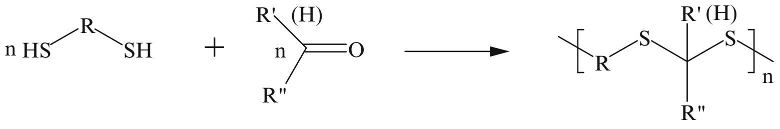
Polymer repeat unit	T_g (°C)
	220
	180
	290
	280
	265
	230



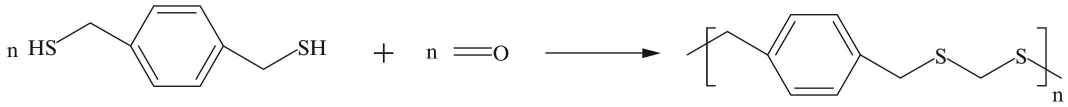
It is estimated, however, that the *ortho* substitution amounts to not more than 5–10%. Removal of the catalyst after the reaction is tedious. Table 7.6 presents the T_g values of some aromatic polysulfones.

7.9.2 Polythiols and Polymercaptans

These polymers form from reactions of di thiols with aldehydes or ketones:

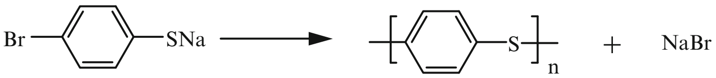


This reaction is used commercially to prepare an aromatic polymercaptan from *p*-bis (mecaptomethyl)benzene:

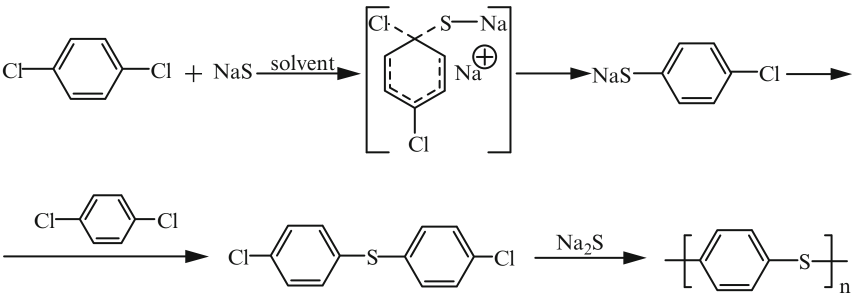


The polymer melts at 150°C and can be spun into fibers [109].

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:

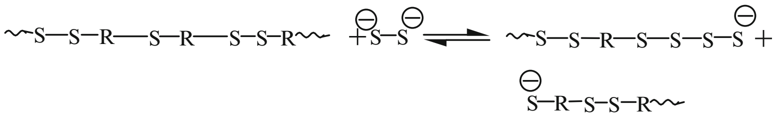
$$-[-\mathrm{R}-\mathrm{S}_x-]_n- \quad \text{where } x = 2-4$$

The most widely used methods of preparation are based on reactions of sodium polysulfides with alkyl dichlorides [110]:

$$n\mathrm{Cl}-\mathrm{R}-\mathrm{Cl} + \mathrm{Na_2S}_x \rightarrow -[-\mathrm{R}-\mathrm{S}_{x\text{-}}]_{n\text{-}} + 2n\mathrm{NaCl}$$

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.

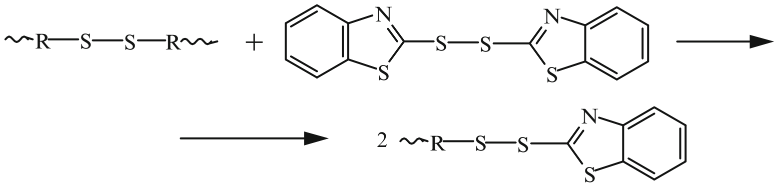
The magnesium chloride forms magnesium hydroxide and acts as a nucleating agent. Bis(2-chloroethyl) formal is then added over 2 h with stirring and external cooling of the exothermic reaction to about 90°C. After addition, this temperature and stirring are usually maintained for additional 2 h to complete the process. The product contains a distribution of polysulfide groups. The polysulfide anions can interchange continuously:



$$\sim S{-}S{-}R{-}S{-}R{-}S{-}S{-}R\sim + \overset{\ominus}{S}{-}\overset{\ominus}{S} \rightleftharpoons \sim S{-}S{-}R{-}S{-}S{-}S{-}\overset{\ominus}{S} + \overset{\ominus}{S}{-}R{-}S{-}S{-}R\sim$$

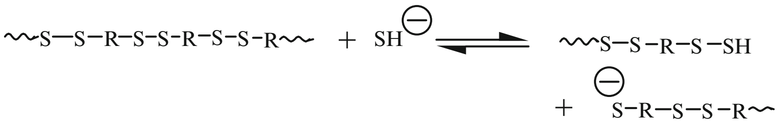
This allows building up the molecular weights of the polymers by additions of excess polysulfide. Also, low molecular weight fractions can be washed out. By such manipulations, molecular weights of 500,000 are readily achieved. It is interesting that in this particular step-growth polymerization, in 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:



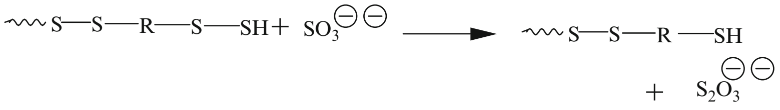
The elastomers are then chain-extended again with metal oxides, like zinc oxide, that couple the terminal hydroxy groups. The same thing can also be done by using diisocyanates.

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:



$$\sim S{-}S{-}R{-}S{-}S{-}R{-}S{-}S{-}R\sim + SH^{\ominus} \rightleftharpoons \sim S{-}S{-}R{-}S{-}SH + \overset{\ominus}{S}{-}R{-}S{-}S{-}R\sim$$

The sulfite ion prevents the reversal of the equilibrium by splitting of the sulfur from the thiothiol:



$$\sim S{-}S{-}R{-}S{-}SH + SO_3^{\ominus\ominus} \longrightarrow \sim S{-}S{-}R{-}SH + S_2O_3^{\ominus\ominus}$$

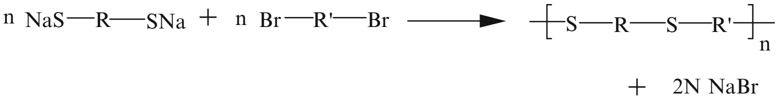
These polymers cross-link by oxidative coupling of the mercaptide groups:

$$\sim SH + [O] + HS\sim \longrightarrow \sim S{-}S\sim + H_2O$$

and by reactions with metal peroxides like lead peroxide. They also react with epoxy resins.

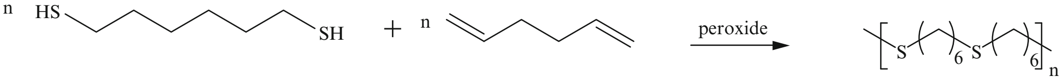
Poly(alkylene sulfide)s are exceptionally oil-resistant elastomers. They also exhibit good resistance to solvents and to weathering. On the other hand, these elastomers lack the strength of synthetic rubbers and possess an unpleasant odor.

Aliphatic polysulfides also form from reactions of di thiols with alkyl dihalides. High molecular weight polymers, however, are hard to form [109]:

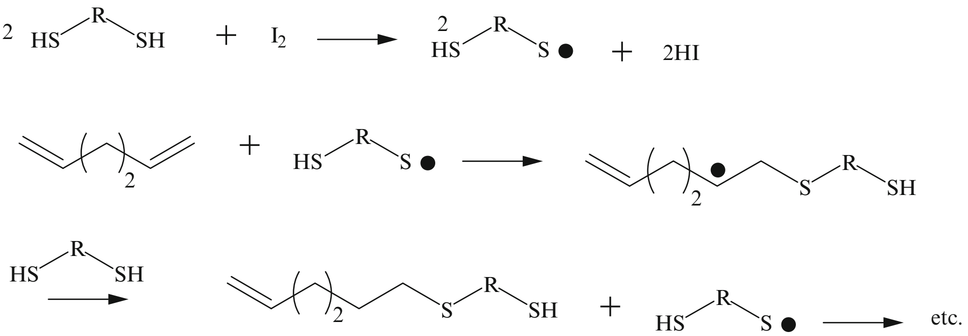


$$n\ NaS{-}R{-}SNa + n\ Br{-}R'{-}Br \longrightarrow \left[S{-}R{-}S{-}R' \right]_n + 2N\ NaBr$$

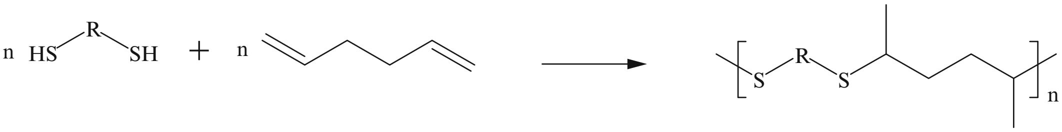
Similar polymers form through addition of di thiols to diolefins [109]. The reaction can take place either by a free-radical mechanism or by an ionic one. A free-radical mechanism requires presence of peroxides to achieve counter Markownikoff additions across the double bonds:



It is a step-growth polymerization process. The additions to the double bonds involve a series of hydrogen exchange reactions [108]:

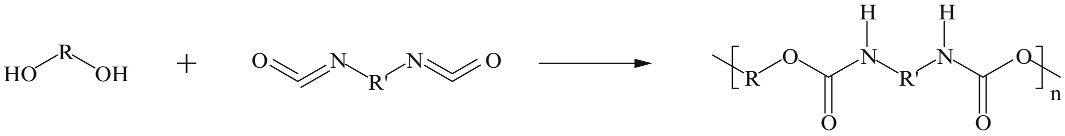


When additions take place by ionic mechanisms, they are catalyzed by either acids or bases. These additions follow the Markownikoff rule:

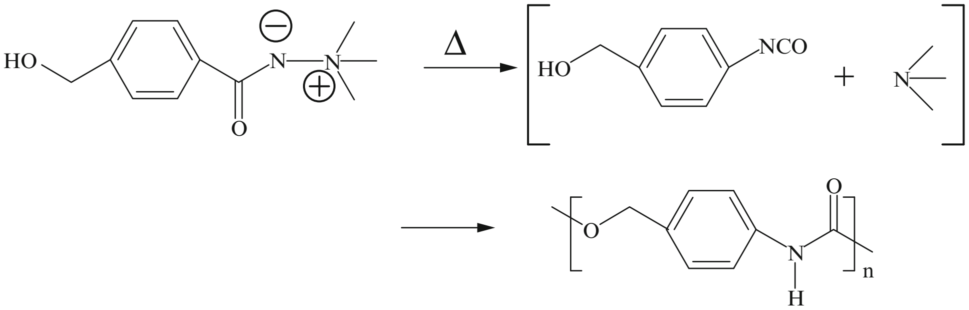


7.10 Polyurethanes

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].

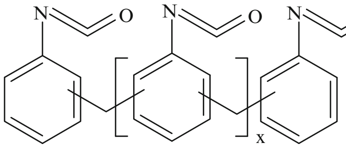
7.10.1 Preparations of Polyfunctional Isocyanates

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:



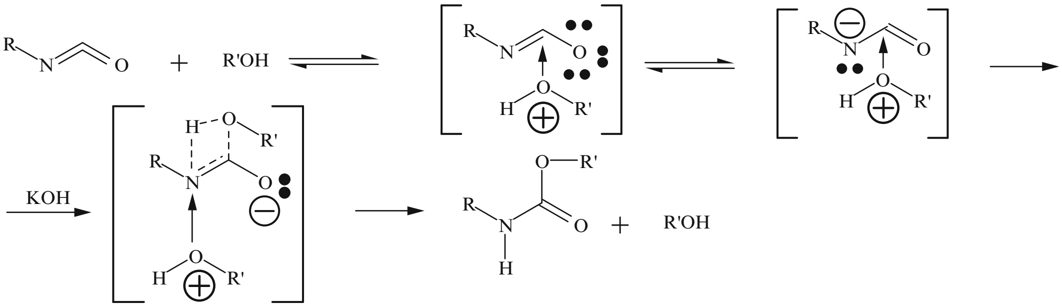
where, x =2 or 3

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.

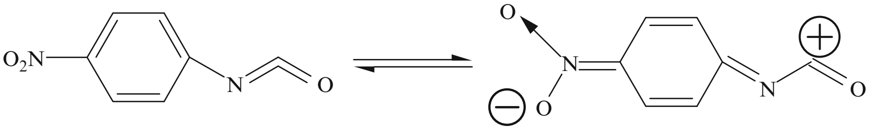
The common aliphatic diisocyanates are hexamethylene diisocyanate, hydrogenated (H_{12}) 4,4′-dipenylmethane diisocyanate, isophorone diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, and 2,4,4-trimethylhexamethylene diisocyanate. Other aliphatic diisocyanates that are commercially used are lysine 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:



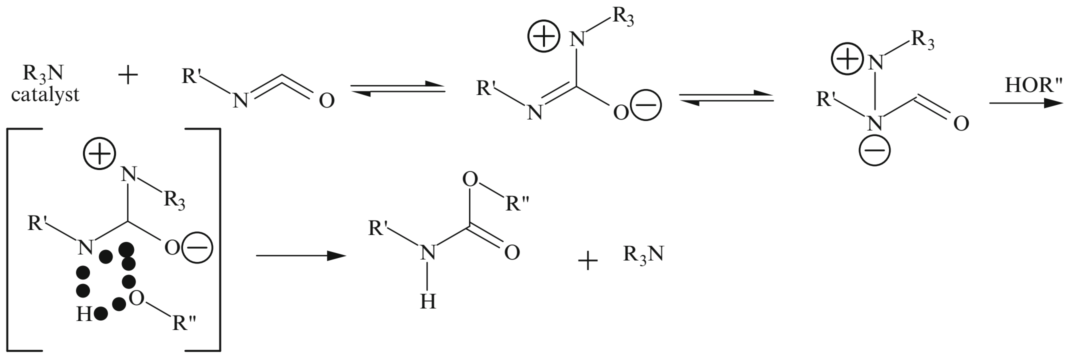
This makes an attack by an electron donor easier and yields a faster reaction. Electron donating groups, therefore, have an opposite effect.

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]:

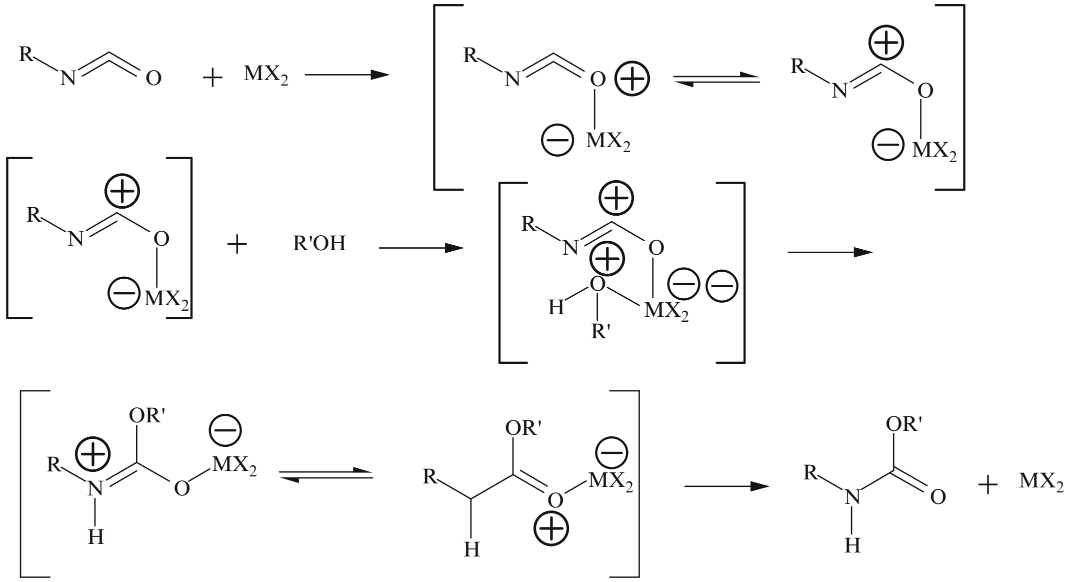


Table 7.8 T_m values of some fiber-forming polyurethanes [126, 132]

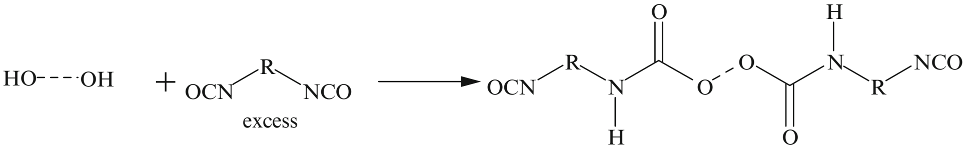
Diisocyanate	Glycol	T_m (°C)
$OCN(CH_2)_4NCO$	$HO(CH_2)_4OH$	190
$OCN(CH_2)_4NCO$	$HO(CH_2)_6OH$	180
$OCN(CH_2)_4NCO$	$HO(CH_2)_{10}OH$	170
$OCN(CH_2)_5NCO$	$HO(CH_2)_4OH$	159
$OCN(CH_2)_6NCO$	$HO(CH_2)_4OH$	183
$OCN(CH_2)_6NCO$	$HO(CH_2)_5OH$	159
$OCN(CH_2)_8NCO$	$HO(CH_2)_4OH$	160
$OCN(CH_2)_8NCO$	$HO(CH_2)_6OH$	153

Table 7.9 The effect of molar ratios on the molecular weight of the product [134–136]

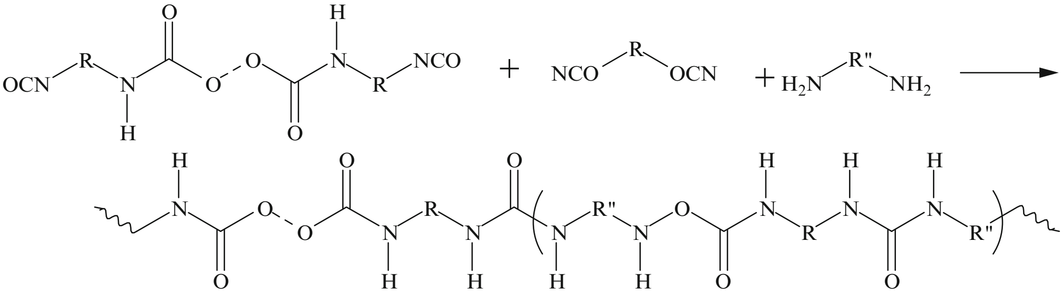
Ratio of epichlorohydrin to phenol	Molecular weight
10.0:1	370
2.0:1	451
1.4:1	791
1.33:1	802
1.25:1	1,133
1.2:1	1,420

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:

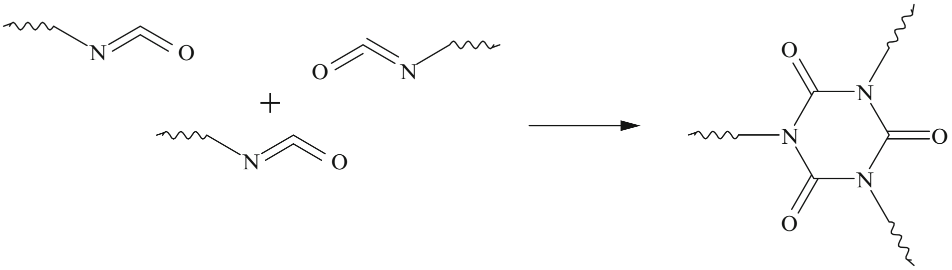


The prepolymers are spun into fibers and subsequently cross-linked, or cross-linked while they are being spun, to obtain resilient elastomeric fibers.

7.10.6 Polyurethane Elastomers

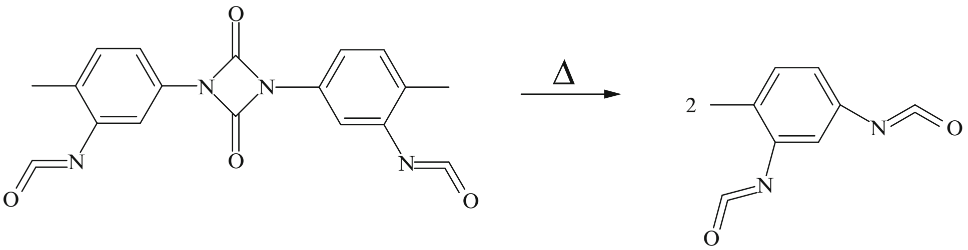
Solid elastomers can be divided into three categories, namely cast, millable, and thermoplastic ones. The cast elastomers are formed by casting liquid reaction mixtures of low molecular weight prepolymers into heated molds where they cross-link and convert to high molecular weight materials. Slightly 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:



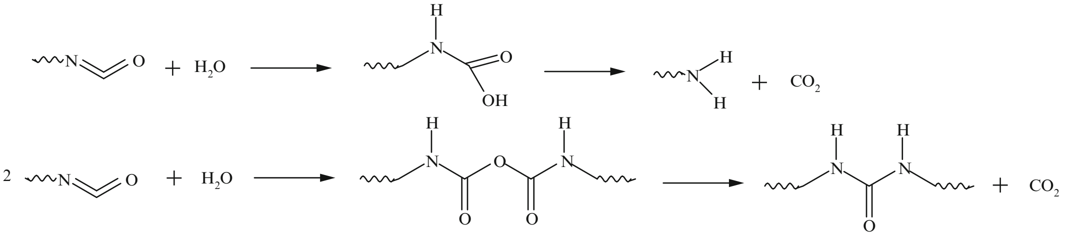
Unsaturated prepolymers cross-link with peroxides or sulfur. This unsaturation can be present in the backbone or in the pendant groups. Vulcanization or cross-linking of elastomers with sulfur or peroxides is discussed in Chap. 8.

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:



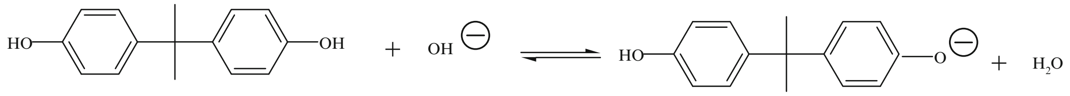
In addition, in many industrial practices, additional carbon dioxide or Freon gas (a major source of environmental pollution) may be introduced into the system as it cures. For rigid foams, a low boiling liquid may be added to form additional bubbles. Appropriate catalysts and foam stabilizers or surfactants 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.

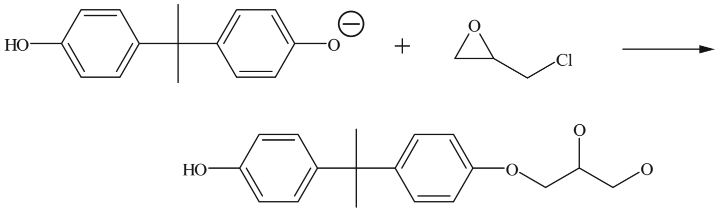
7.11 Epoxy Resins

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.

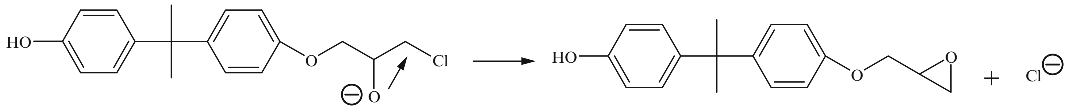
7.11.1 Preparation of Commercial Epoxy Resins

The earliest developed commercial epoxy resins were diglycidyl ethers of 4,4′-isopropylidinediphenol (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]:

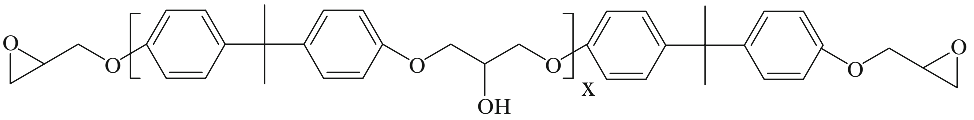




This is followed by ring closures through internal displacement of chloride ions:



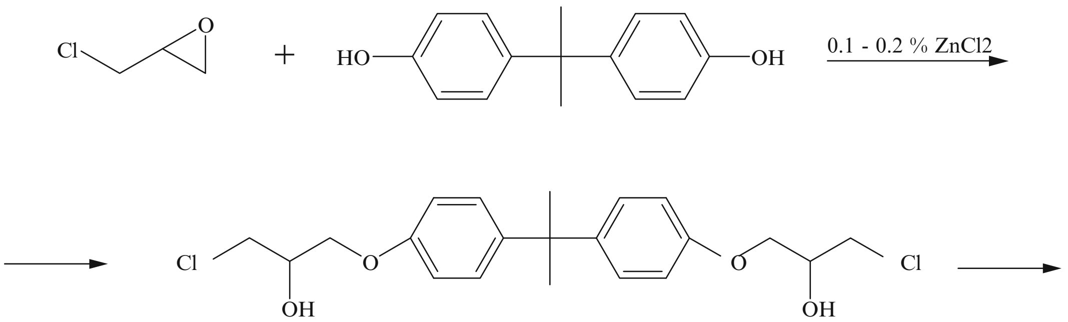
As explained in the discussion on phenoxy resins, a reaction of two moles of epichlorohydrin with one mole of the diphenol yields higher molecular weight by-products and only 10% of the diether:

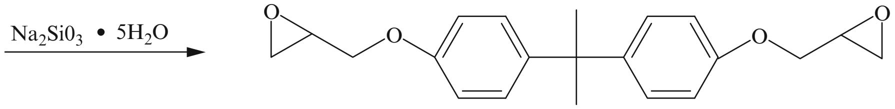


where $x = 1$–10

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.

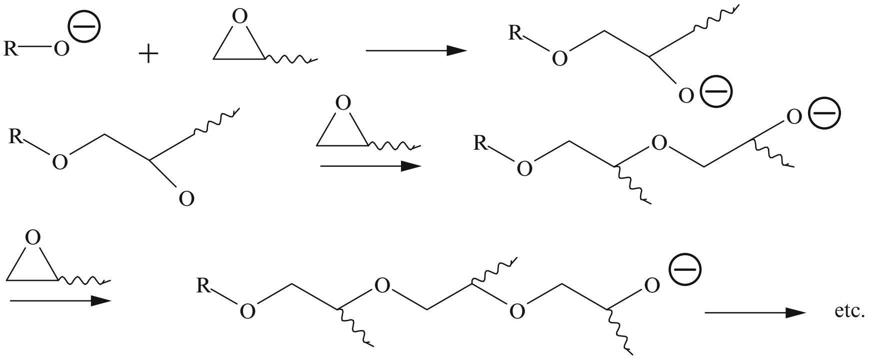
7.11.2 The Cross-linking Reactions

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:

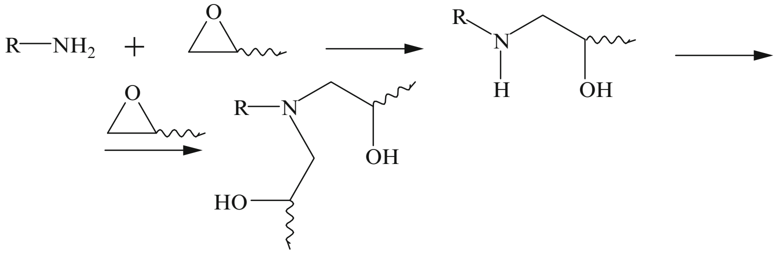
The product reacts with hydroxyl compounds to form anions:

The anions in turn initiate polymerizations of the epoxy groups:

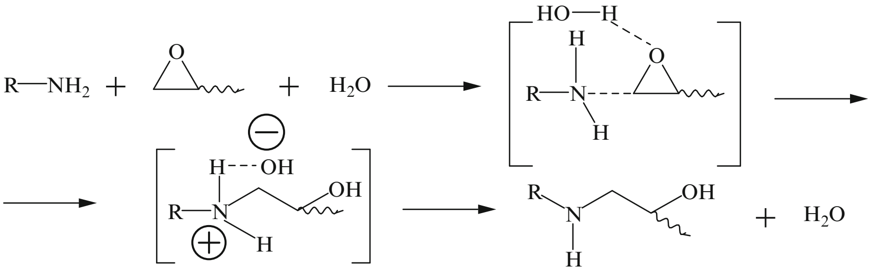


Because the monomer is a diepoxide, a three-dimensional lattice results. A similar three-dimensional product forms from reactions with other cross-linking materials, like boron trifluoride-etherate, boron trichloride-amine complexes, and imidazole derivatives. All these compounds initiate polymerizations 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]:

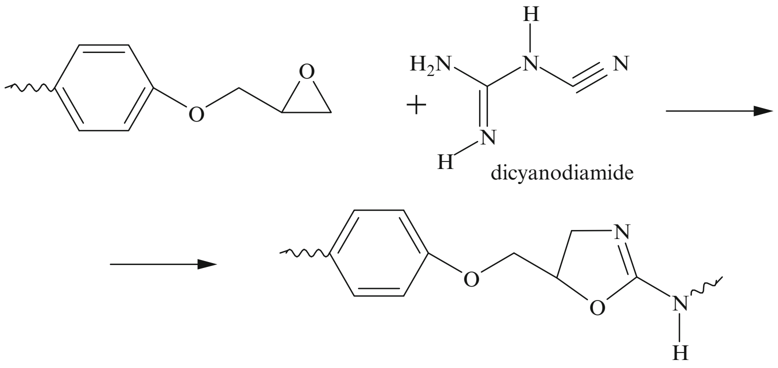


Epoxy resins can also be cured with the aid of ionic liquids [136]. The cross-linking reaction takes place at elevated temperatures

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.

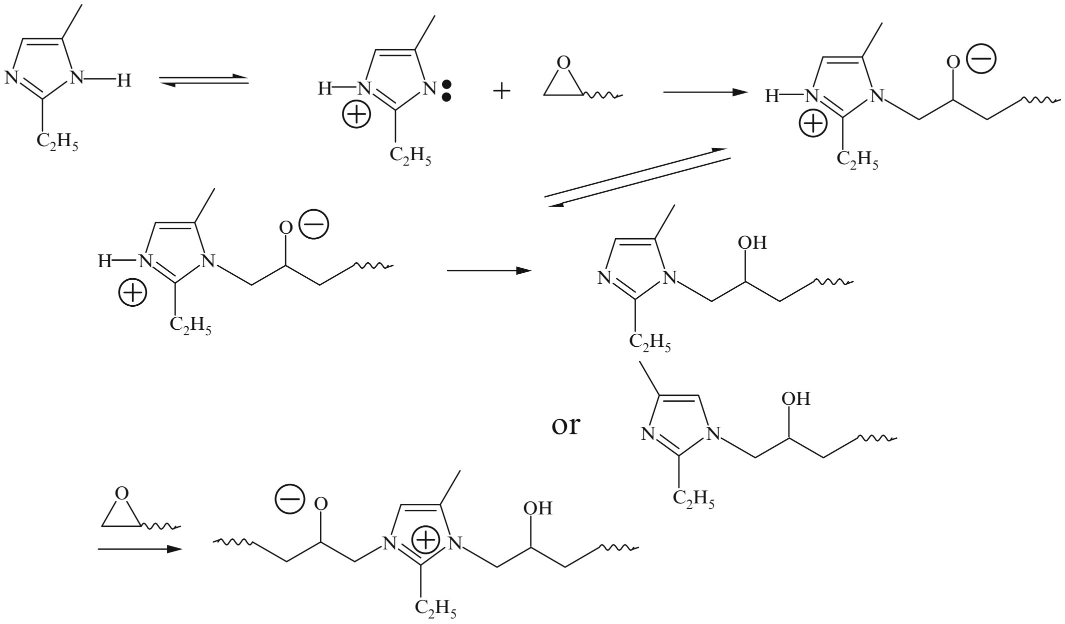
Many different aliphatic and aromatic polyamines are available for cross-linking epoxy resins. Some of these are ethylenediamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, and many others. Among the aromatic polyamine are *p*-phenylene diamine, *m*-phenylene diamine, 4,4′-diaminodiphenyl-methane, 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]:

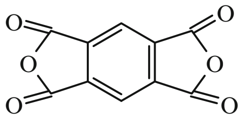


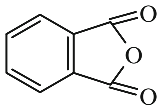
Earlier, however, it was speculated that guanidyl urea forms [140].

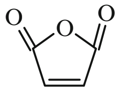
The curing mechanism of epoxy resins with imidazole was investigated. The following mechanism was proposed [137]:

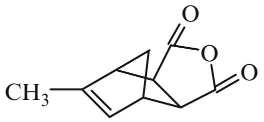


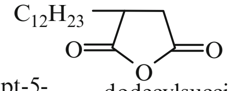
Many cyclic acid anhydrides are used industrially for cross-linking epoxy resins. These are mono and polyanhydrides. Following are some typical commercially used anhydrides:

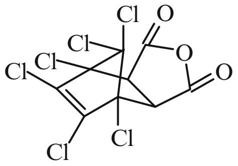

pyromellitic dianhydride

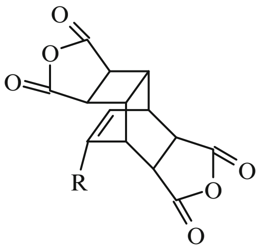

phthalic anhydride


maleic anhydride

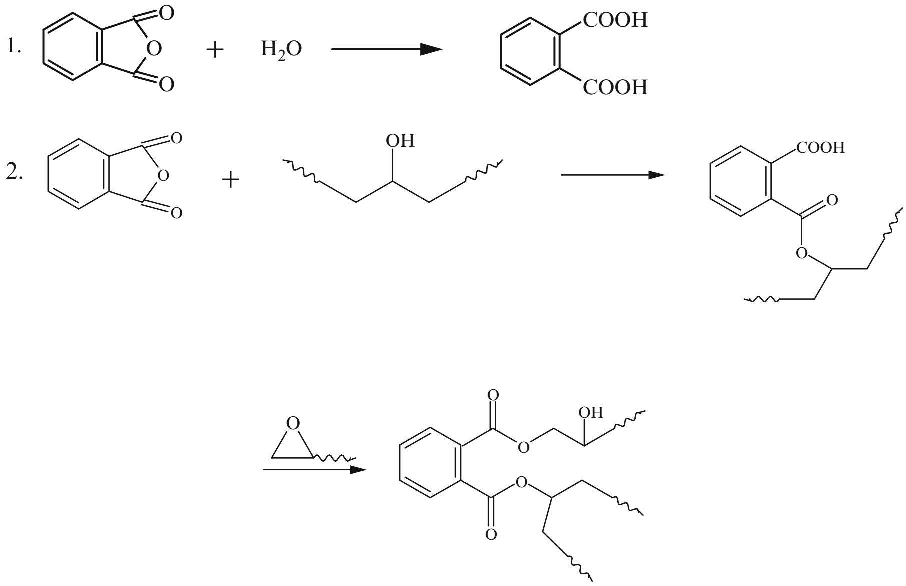

methylbicyclo [2,2,1]hept-5-ene-2,3-dicarboxylic acid anhydride


dodecylsuccinic anhydride

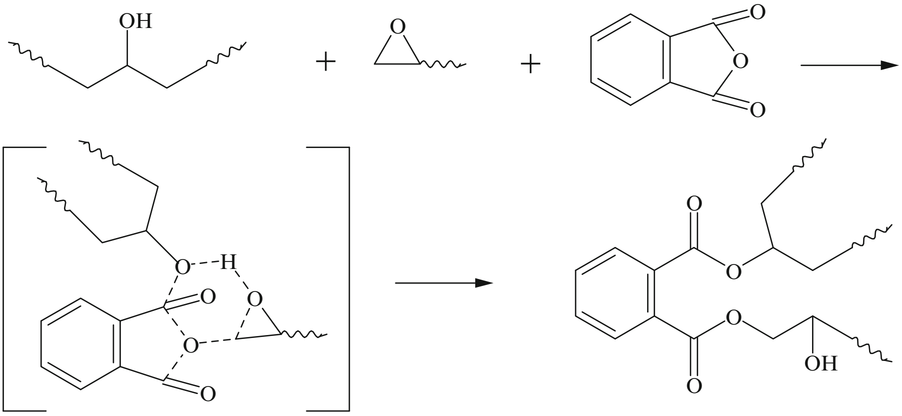

chlorendic anhydride


photoadduct of alkylbenzene and maleic anhydride[138]

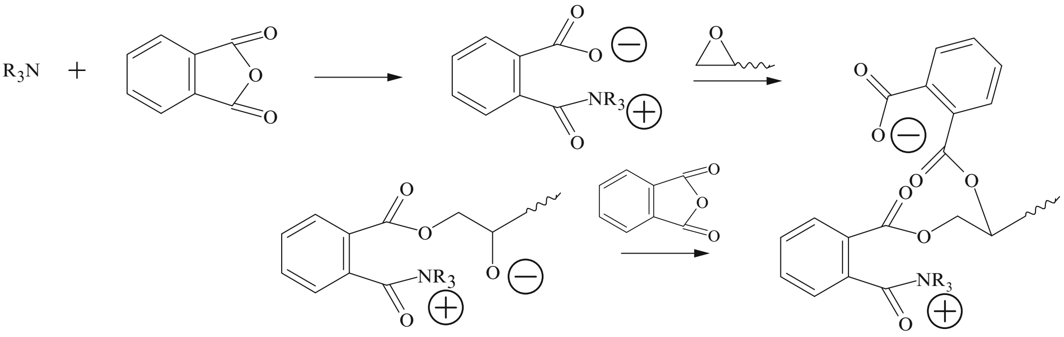
The anhydrides react with traces of moisture or with pendant hydroxyl groups first. This opens the anhydride groups and frees the carboxylic acids for reactions with the epoxy rings:



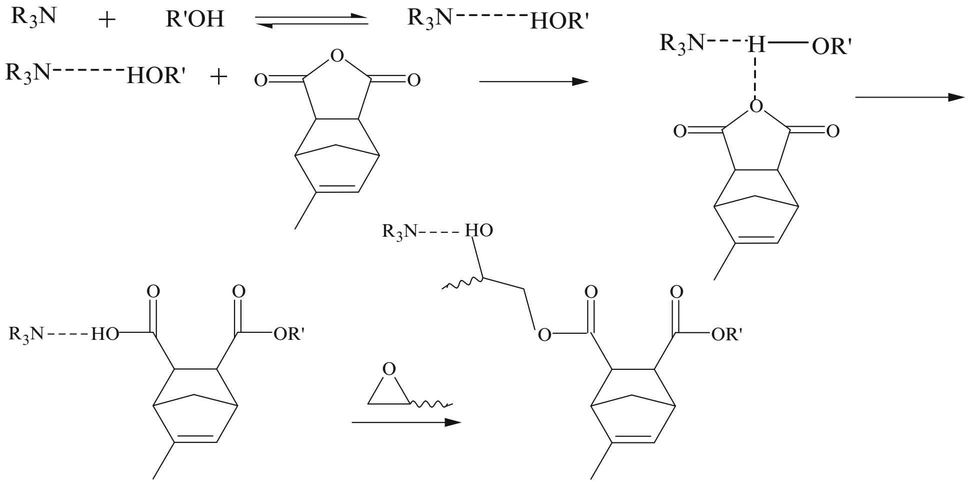
When only epoxy and hydroxyl groups are present, very little reaction takes place even at elevated temperatures, as high as 200°C. Proton donors, however, catalyze the reaction [139]. When anhydrides are present in the reaction mixtures, diesters form as a result of termolecular transition states. Kinetic data support that [136]:



Tertiary amines are very effective in catalyzing reactions of anhydrides with epoxies:

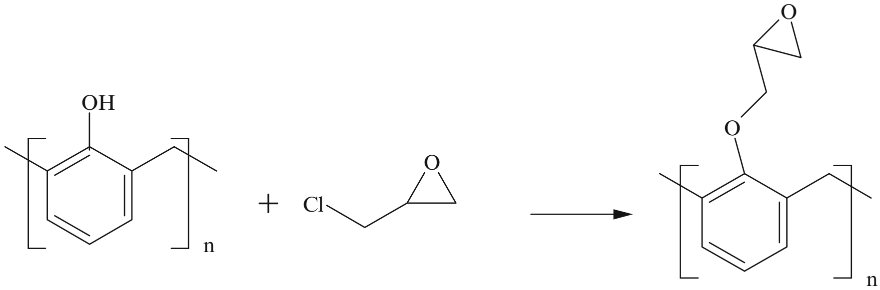


Reactions in the presence of alcohols take a somewhat different path [142, 143]:

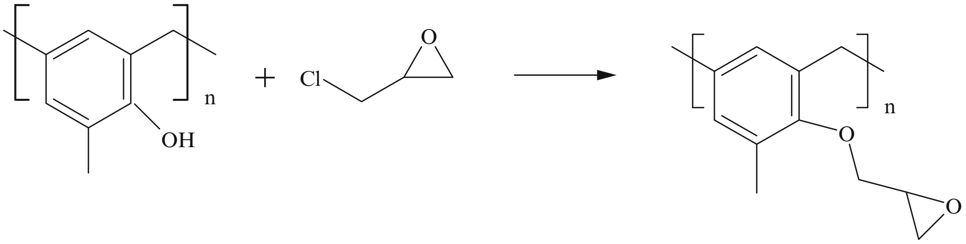


where, R′OH represents both epoxide molecules with hydroxyl function and other alcohols in the system.

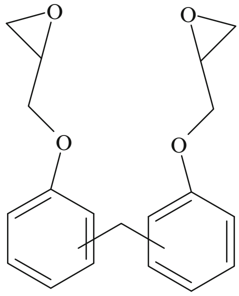
Another similar group of epoxy resins, called *epoxy novolacs*, forms from reactions of epichlorohydrin with low molecular weight phenolic novolacs (phenolic novolac resins are discussed in the next section):



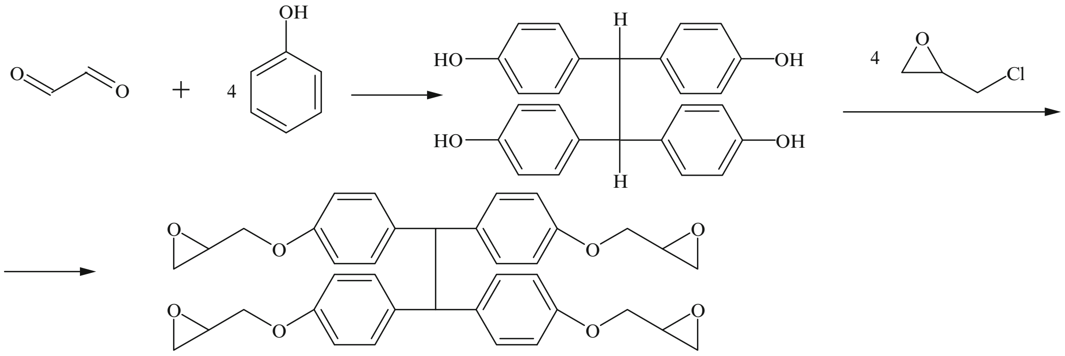
also



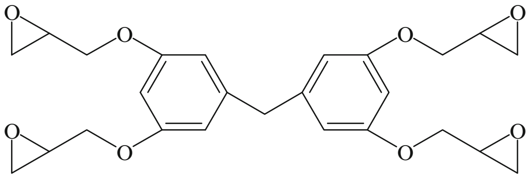
where, *n* is typically 2.2–3.8 for liquid epoxy novolacs and 3–7 for solid resins. Epoxy resins are also prepared commercially from Bisphenol F that is a blend of *ortho* and *para* diphenol methanes:



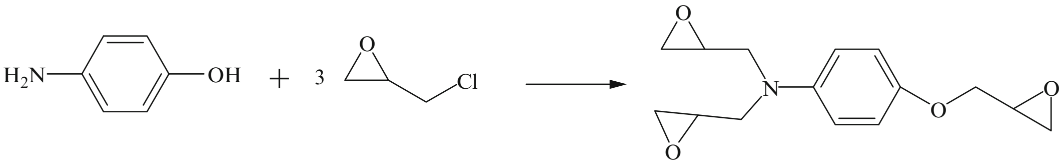
Another material is based on a condensation product of glyoxal with phenol:



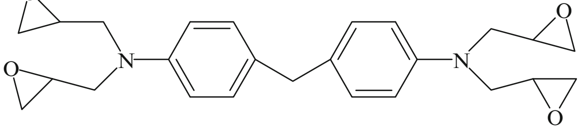
Epoxy resins formed by condensations of epichlorohydrin with resorcinol-based phenolic resins are also formed commercially:



Several nitrogen-containing aromatic epoxy resins were also commercialized. These are condensation products of aromatic amines with epichlorohydrin. Following are some examples [140]:



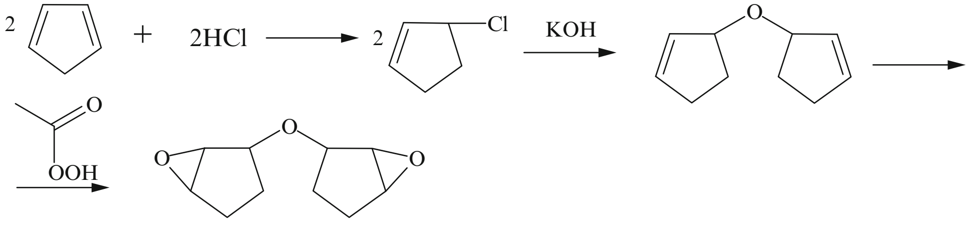
as well as:



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.

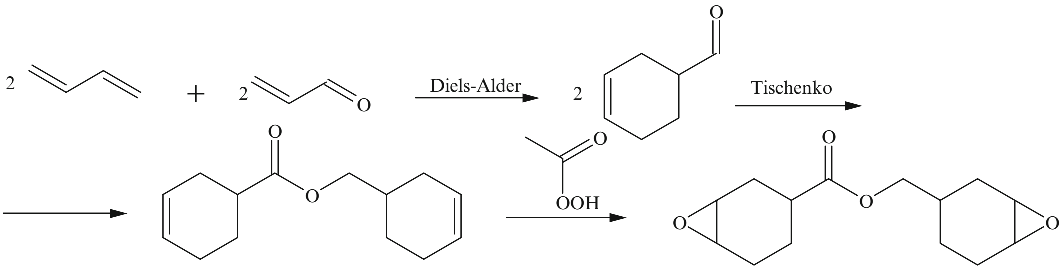
7.11.3 Cycloaliphatic Epoxides

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:

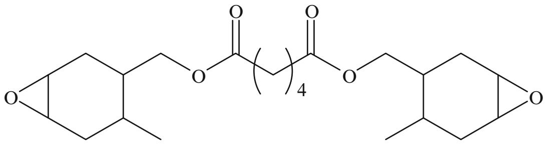


bis(2,3-epoxycyclopentyl) ether

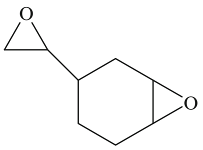
Another group of cycloaliphatic epoxy resins are prepared via Diels–Alder additions, followed by a Tischenko reaction, and completed by epoxidation. A preparation, for instance, may start with butadiene and acrolein:



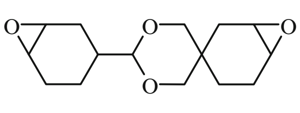
Examples of some other cycloaliphatic epoxy resins are:



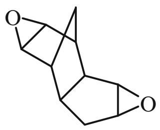
bis(3,4-epoxy-6-mehyl-cyclohexyl)adipate



vinyl cyclohexyl dioxide



2-(3,4-epoxycyclohexyl)-5,5-
spiro(3,4-epoxy)cyclohexane-*m*-dioxane



dicyclopentadiene dioxide

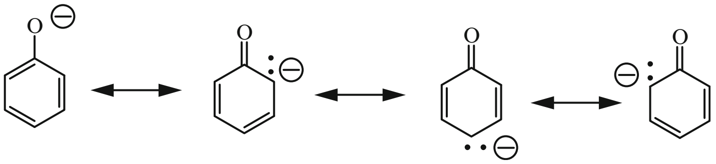
Acid anhydrides are more effective curing agents for cycloaliphatic epoxy resins than are the amines. In addition, the amines might also react with ester groups that are present in some of these materials and form undesirable by-products.

7.12 Phenol-Formaldehyde Resins

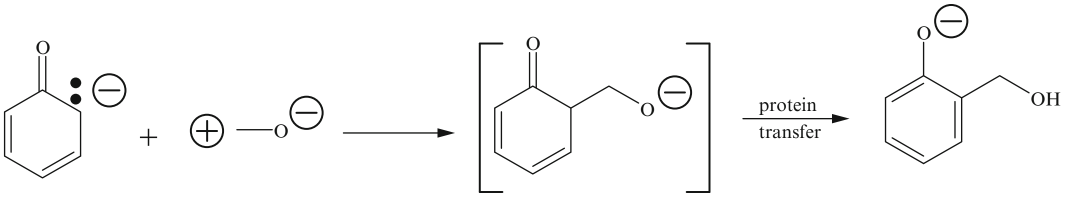
The phenolic resins are condensation products of phenol and formaldehyde [144–146, 148]. These materials were among the earliest commercial synthetic plastics. Two different methods [144–146] are used to prepare them. In the first one, the condensations are base catalyzed, while in the second one, they 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

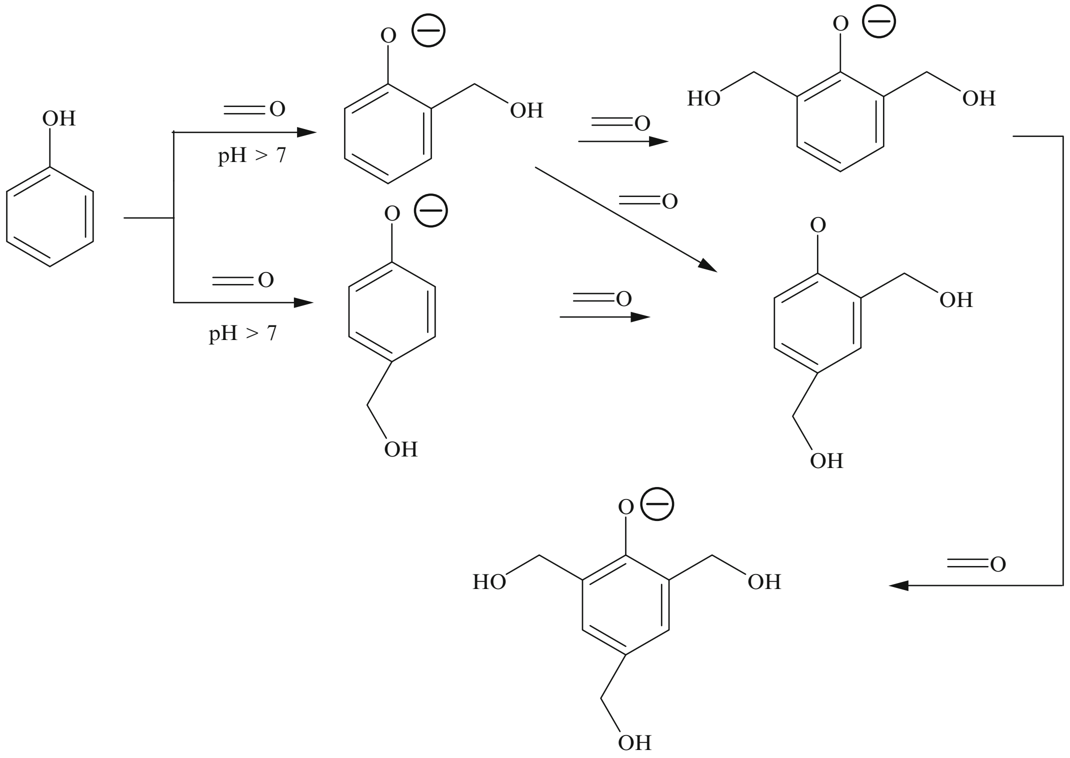
These thermosetting resins form in reactions of phenols with formaldehyde in water in the presence of catalytic amounts of bases. Under these conditions, phenol exists as a resonance-stabilized anion:



The addition of the phenol anion to formaldehyde is a typical nucleophilic reaction:



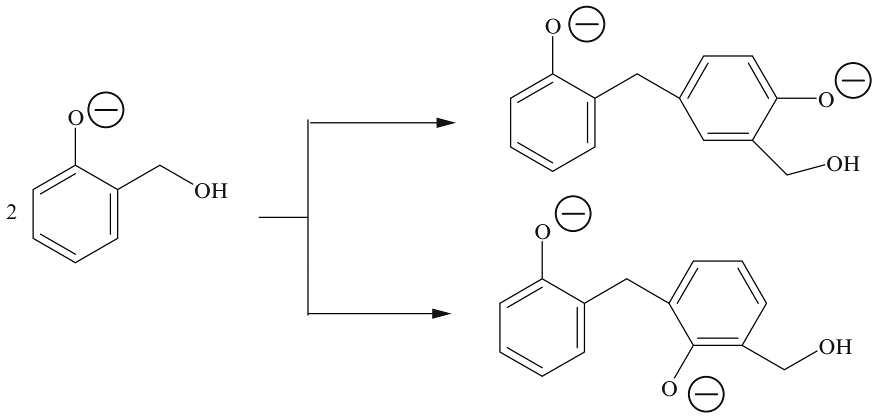
Both *ortho* and *para* methylolphenols form in the above reaction. Phenol is very reactive and monosubstituted phenols are hard to isolate from the reaction mixture, because di- and trisubstitution occurs rapidly. No substitutions were ever shown to take place in the *meta* position. The overall reaction is as follows:



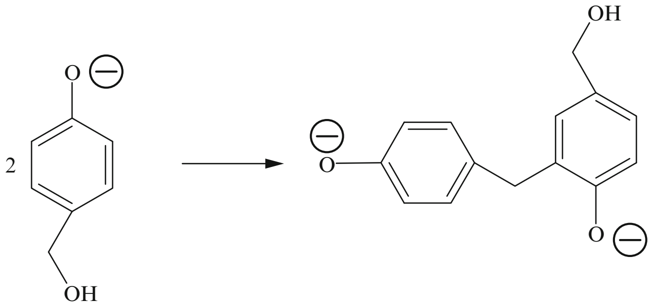
When an aqueous reaction of phenol and formaldehyde, catalyzed by sodium hydroxide, is carried out at 30°C for 5 h, the products are [147]:

2,4,6-trimethylolphenol	37%
2,4-dimethylolphenol	24%
2,6-dimethylolphenol	7%
p-methylolphenol	17%
o-methylolphenol	12%

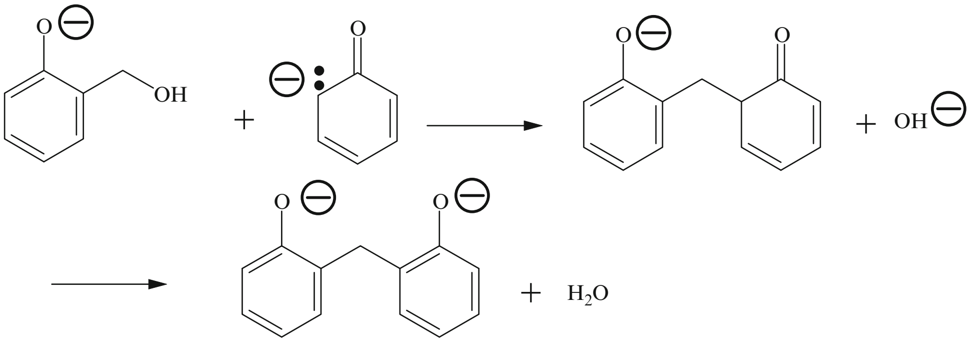
The remaining 3% is unreacted phenol. As the reaction continues, methylolphenols condense with each other to form methylene bridges:



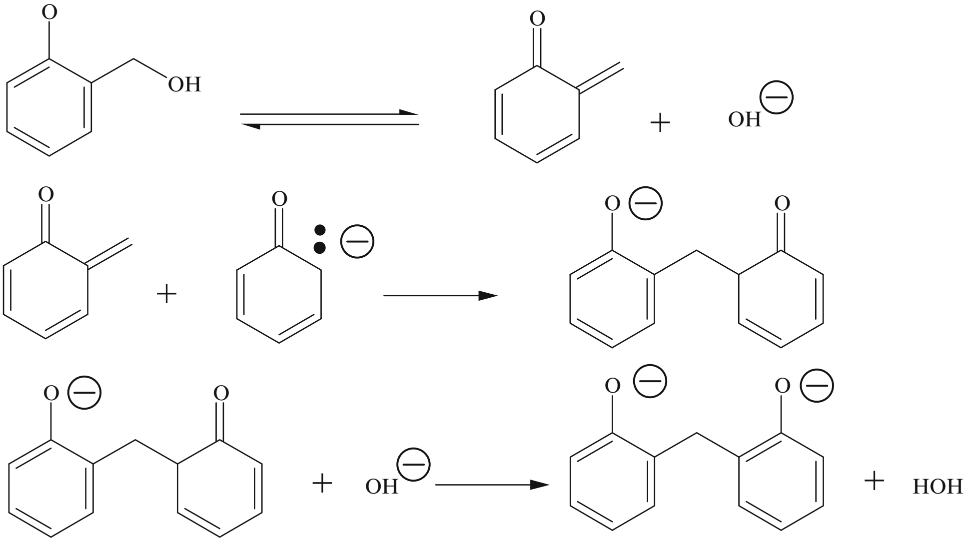
The *para* substituted methylolphenols, of course, react in the same manner:



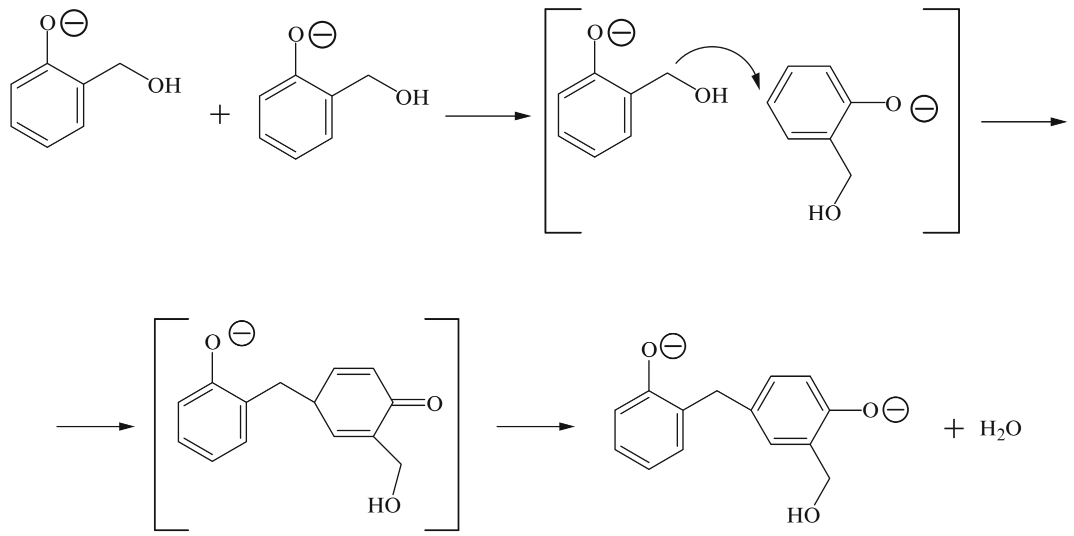
Formation of methylene bridges take place by one of two mechanisms. One is a direct S_N2 displacement:



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]:

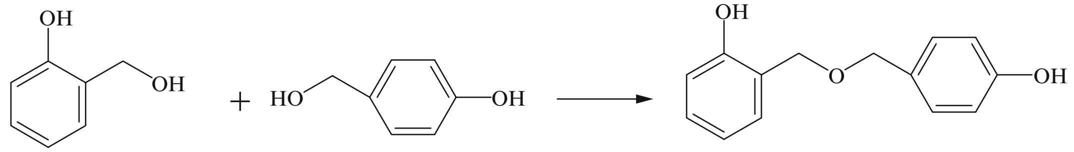


Two methylol-substituted phenols react with each other by the same mechanism:

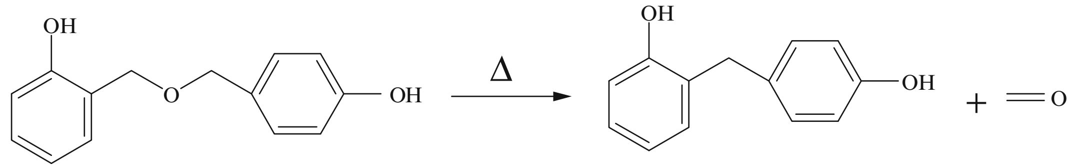


The same can be shown for *para* substituted methylolphenols. As the reaction continues, it leads to formation of trinuclear and tetra nuclear phenolic resins.

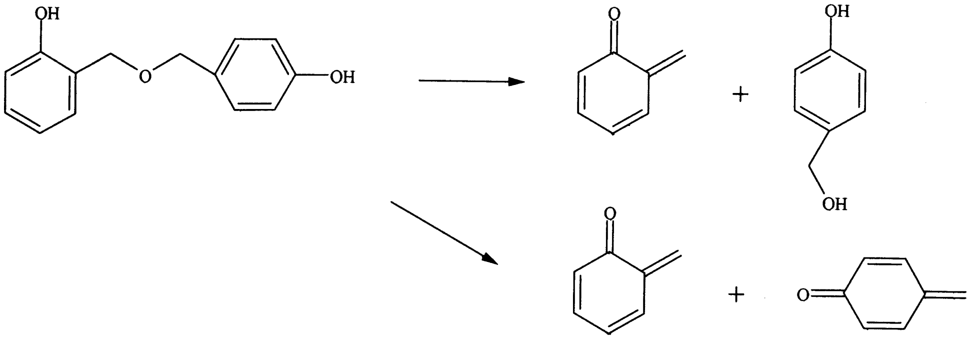
A typical liquid resole is quite low in molecular weight. It may contain no more than two or three benzene rings. Carried a little further, the condensation yields a solid resole. The pH is usually adjusted to neutral before the resoles are heated further for cross-linking. Under neutral or slightly acidic conditions, the methylol groups tend to form dibenzyl ethers:



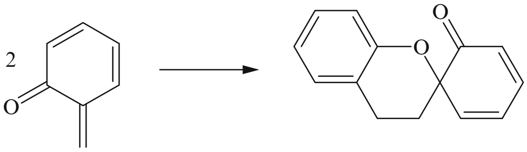
These dibenzyl ethers are unstable at higher temperatures, such as 150°C, and decompose to yield methylene bridges and formaldehyde [147]:



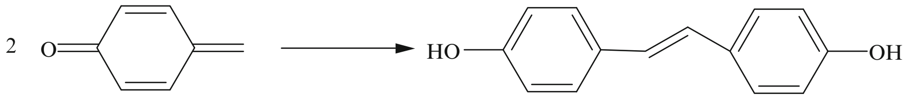
The structure of a typical resole contains both dimethylene ether and methylene bridges as well as methylol groups. Fusible and soluble resols are called A-stage resins. Further reactions cause these resins to pass through a rubbery stage where they can still be swollen by solvents. This is called B-stage. 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:

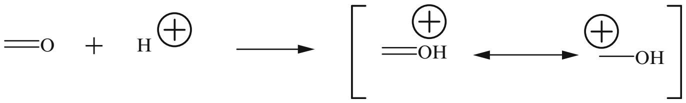


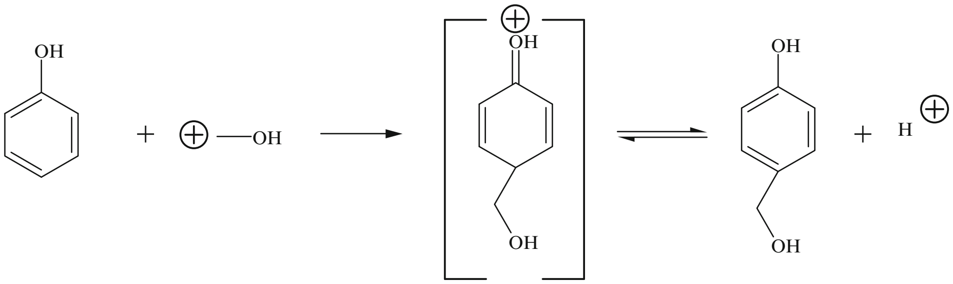
The *para* quinone methides can couple:

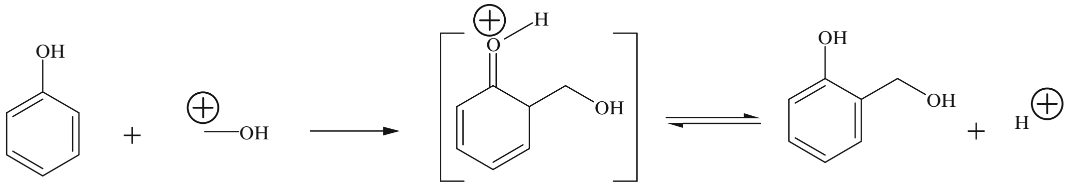


7.12.2 Novolacs

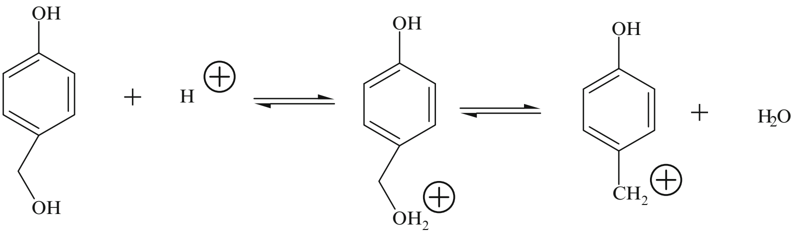
The phenolic resins that form in acid-catalyzed condensations of phenols with formaldehyde are different from resols. At pH below seven protonation of the carbonyl group of formaldehyde takes place first and is followed by electrophilic aromatic substitution at the *ortho* and *para* positions of the 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:

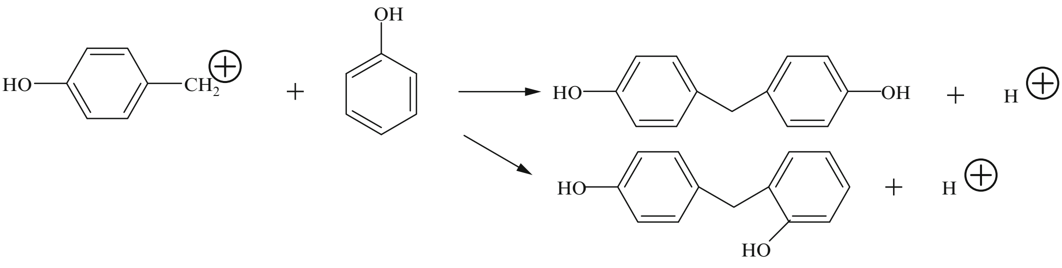






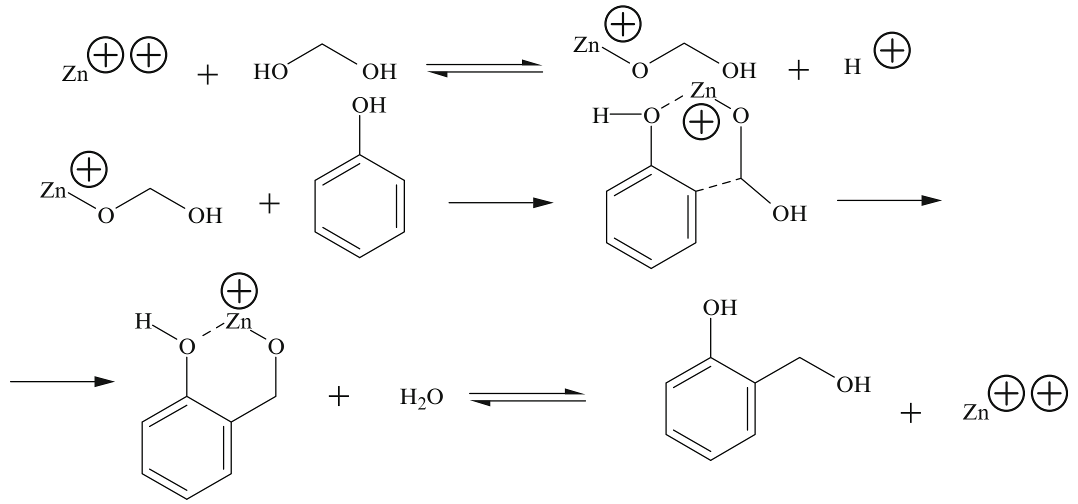
Because the reaction is taking place at pH below 7, the above shown *p*- and *o*-methylolphenols are transitory and are present in small concentrations only. Hydrogen ions convert them to benzylic carbocations that react rapidly with free phenol. This can be illustrated as follows:

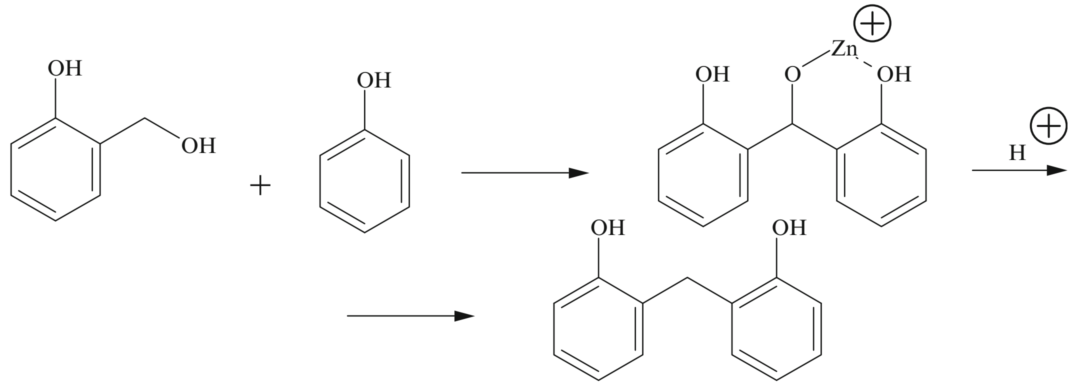




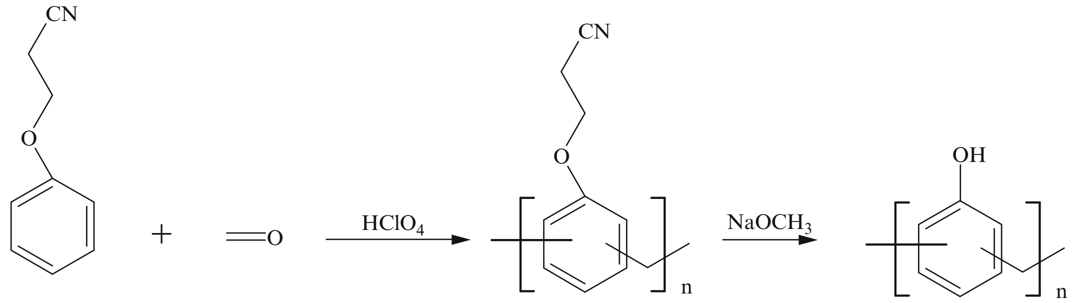
The *ortho* substituted methylolphenols react in the same manner.

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:

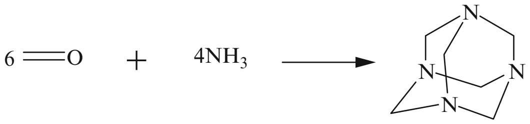




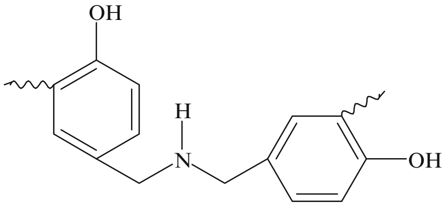
It is possible to form high molecular weight novolacs by carrying out the reactions of alkyl phenyl ethers with formaldehyde in acetic acid in the presence of perchloric acid [149]:



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:



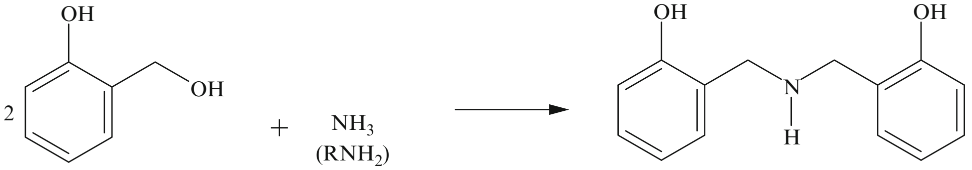
Hexamethylenetetramine decomposes to formaldehyde and ammonia upon heating. Some of the ammonia is picked up by the novolacs with the result that there are some benzylamine bridges in the product:



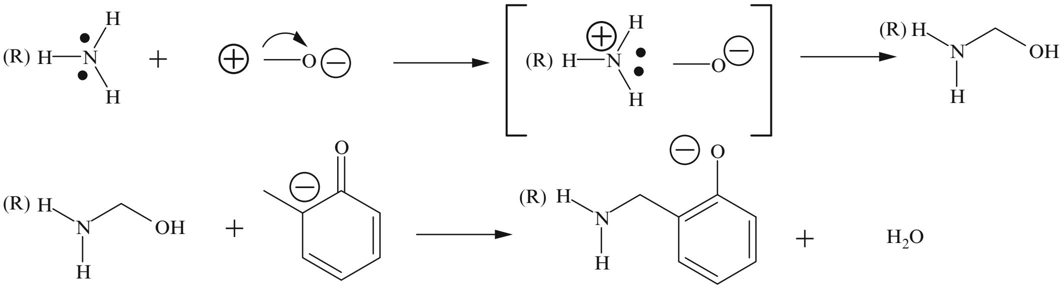
The mechanism of this reaction is discussed in the next section.

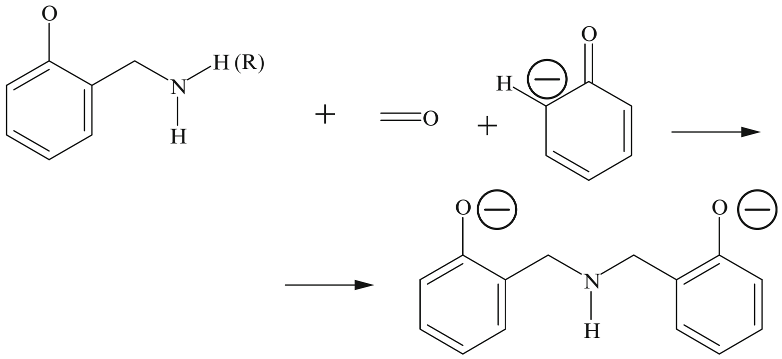
7.12.3 Ammonia-Catalyzed Phenolic Resins

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.

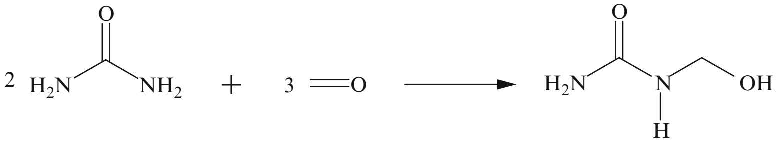
Xylenols (all six isomers) are now also in common use to form alkali-resistant grades of phenolic resins. High 3,5-xylenol mixtures are preferred. Also, resorcinol, which forms very reactive phenolic resins, is used in preparations of cold-setting adhesives. Higher homologues of phenol, like Bisphenol A, are used to prepare special phenol-formaldehyde condensates.

7.13 Amino Polymers

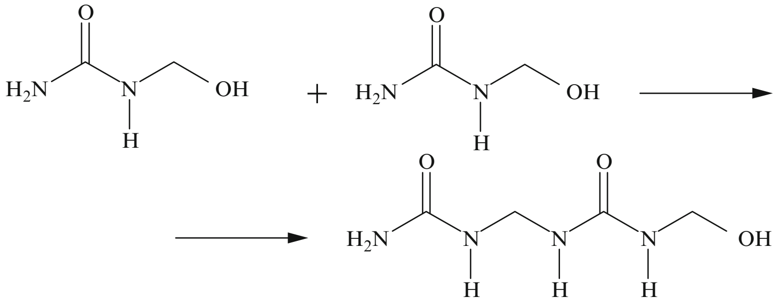
Currently, the bulk of the commercial polymers that would fit into this category are urea-formaldehyde and melamine-formaldehyde resins [151]. Over the years, however, many other materials that might fit into this group were prepared but not adopted for use for various reasons.

7.13.1 Urea-Formaldehyde Resins

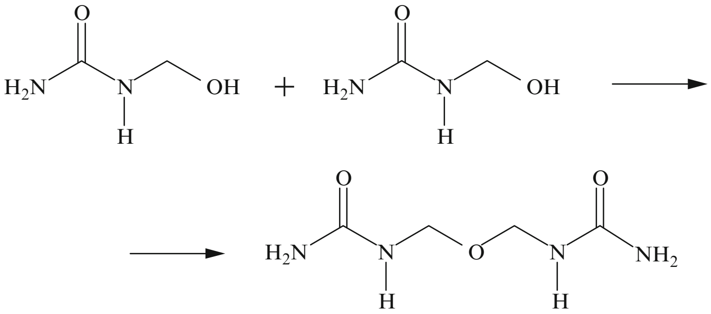
These thermosetting resins find applications in coatings, adhesives, laminating, and molding compositions. The materials are formed in water at a pH above 7 at the start of the reaction, because the methylol derivatives that form condense rapidly at acidic conditions. The initial step, where urea undergoes 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:



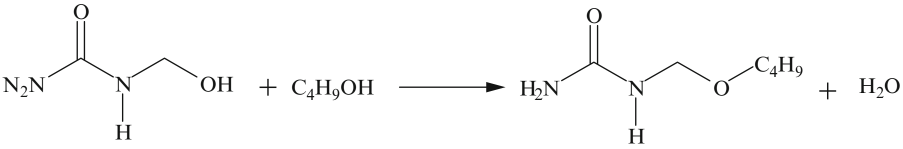
Under alkaline conditions, on the other hand, dimethylene ether groups form instead [152]:



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.

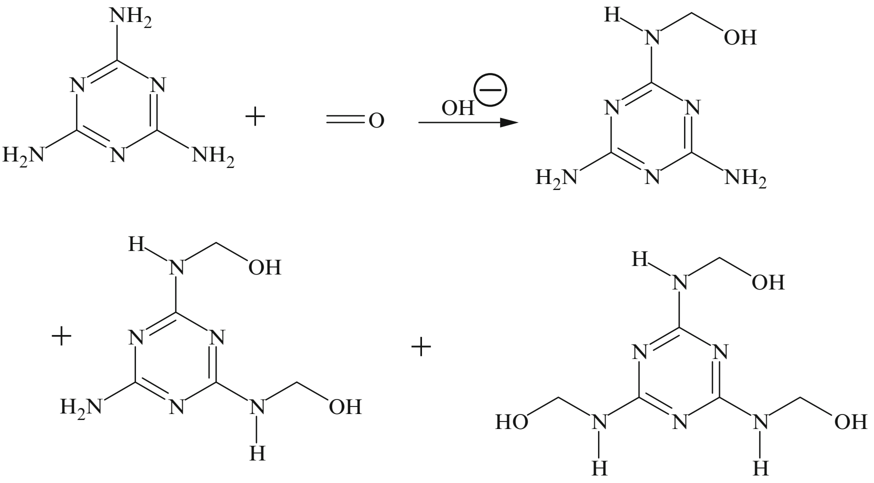
Urea-formaldehyde resins for surface coatings are commonly modified for solubility in organic solvents by reacting them with alcohols to form ether groups. Usually, *n*-butyl alcohol is used. The reaction is carried out under basic conditions, before acidification:



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.

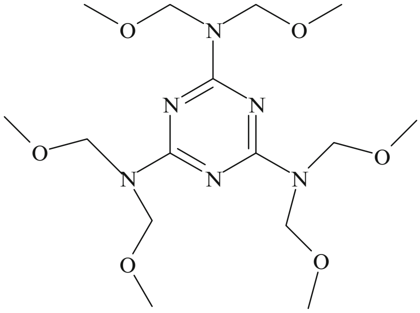
7.13.2 Melamine-Formaldehyde Resins

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.

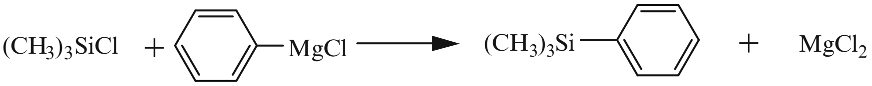
The starting materials can be prepared through hydrolyses of alkyl or arylsilicone halides [156–160]. Organosilicone halides, in turn, are made commercially by heating alkyl or aryl halides with silicon at 250–289°C. Copper catalyzes this reaction:

$$RCl + Si \xrightarrow[Cu]{250\text{ - }280\ ^{o}C} SiCl_4 + RSiCl_3 + R_2SiCl_2 + R_3SiCl$$

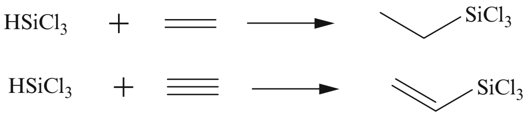
The same materials can also be formed by the Grignard reaction:

$$RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$$

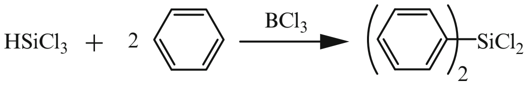
$$RMgCl + R_2SiCl_2 \longrightarrow R_3SiCl + MgCl_2$$



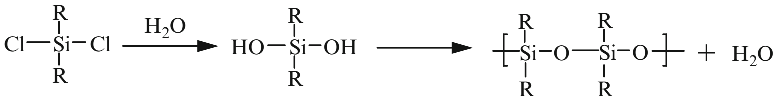
Alkyl silanes can also be prepared by additions of trichlorosilanes to ethylene or acetylene:



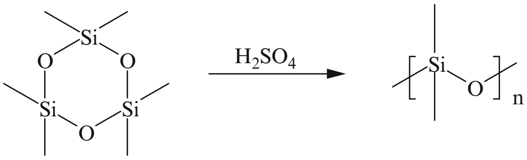
Trichlorosilane reacts with aromatic compounds in the presence of boron trichloride:



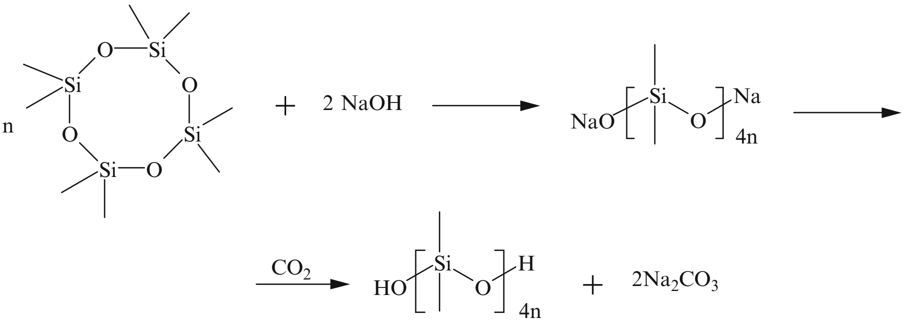
The siloxane linkages can result from hydrolysis of the halides. The products of hydrolyses, silanols, are unstable and condense:



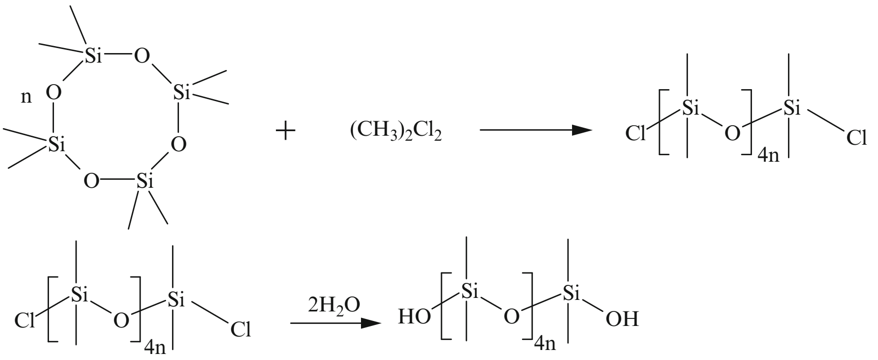
The above shown reaction is one possible route to siloxane polymers. As a general method, however, this approach is not very satisfactory, because ring formations accompany the reactions. Some rings that form from hydrolyses of trichlorosilanes are structurally complex [161]. They may even possess three-dimensional 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.



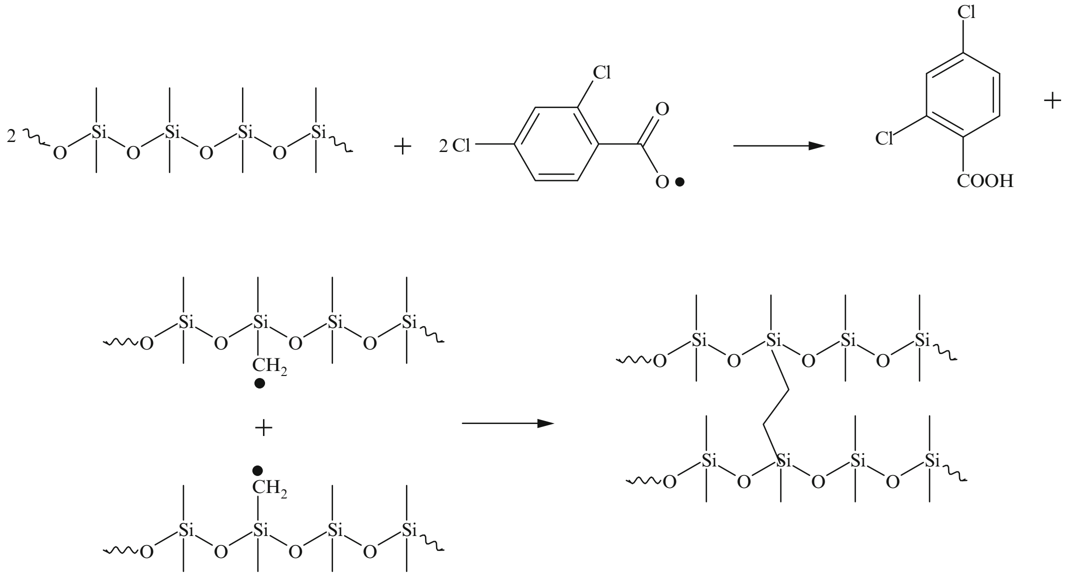
Another method of forming polydialkyldisiloxanes is by reacting difunctional oligomers with cyclic organisilicons:



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.

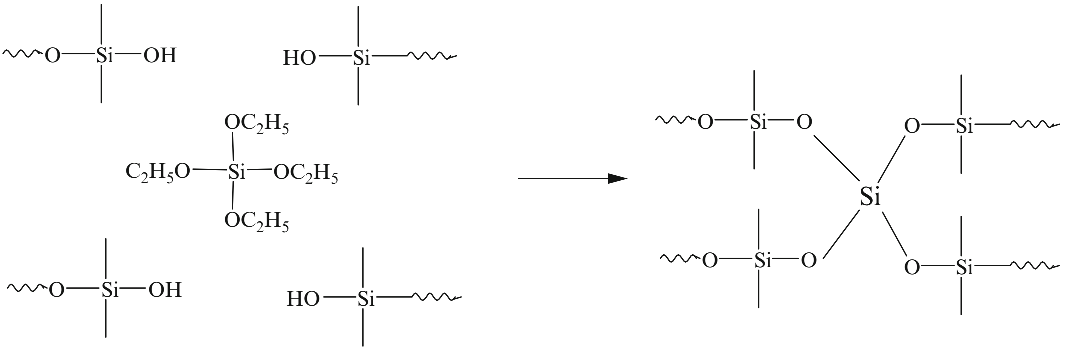
7.14.2 Silicone Elastomers

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:



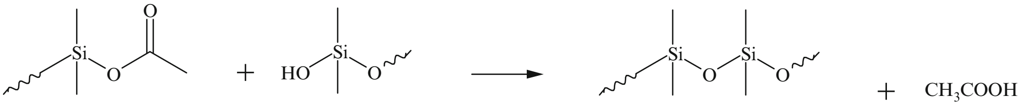
The same can be accomplished by replacing a small quantity of the methyl groups with vinyl ones. This can be done by including a small amount of vinyl methyldichlorosilane into the monomer mix (about 0.1%). The product with a small quantity of pendant vinyl groups cross-links readily by free-radical 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:

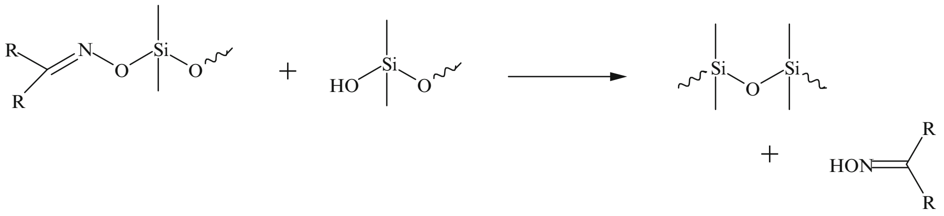


In the second one, polysiloxanes terminated by hydroxyl groups are either: (1) acetylated, (2) converted to ketoximes, or (3) etherified. The cross-linking is activated by reaction with atmospheric moisture:

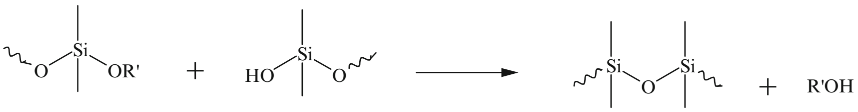
(1)



(2)



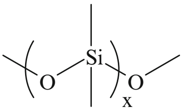
(3)



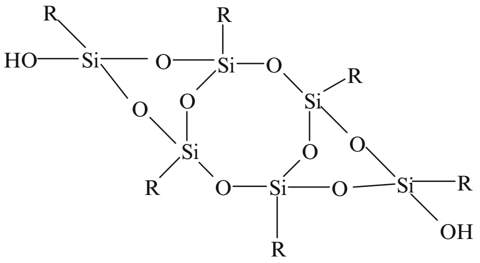
The acetate-capped RTV-s exhibit good adhesion to substrates, but the released acetic acid can be corrosive.

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:



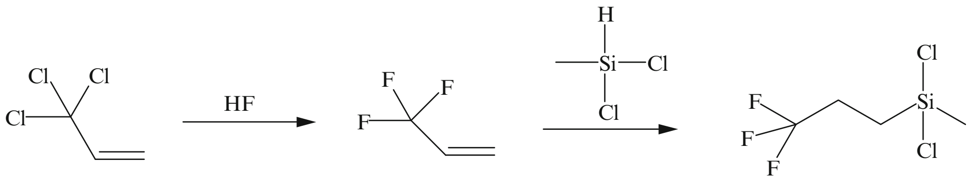
and



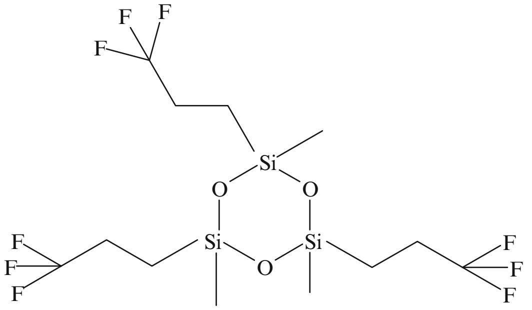
where $x = 3$–6.

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:



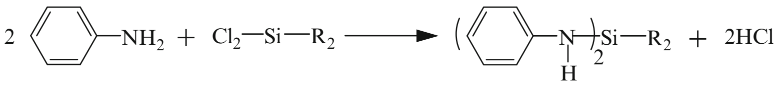
The above dichloro silane is converted to a cyclic trimer:



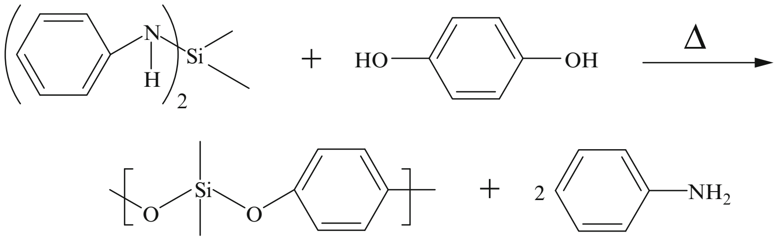
Ring opening polymerizations with basic catalysts convert the trimers to polymers at elevated temperatures. Some vinyl silane is usually copolymerized with the material for subsequent cross-linking. These elastomers are reported to be capable of maintaining their original strengths at temperatures as high as 205°C for long periods of time.

7.14.5 Polyarylsiloxanes (Also See Sect. 7.17.4)

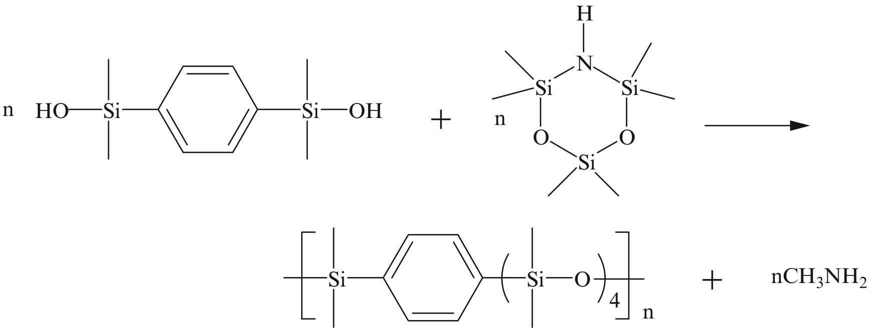
Many different polyarylsiloxanes were reported in the literature. Only a few of them are in general industrial use at present, though many exhibit interesting physical properties and might be used in the future. Preparation of one such material [164] starts with a reaction of aniline with dichlorosilane in the presence of an HCl scavenger:



The product, dianilinosilane, is reacted with diphenols, like hydroquinone:



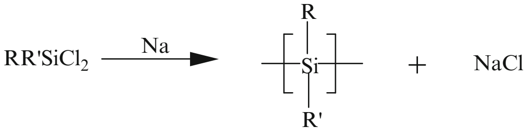
Polymers prepared by the above procedure have molecular weights up to 80,000 [164]. It is also possible to start with diphenoxysiloxane and catalyze the reaction with sodium or lithium metals. Reactions of cyclic silazanes with arylene disalanols yield polymers with molecular weights as high as 900,000 [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]:



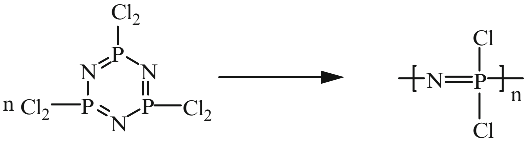
$$RR'SiCl_2 \xrightarrow{Na} \left[\overset{R}{\underset{R'}{Si}} \right] + NaCl$$

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].

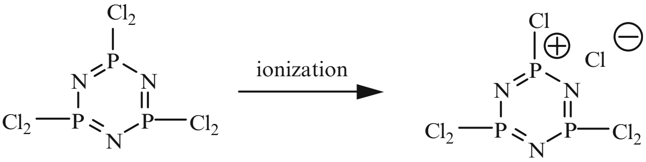
Recently, an ambient temperature sonochemical reductive coupling process was developed [172]. The reaction is carried out in the presence of an ultrasound and results in relatively high (M_n = 50,000–100,000) molecular weight materials with narrow molecular weight distributions. In addition, it was reported [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

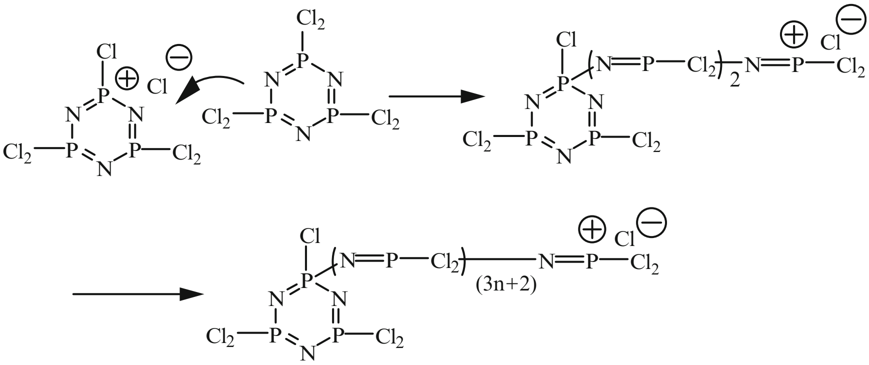
These polymers, also called *polyphosphazenes*, are useful materials when they are substituted with organic compounds [173]. They are prepared from hexachloro-cyclotriphosphazenes by ring opening polymerizations:



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]:

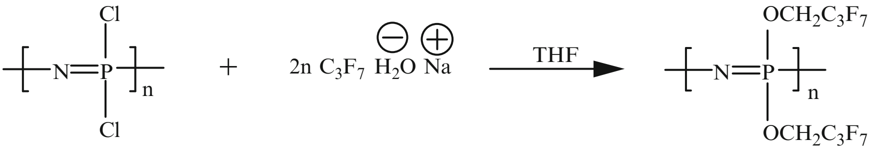


This is followed by an attack on another monomer molecule:



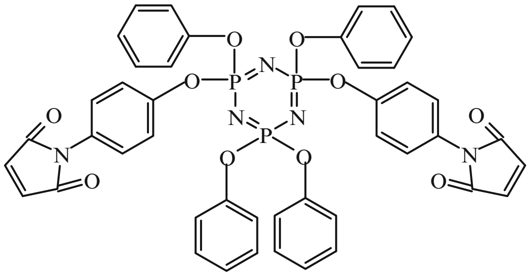
Alkyl, aryl, alkoxy, and aminocyclotriphosphazenes fail to polymerize. This is believed to be due to an absence of easily ionizable halogen to phosphorus bonds. At the same time, materials that presumably facilitate ionization of the phosphorus to halogen bonds, such as water, carboxylic acids, and metals, 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:

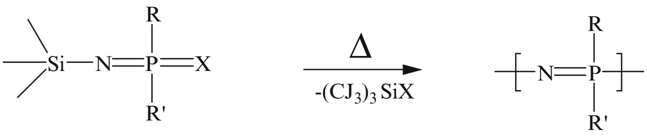


Mixed fluoroalkoxy compounds can be used to obtain a variety of properties. The materials find application as elastomers, because they exhibit good chemical resistance and good thermal stability. In addition, many retain the useful elastomeric properties at low temperature. As a result, among other applications, 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.

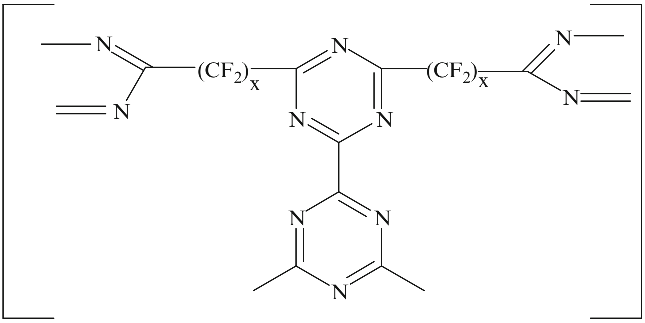
In developing tough, heat-resistant polymers the chemists pursued several goals [191]. These were:

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

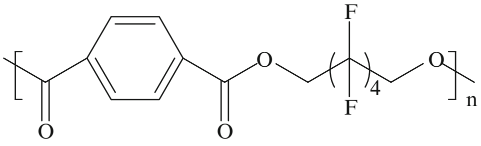
The high strength of the carbon-fluorine bonds and the shielding effect of the highly electronegative fluorine atoms improve heat stability. One such material was synthesized by heating perfluoroalkyl amidines above their melting points. Ammonia evolves and triazine ring containing polymers form [174]:



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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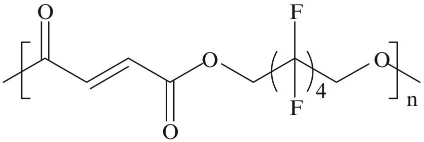

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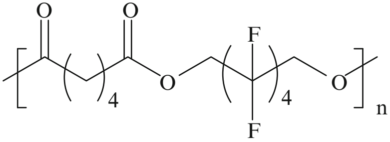
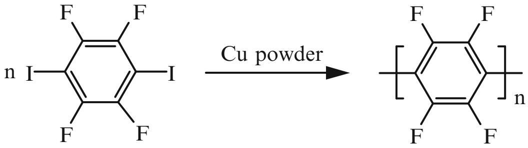
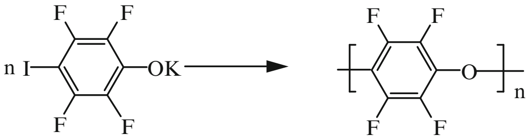


Their heat stability and other physical properties, however, do not appear to be superior to conventional materials. The Ullmann reaction can be used to prepare polyperfluorophenylene [176]. The products, however, are low in molecular weight:

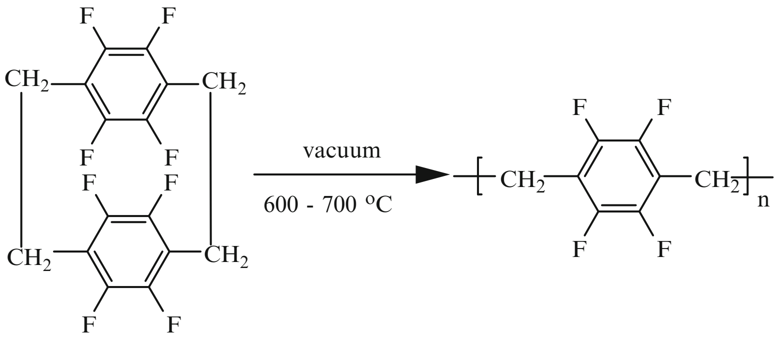


Higher molecular weight materials, like poly(perfluorophenylene ether), form from potassium pentafluorophenoxide [177], where M_n is about 12,500:



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($\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-*p*-xylylene) by a polymerization technique that closely resembles the preparation of poly(*p*-xylylene) by vacuum pyrolysis of a dimer [181]:

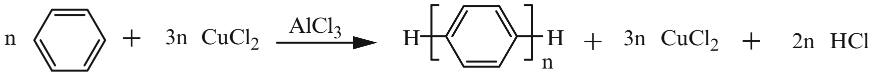


The resultant polymers maintain useful mechanical properties for up to 3,000 h in air at 250°C.

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.

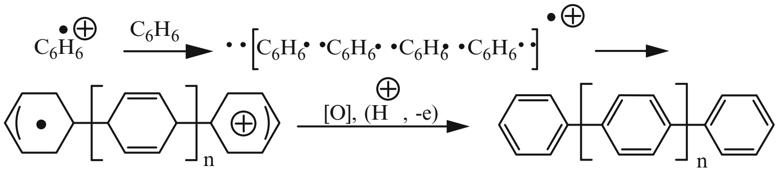
7.17.2 *Polyphenylene*

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]:



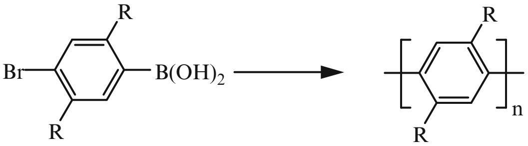
The yield of polymers reaches a maximum value (close to quantitative) at an aluminum chloride to cupric chloride molar ratio of 2:1 [180]. Solvents, concentrations, and temperatures affect the molecular weights of the products [189]. Other Lewis acids that are effective in benzene polymerizations are $MoCl_5$, $FeCl_3$, 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.

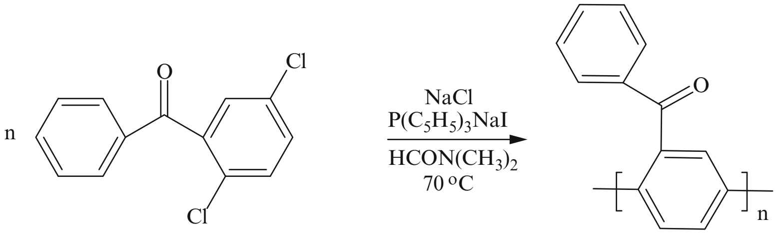
The polymer is very stable up to 500–600°C and oxidizes very slowly. It is, however, quite insoluble with a very high melting point that makes is difficult to process and even to determine its molecular weight. Introduction of irregularity into the polymeric structure by copolymerizing terphenyl, biphenyl, 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].

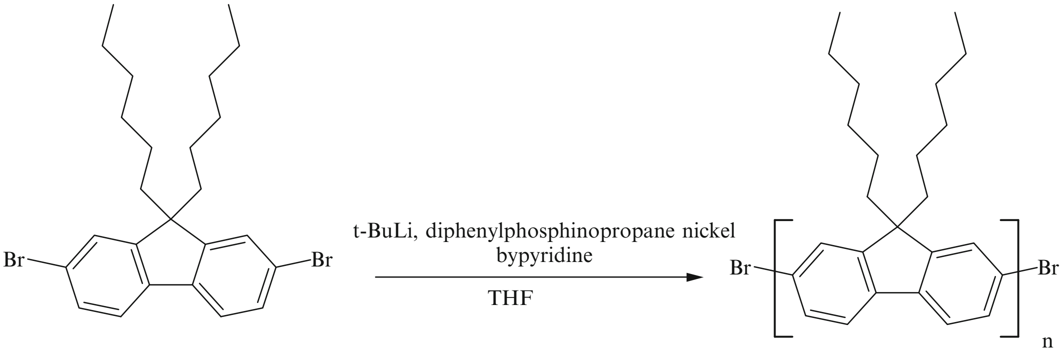
Goodson et al. [246] reported formation of soluble derivatives of poly(*p*-phenylene) of high molecular weight via Suzuki coupling reactions catalyzed by palladium (0) precursors in the presence of either triphenylphosphine or tri(*o*-tolyl)phosphine. Use of triphenylphosphine, however, apparently resulted in incorporation of the phosphine [246].

Formation of poly(benzoyl-1,4-phenylene) with the aid of a nickel-catalyzed reaction was reported [247]:



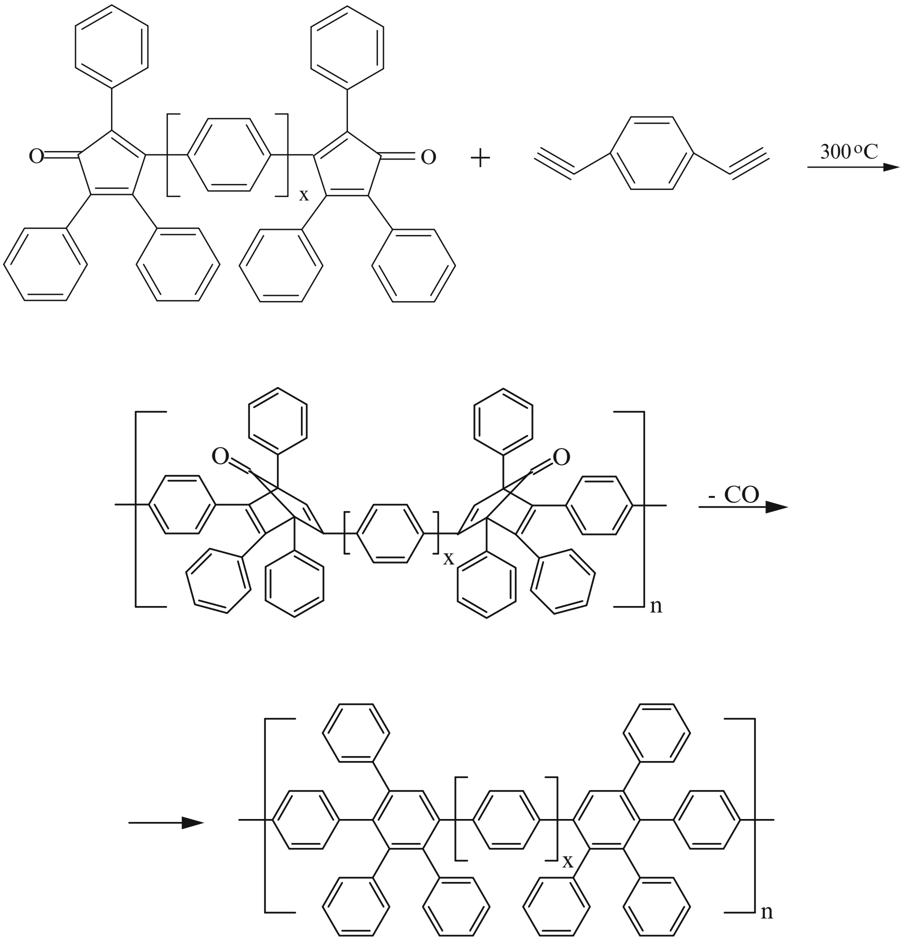
When sodium iodide is replaced with 2,2′-bipyridine, the reaction proceeds faster. The polymers prepared with bipyridine exhibit a glass transition of 217°C and loose only 3% of their weight at 500°C either in air or in nitrogen [247].

Carter et al. [247] used organolithium-activated nickel catalysts to synthesize polyarylates



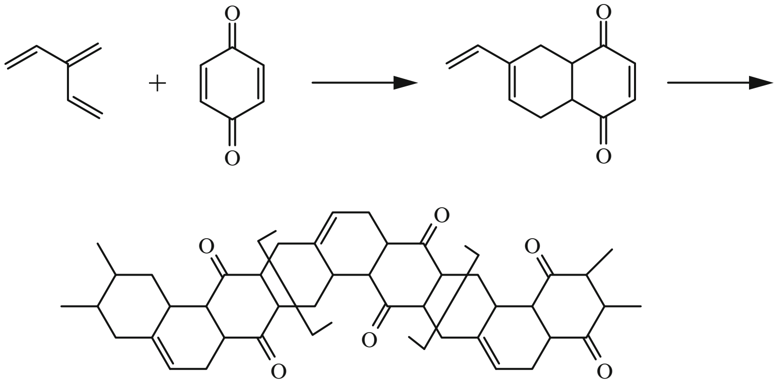
7.17.3 Diels–Alder Polymers

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:



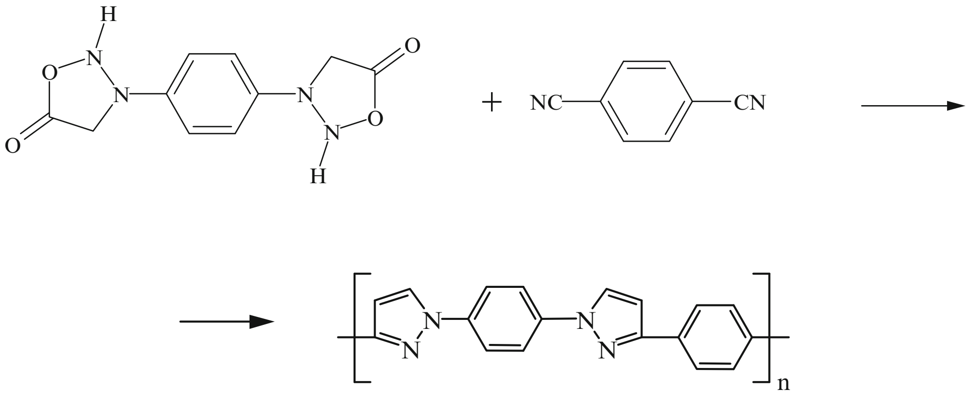
where $x = 1,2$. These polymers are amorphous and form clear films that are stable in air up to 550°C.

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]:

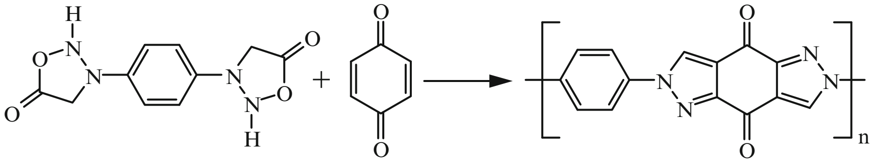


This double-stranded polymer, shown above, is soluble only in hexafluoroisopropyl alcohol [198] and is infusible. When, however, some of the rings are made flexible by condensing 2-vinyl-1,3-butadiene with a large ring bis fumarate, the solubility improves [198].

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]:

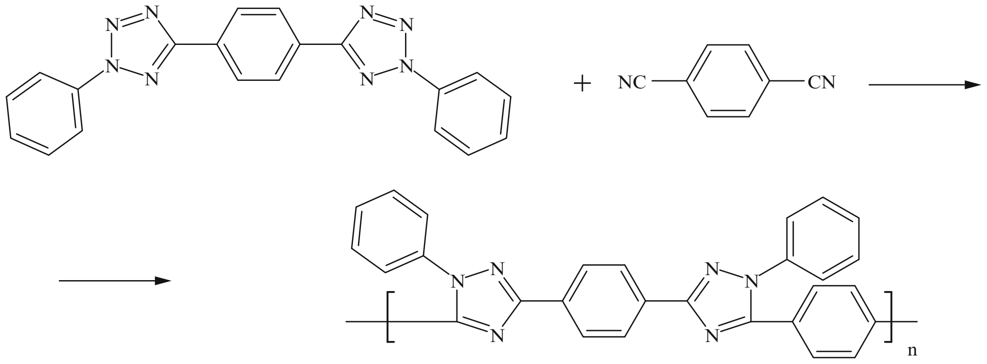


Similarly, bis-sydnones condense with quinone [199]:

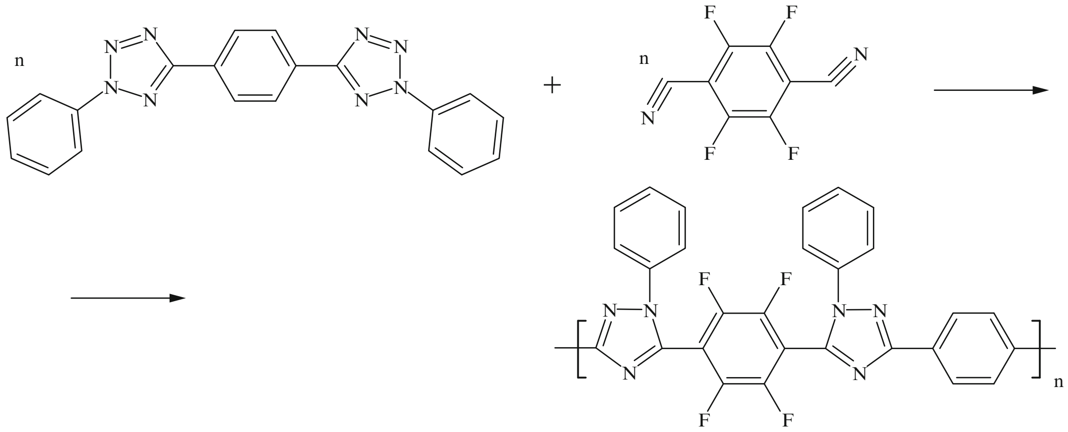


The resultant polymers are not high in molecular weights and only slightly soluble in solvents like dimethylformamide. Their powders decompose near 420°C in air and near 500°C in a nitrogen atmosphere.

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:

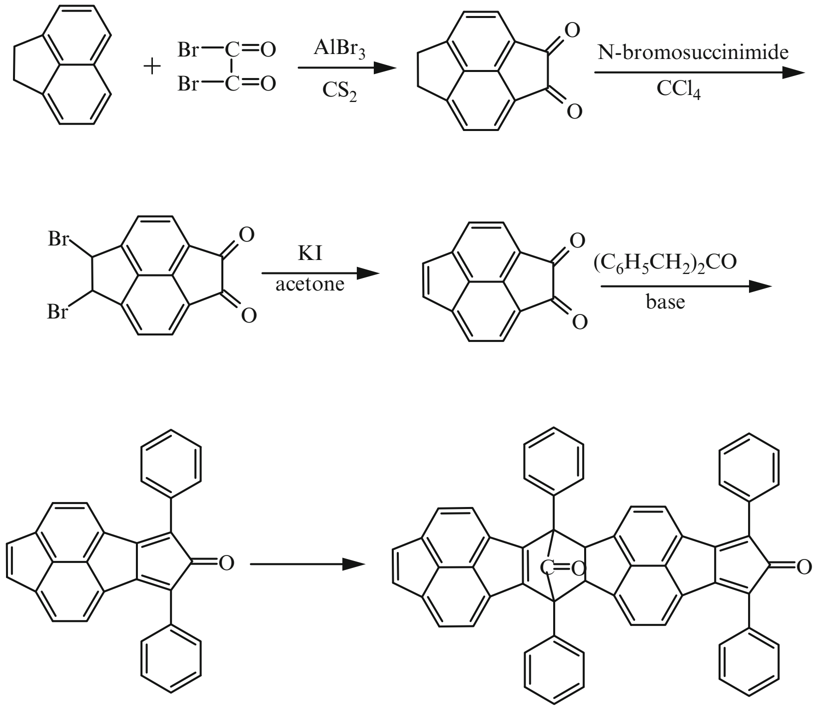


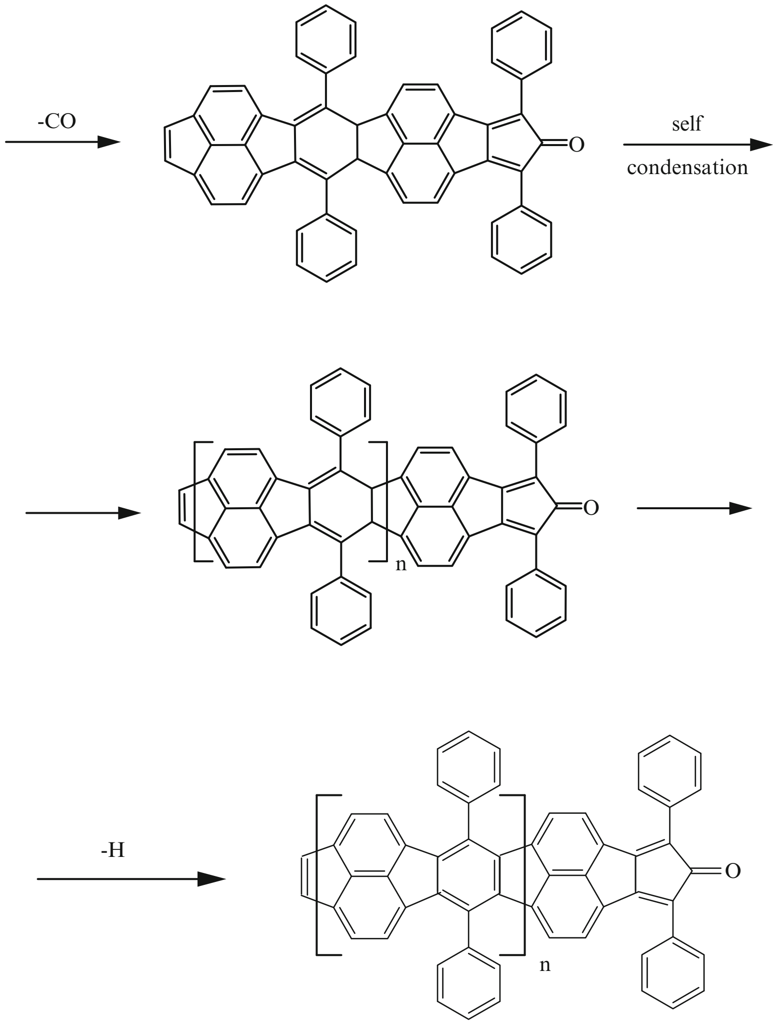
and



By this condensation, high molecular weight polymers can form [200]. They decompose near 500°C in air or in nitrogen atmosphere.

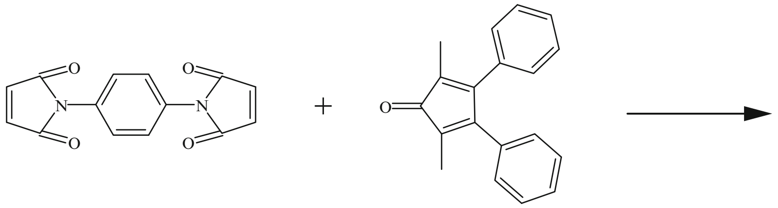
Cyclopentadienone derivatives condense by the Diels–Alder reaction in homopolycycloaddition. The reactions involve a series of steps consisting of initial cycloaddition, followed by loss of carbon monoxide through an expulsion of a bridge carbonyl group [201]:

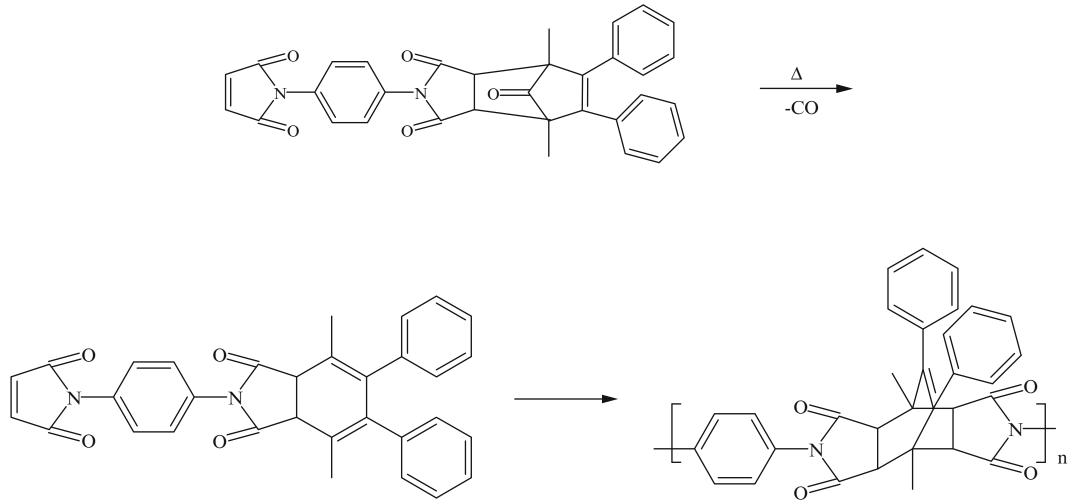




The products are ladder polymers of varying molecular weights. They loose approximately 30% [201] of their weight at 700°C in a nitrogen atmosphere.

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]:

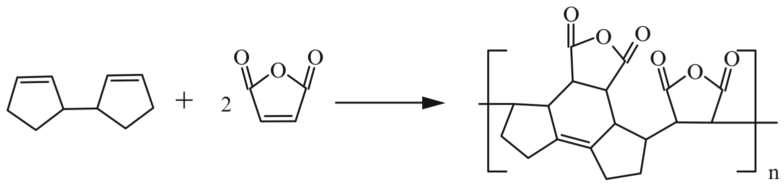
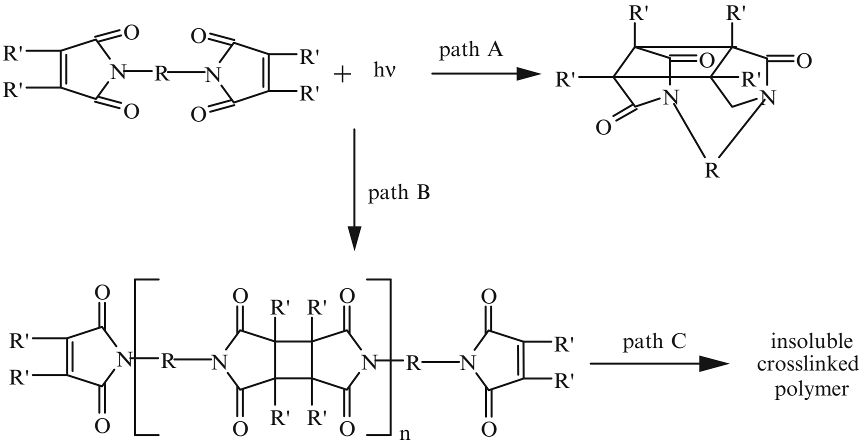


Photo-cycloaddition reactions also form low molecular weight polymers with heterocyclic rings in the backbone. The reactions are photoinitiated with benzophenone to obtain repeated $2\pi + 2\pi$ photocycloadditions of bismaleimides [205]:



where, $R = (CH_2)_x$.

These polymeric materials form transparent, flexible films [205].

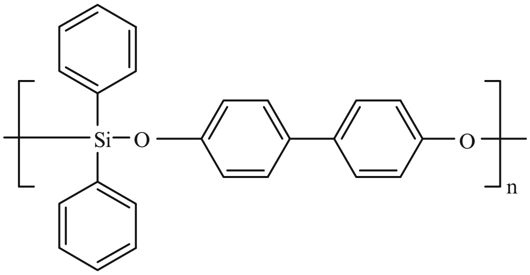
Diels–Alder reaction can also be used to modify the chemical structures of some aromatic polyamides. This improves their heat stability, raises their T_g value, and makes them rigid at higher temperatures [203].

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]:

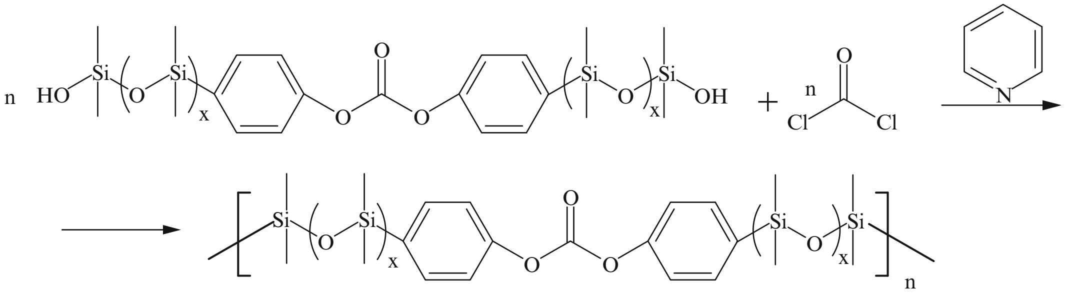
$$\begin{matrix} R_2Si(OR)_2 \\ \text{or} \\ R_2SiCl_2 \end{matrix} + HO{-}Ar{-}OH \longrightarrow \left[-\overset{\overset{\large R}{|}}{\underset{\underset{\large R}{|}}{Si}}-O-Ar-O- \right]_n$$

Many of these polymers are soluble and exhibit good heat stability. An example is one such material prepared by this procedure and shown below:



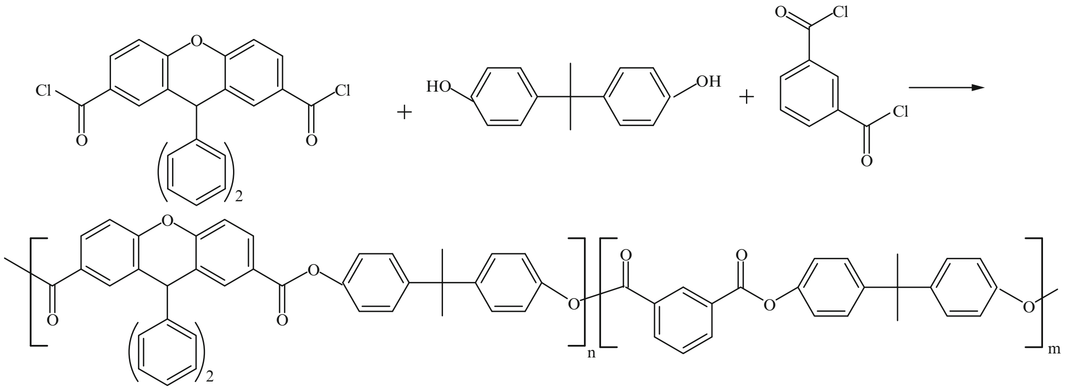
It looses only 10% of its weight at 600°C [191].

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].

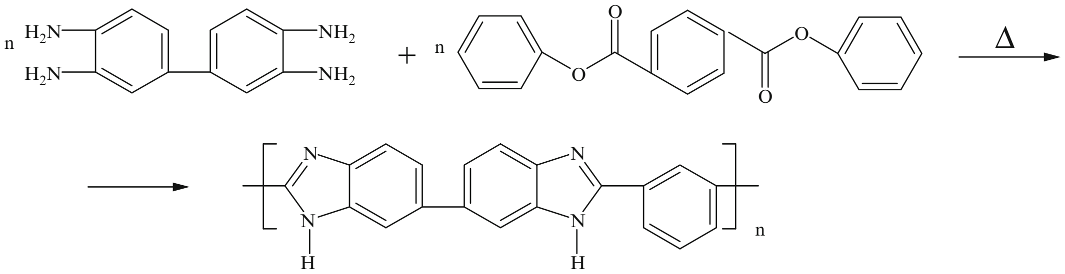
There are also reports in the literature of attempts to modify polysiloxane backbones to increase heat stability. These modifications consist of making changes in the electronic character of the Si–O bonds to prevent rearrangements at high temperatures to low molecular weight cyclic products. It is known 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.

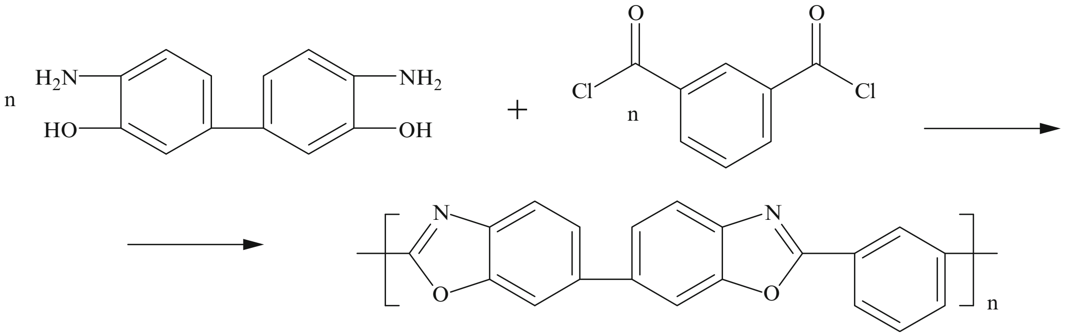
7.17.5.1 Polyimidazoles, Polybenzthiazoles, and Related Polymers

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]:

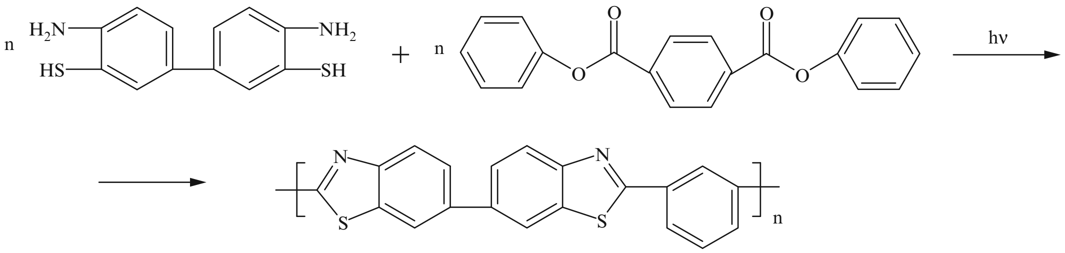


Films and fibers from this material exhibit good mechanical properties up to a temperature of 300°C. Above that temperature, however, they degrades rapidly in air [206].

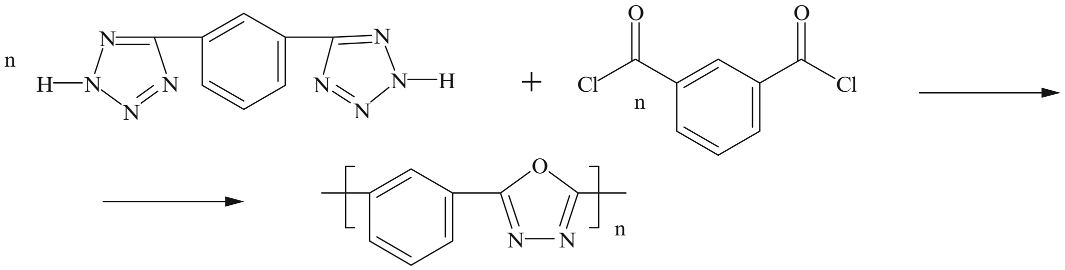
Similar polymers are *polybenzoxazoles* [207, 208]:



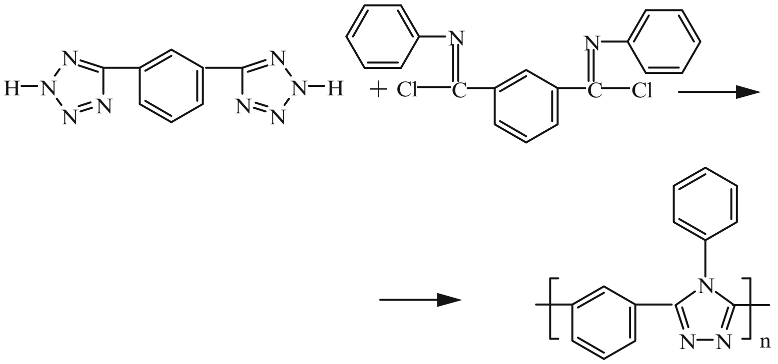
The same is true of *polybenzthiazoles* [209]:



Polyoxidiazoles also belong to this general class of materials [210]:

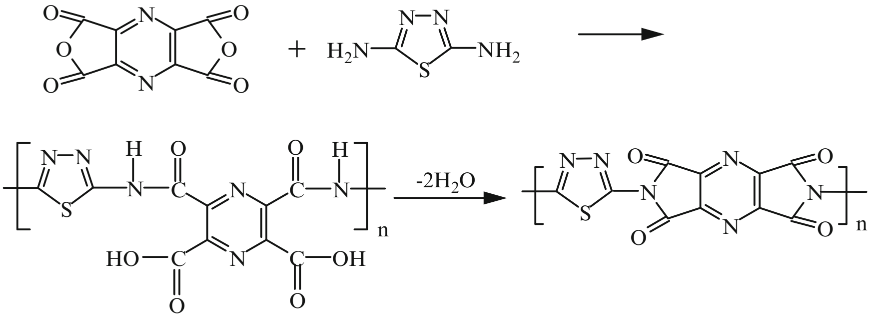


and *polybenztriazoles* [211]:



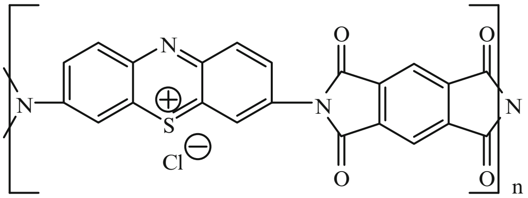
All of the above materials maintain useful properties up to 300°C in air and can be formed into fibers.

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:

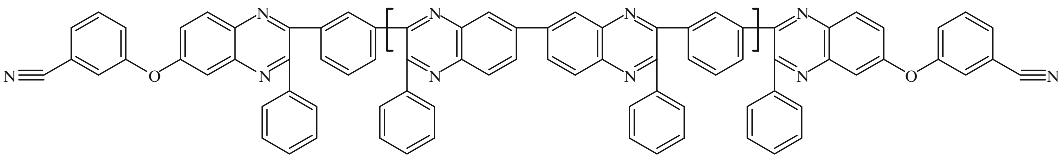


Many polymers that are described in this section can be prepared in either one or in two steps. In the one-step process, polyphosphoric acid is often employed as a solvent. It is a proton donor, promotes condensation, and acts as a cyclodehydrating agent, frequently yielding polymers of high molecular 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.

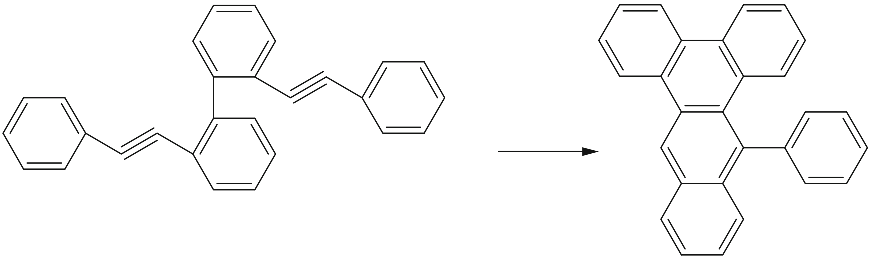
7.17.6 Oligomers with Terminal Functional Groups

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:



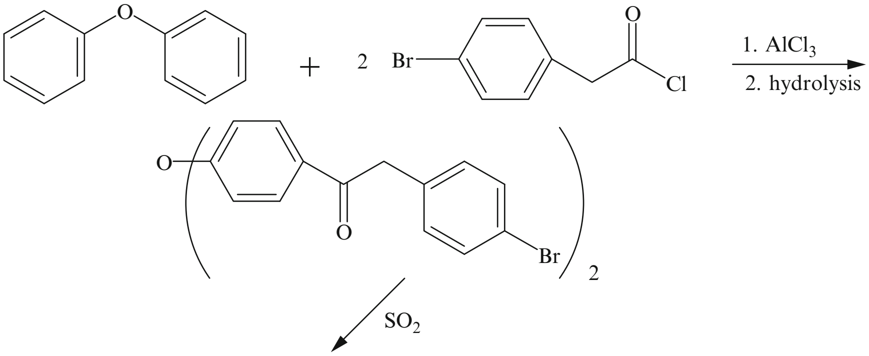
No volatiles can be detected by mass spectrometry [215, 216] or by thermo gravimetric analyses during the cross-linking reaction. The thermo oxidative stability of the resultant polymers is at least equivalent to polyphenylquioxalines not terminated by acetylene. The cross-linking reaction was shown on a model compound to be an intramolecular cyclization [215–217]:

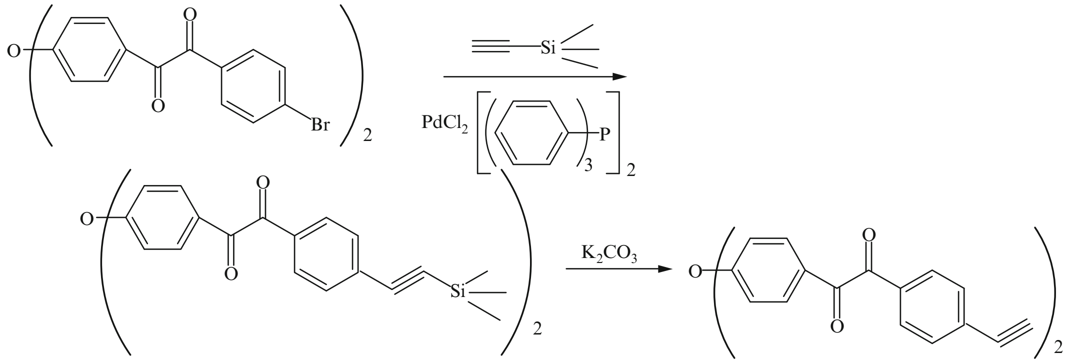


It is not necessary for the acetylenic groups to be on the terminal ends of the prepolymers. They can also be located as pendant structures [216].

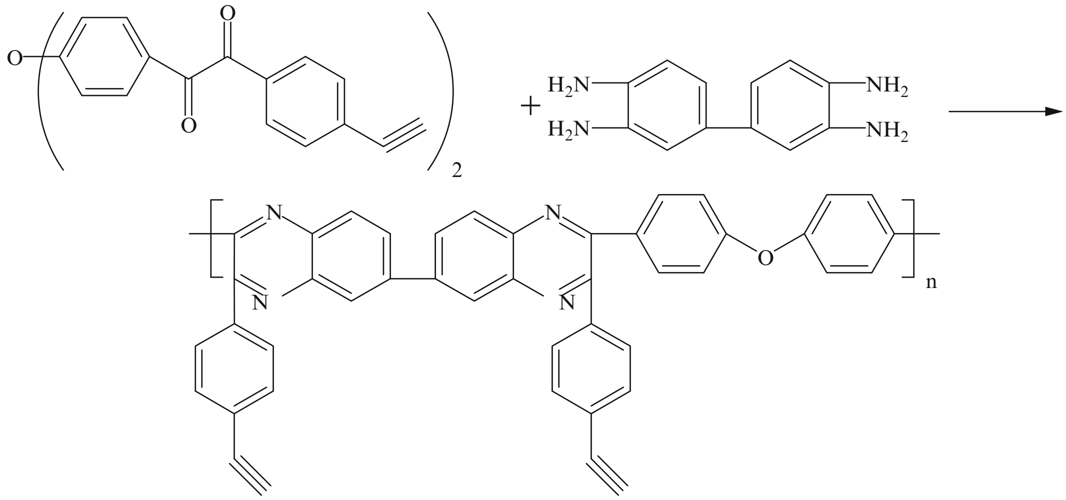
Aromatic polyamides with terminal acetylenic groups [218] were formed from 2,2′-diiododiphenyl-4,4′-dicarbonyl chloride reacted with aromatic diamines. The phenylethynyl groups were introduced by reacting the iodine moieties with copper phenyl acetylide. Thermal treatment converted the prepolymers to 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:





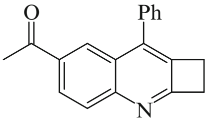
The synthesis is completed by condensation with a tetramine:



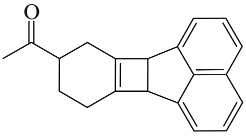
Above shown reactions yield polymers with high T_g values. The materials, however, exhibited lowered thermo oxidative stability. The same was found to be true when the ethynyl moieties were replaced by phenylethynyl groups [219].

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

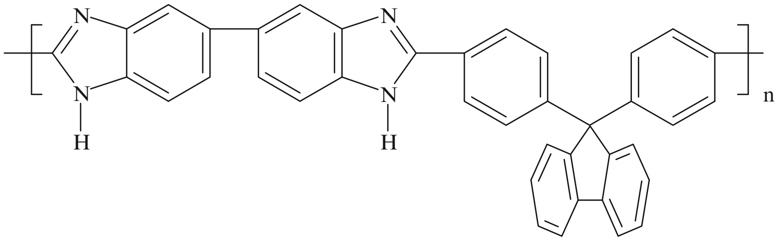


BCBAN

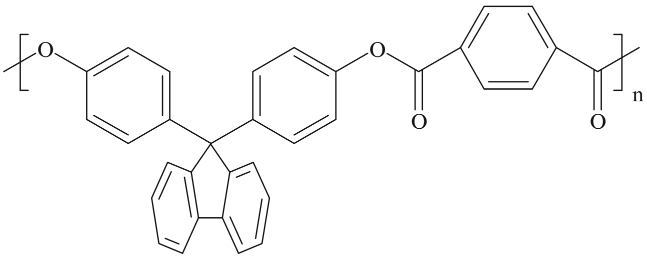
It was reported [230] that the oligomer capped with BCBAN yields a cured film that exhibits good flexural moduli and superior heat stability in air at 400°C.

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]:

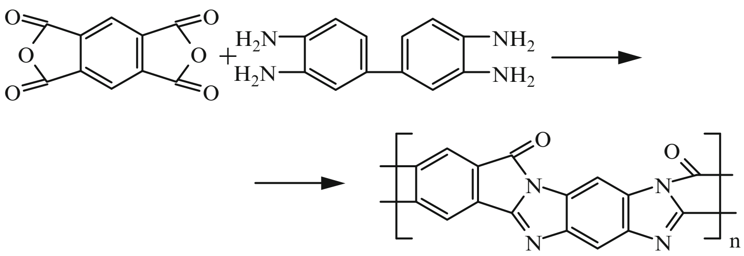


Many cardo polymers exhibit improved solubility in different solvents with little sacrifice in properties. A survey was made of the physical properties of different cardo copolyimides with varying microstructures [220]. As might be expected, copolyimides with increasing aliphatic fragment content were shown to exhibit the highest impact and flexural strength.

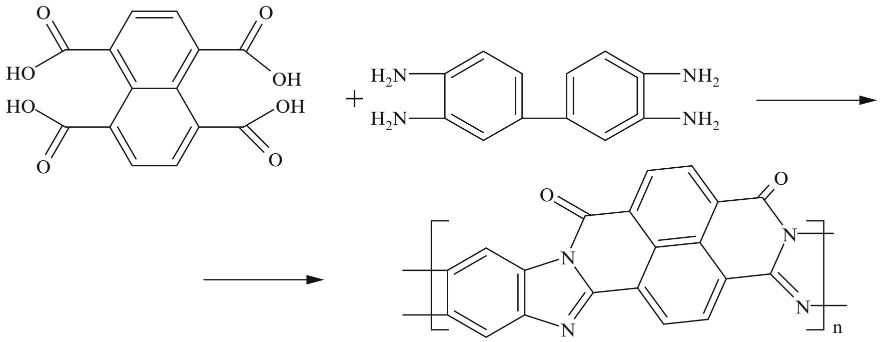
7.17.8 Double-Stranded Polymers

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:

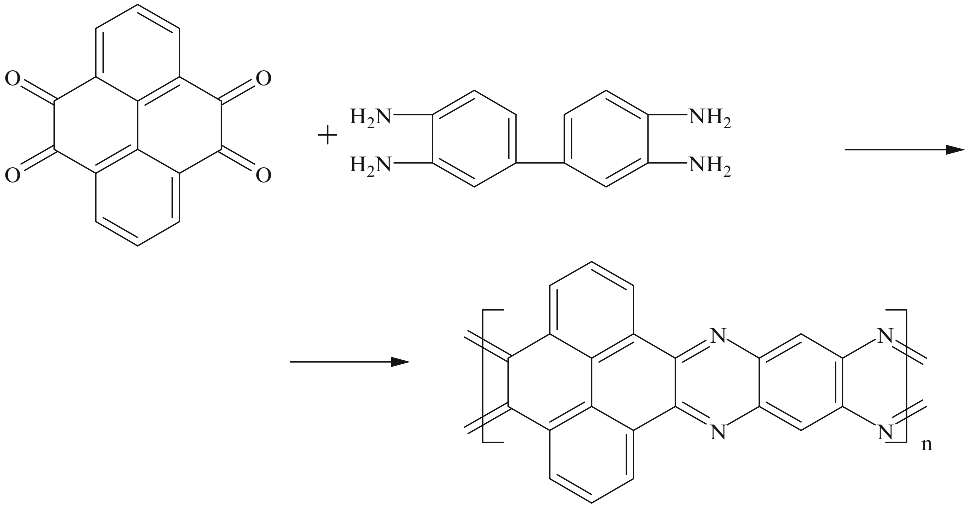
1.



2.



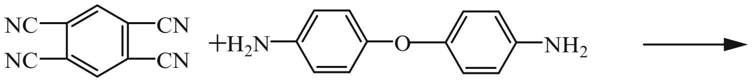
Different ladder polyquinoxalines were prepared as well. One example is shown below [233]:

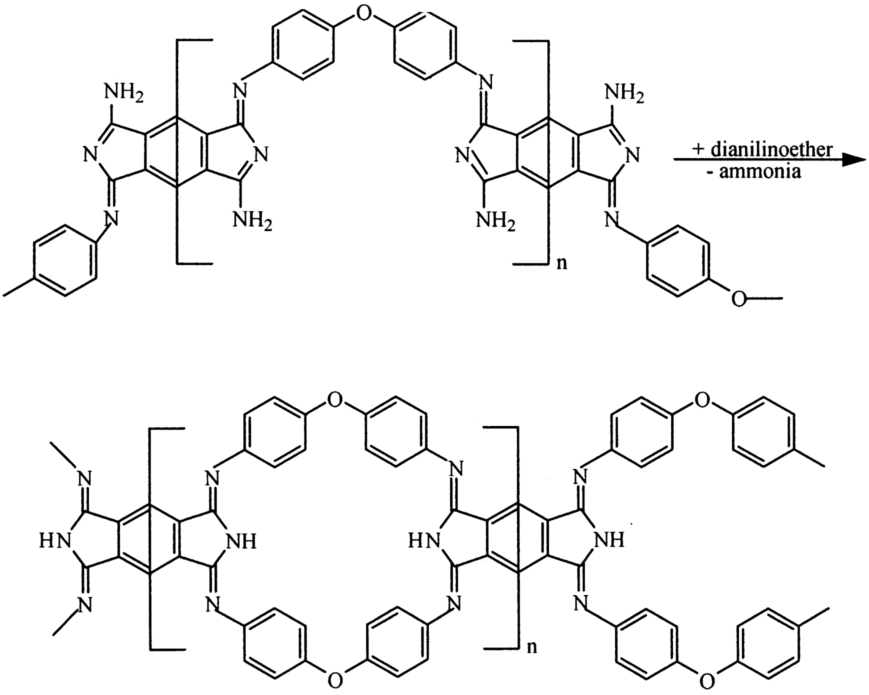


Some ladder polyquinoxalines were found to be stable in air at 460°C and in nitrogen up to 683°C.

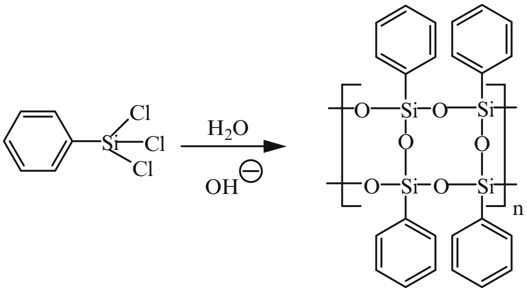
Not all attempts at formations of ladder polymers yielded completely cyclized fused ring structures. For instance, an attempt to form a polymer from tetraaminonaphthalene with naphthalene tetracarboxylic acid dianhydride failed to yield complete cyclizations [222].

An interesting polymer containing macrocyclic rings was formed from pyromellitic tetranitrile by condensation with dianilino ether [223]:



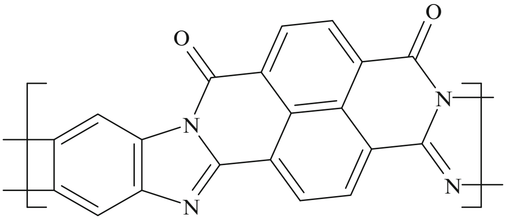


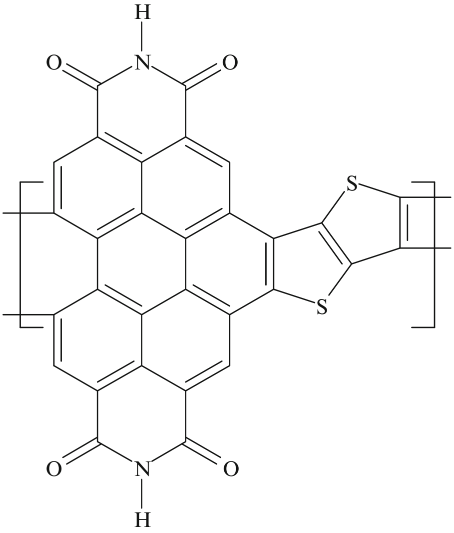
The description of all the double-stranded polymers that were synthesized and reported in the literature is beyond the scope of this book. This section is concluded by mentioning two more materials. One prepared by an alkali catalyzed polymerization of phenyltrichlorosilane [224]:



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:

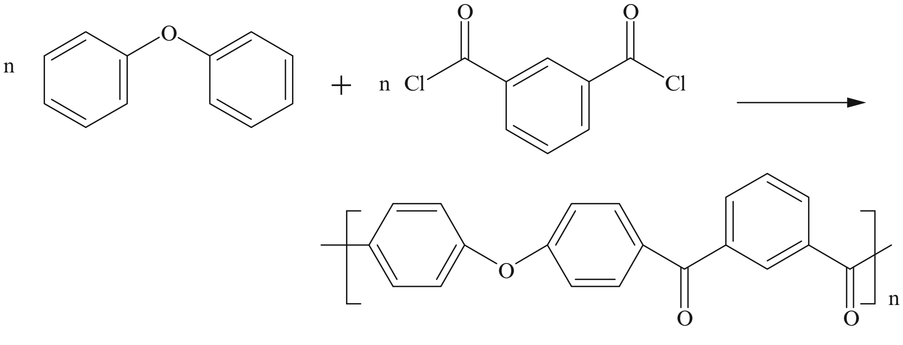




7.17.9 Poly(arylene ether)s and Poly(arylene ether ketone)s

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.

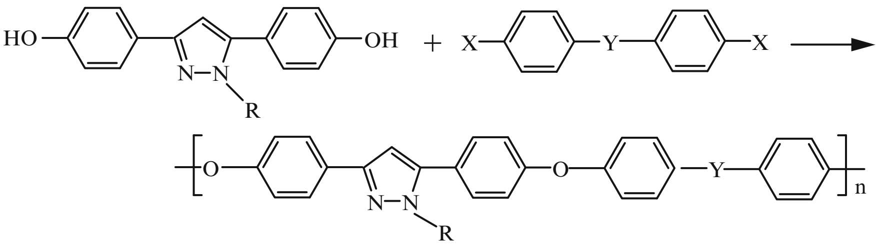
Commercial poly(ether ketone)s that are also poly(arylene ether)s are formed from diacid chloride by the Friedel–Craft reaction [234].



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.

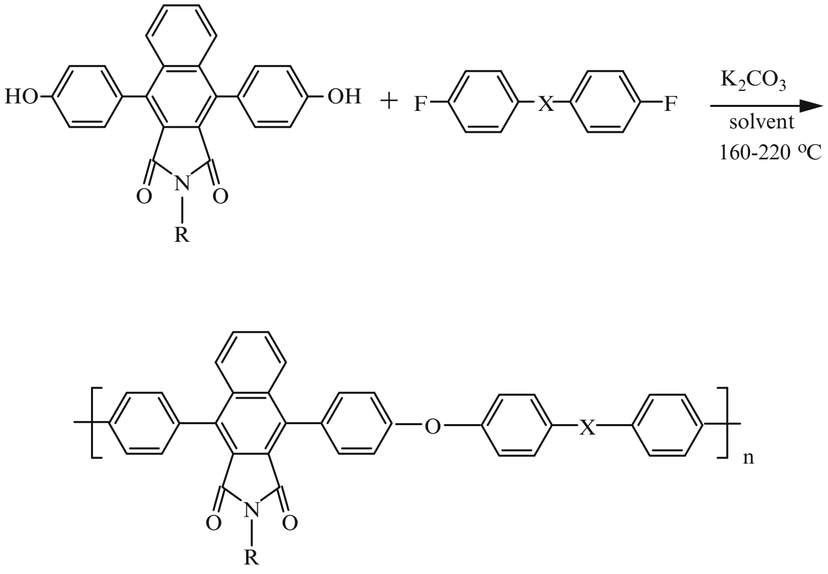
Some current preparations of poly(arylene ether)s are carried out by nucleophilic displacements of activated aromatic dihalides or dinitro groups by alkali metal bisphenates. The reactions take place in polar aprotic solvents. The glass transition temperatures, tensile strengths, and tensile moduli of 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:



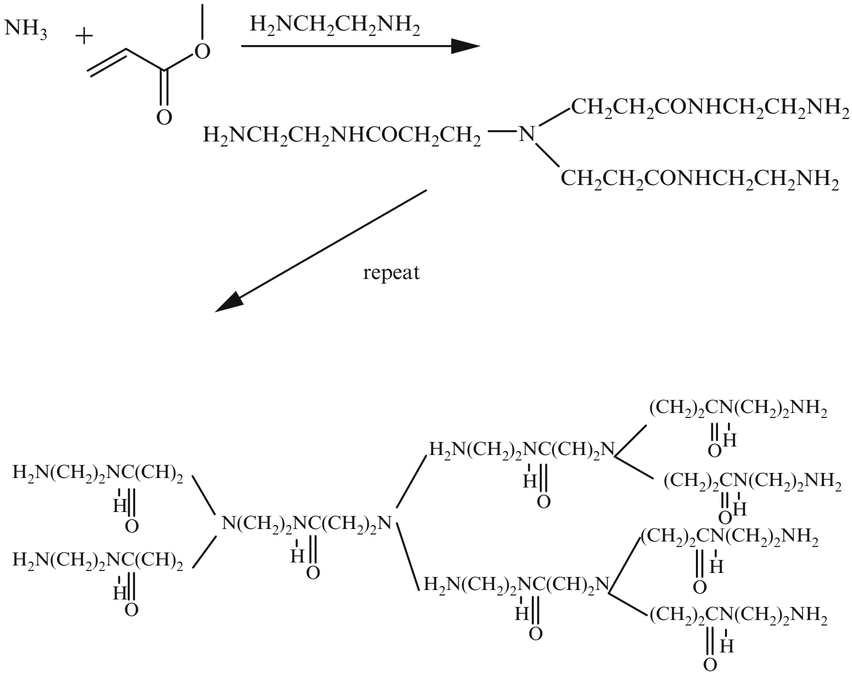
where: R = CH_3; $CH_3(CH_2)_{11}$; Phenyl; X = SO_2; CO; Isophthaloyl; Based on thermogravimetric analyses, the phenyl substituted polymers lose only 10% of their weight in air and in nitrogen at 550°C. In addition, the polymers have high glass transition temperatures and remain soluble in common solvents, 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

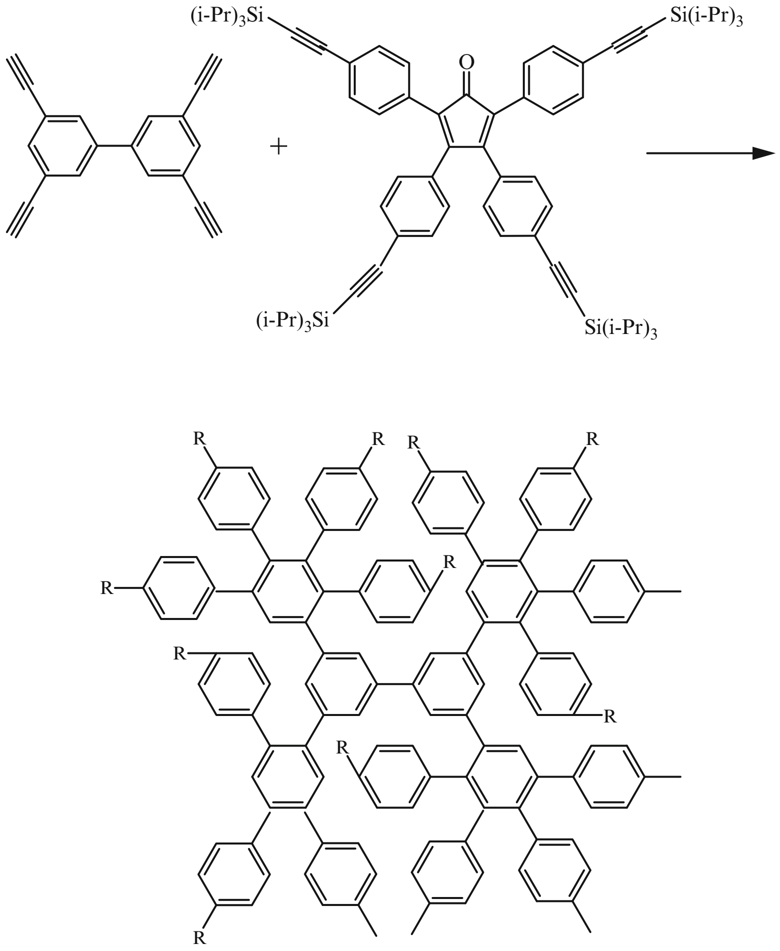
Highly branched polymeric materials with large number of end groups can offer unique physical properties. Dendrimers (described in Chap. 1) differ from linear polymers in viscosity and thermal behavior. A variety of applications have been forecast for these highly branched globular macromolecules. One 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:

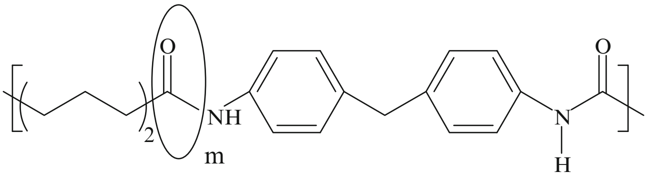


The above condensation reactions were carried out at 180–200°C in aromatic solvents [250].

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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