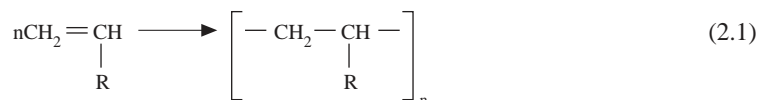# Polymerization Mechanisms

I. INTRODUCTION

As discussed in Chapter 1, under a scheme proposed by Carothers, polymers are classified as addition or condensation polymers depending on the type of polymerization reaction involved in their synthesis. This classification scheme, however, does not permit a complete differentiation between the two classes of polymers. A more complete but still oversimplified scheme that is still based on the different polymerization processes places polymers into three classes: condensation, addition, and ring-opening polymers. This scheme reflects the structures of the starting monomers. Probably the most general classification scheme is based on the polymerization mechanism involved in polymer synthesis. Under this scheme, polymerization processes are classified as step-reaction (condensation) or chain-reaction (addition) polymerization. In this chapter, we will discuss the different types of polymers based on the different polymerization mechanisms.
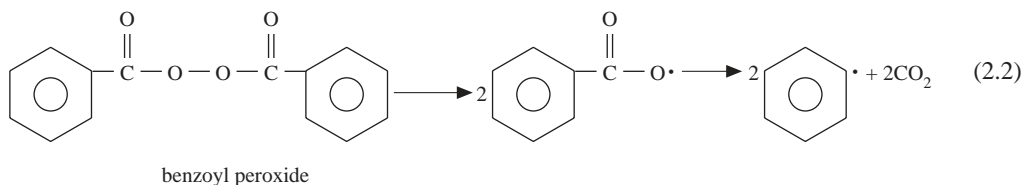
II. CHAIN-REACTION POLYMERIZATION

Chain-reaction polymerization, an important industrial method of polymer preparation, involves the addition of unsaturated molecules to a rapidly growing chain. The most common unsaturated compounds that undergo chain-reaction polymerization are olefins, as exemplified by the following reaction of a generalized vinyl monomer.

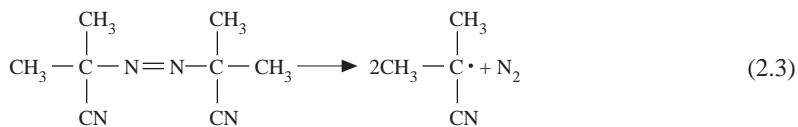$$nCH_2=CH \longrightarrow \left[-CH_2-CH- \right]_n \tag{2.1}$$

The growing polymer in chain-reaction polymerization is a free radical, and polymerization proceeds via chain mechanism. Chain-reaction polymerization is induced by the addition of free-radical-forming reagents or by ionic initiators. Like all chain reactions, it involves three fundamental steps: initiation, propagation, and termination. In addition, a fourth step called chain transfer may be involved.
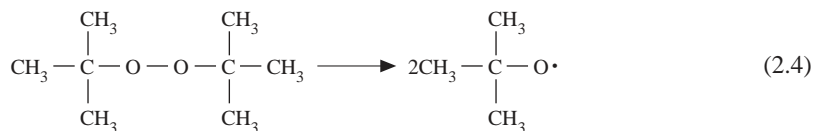
A. INITIATION

Initiation involves the acquisition of an active site by the monomer. This may occur spontaneously by the absorption of heat, light (ultraviolet), or high-energy irradiation. But most frequently, initiation of free-radical polymerization is brought about by the addition of small quantities of compounds called initiators. Typical initiators include peroxides, azo compounds, Lewis acids, and organometallic reagents. However, while initiators trigger initiation of the chain and exert an accelerating influence on polymerization rate, they are not exactly catalysts since they are changed chemically in the course of polymerization. An initiator is usually a weak organic compound that can be decomposed thermally or by irradiation to produce free radicals, which are molecules containing atoms with unpaired electrons. A variety of compounds decompose when heated to form free radicals. Dialkyl peroxides (ROOR), diacylperoxides (RCO–O–O–CO–R), hydroperoxides (ROOH), and azo compounds (RN›NR) are typical organic compounds that can be decomposed thermally to produce free radicals. Benzoyl peroxide, azobisisobutyronitrile, and di-*t*-butylperoxide are commonly used free-radical initiators, as illustrated in Equations 2.2–2.4.
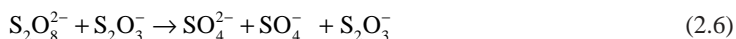

$$\tag{2.2}$$

benzoyl peroxide

$$CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow 2CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot + N_2 \qquad (2.3)$$

<div align="center">azobisisobutyronitrile (AIBN)</div>

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow 2CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O\cdot \qquad (2.4)$$
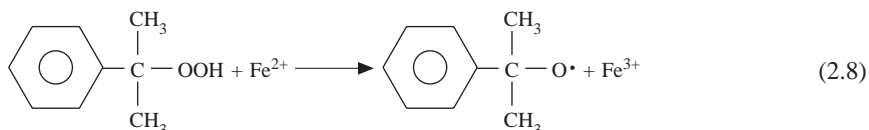
<div align="center">di-t-butylperoxide</div>

The thermal decomposition of benzoyl peroxide, which takes place between 60 and 90°C, involves the homolytic cleavage of the O–O bond to yield benzoyl free radicals that may react to yield phenyl radicals and carbon dioxide. An example of photochemically induced free-radical formation is the decomposition of azo-bisisobutyronitrile by short-wavelength visible light or near-ultraviolet radiation at temperatures as low as 0°C, where no thermal initiation occurs.

In free-radical polymerization carried out in aqueous medium, the decomposition of peroxide or persulfate is greatly accelerated by the presence of a reducing system. This method of free-radical initiation is referred to as redox initiation. The initiation resulting from the thermal decomposition of organic compounds discussed above is appropriate only for polymerizations carried out at room temperature or higher. The enhanced rate of free-radical formation in redox reactions permits polymerization at relatively lower temperatures. Typical redox reactions for emulsion polymerization are shown in Equations 2.5–2.7.

$$S_2O_8^{2-} + HSO_3^- \rightarrow SO_4^{2-} + SO_4^- + HSO_3 \qquad (2.5)$$

$$S_2O_8^{2-} + S_2O_3^- \rightarrow SO_4^{2-} + SO_4^- + S_2O_3^- \qquad (2.6)$$

$$HSO_3^- + Fe^{3+} \rightarrow HSO_3 + Fe^{2+} \qquad (2.7)$$

Persulfate ion initiator (e.g., from $K_2S_2O_8$) reacts with a reducing agent such as a bisulfite ion (e.g., from $NaHSO_3$) to produce radicals for redox initiation (Equations 2.5 and 2.6). Ferric ion may also be used as a source of radicals (Equation 2.7). Other redox reactions involve the use of alkyl hydroxides and a reducing agent such as ferrous ion (Equation 2.8).

$$\text{C}_6\text{H}_5-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OOH + Fe^{2+} \longrightarrow \text{C}_6\text{H}_5-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O\cdot + Fe^{3+} \qquad (2.8)$$

As indicated earlier, free-radical polymerization of some monomers can be initiated by heating or exposing the monomers to light or high-energy irradiation such as X-rays, γ-rays, and α-rays. High-energy irradiation of monomers can be carried out either in bulk or in solution. It is certainly not as selective as photolytic initiation.
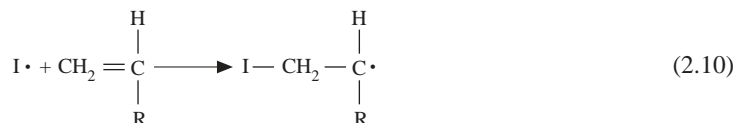
When choosing an initiator for free-radical polymerization, the important parameters that must be considered are the temperature range to be used for the polymerization and the reactivity of the radicals formed. The presence of certain promoters and accelerators and the nature of the monomer often affect the rate of decomposition of initiators. For example, the decomposition of benzoyl peroxide may be accelerated at room temperature by employing ternary or quaternary amines. Free-radical initiation

processes do not require stringent exclusion of atmospheric moisture, but can be inhibited by substances such as oxygen. Free radicals are inactivated by reaction with oxygen to form peroxides or hydroperoxides. For monomers such as styrene and methylmethacrylate that are susceptible to such inhibition, initiation reactions are carried out in an oxygen-free atmosphere such as nitrogen. It must be emphasized also that organic peroxides, when subjected to shock or high temperature, can detonate. Therefore these compounds must be handled with caution.

The initiation of polymerization occurs in two successive steps. The first step involves the formation of radicals according to the processes discussed above. This may be represented broadly as:
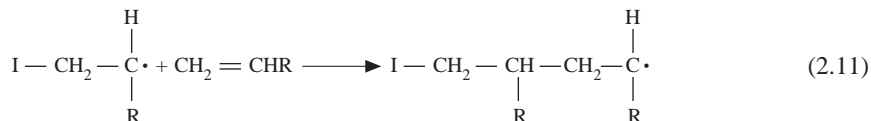
$$I\text{-}I \rightarrow 2I\cdot \tag{2.9}$$

The second step is the addition of the initiator radical to a vinyl monomer molecule:

$$I\cdot + CH_2 = \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}} \longrightarrow I - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}\cdot \tag{2.10}$$

Initiator fragments have been shown by end-group analysis to become part of the growing chain. In commercial practice, 60 to 100% of all the free radicals generated do initiate polymerization.
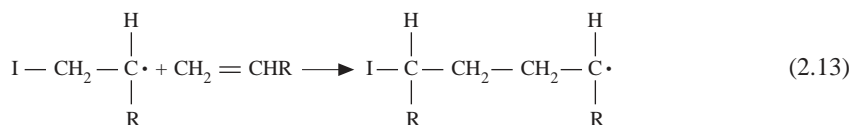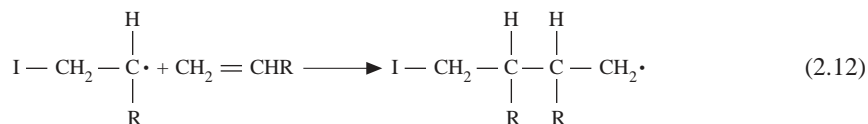
B. PROPAGATION

During propagation, the initiated monomer described above adds other monomers — usually thousands of monomer molecules — in rapid succession. This involves the addition of a free radical to the double bond of a monomer, with regeneration of another radical. The active center is thus continuously relocated at the end of the growing polymer chain (Equation 2.11).

$$I - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}\cdot + CH_2 = CHR \longrightarrow I - CH_2 - \underset{\underset{\displaystyle R}{|}}{CH} - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}\cdot \tag{2.11}$$
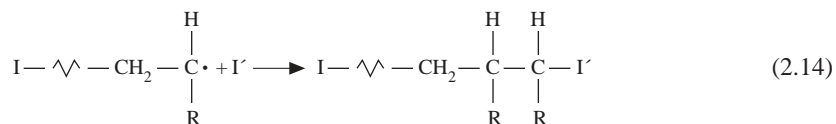
Propagation continues until the growing chain radical is deactivated by chain termination or transfer as discussed below.

The substituted carbon atom is regarded as the head and the unsubstituted carbon atom the tail of the vinyl monomer. There are, therefore, three possible ways for the propagation step to occur: head-to-tail (Equation 2.11), head-to-head (Equation 2.12), and tail-to-tail (Equation 2.13). A random distribution of these species along the molecular chain might be expected. It is found, however, that head-to-tail linkages in which the substituents occur on alternate carbon atoms predominate; only occasional interruptions of this arrangement by head-to-head and tail-to-tail linkages occur. In addition, exclusive head-to-head or tail-to-tail arrangements of monomers in the chain are now known.

$$I - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}\cdot + CH_2 = CHR \longrightarrow I - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}} - CH_2\cdot \tag{2.12}$$

$$I - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}\cdot + CH_2 = CHR \longrightarrow I - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}} - CH_2 - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}\cdot \tag{2.13}$$
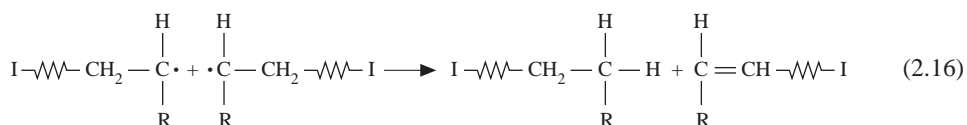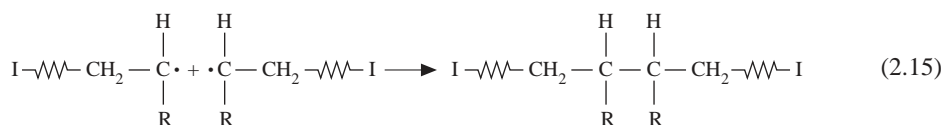
C. TERMINATION

In termination, the growth activity of a polymer chain radical is destroyed by reaction with another free radical in the system to produce polymer molecule(s). Termination can occur by the reaction of the polymer radical with initiator radicals (Equation 2.14). This type of termination process is unproductive and can be controlled by maintaining a low rate for initiation.

$$I - \wedge\wedge - CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \cdot + I' \longrightarrow I - \wedge\wedge - CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - I' \tag{2.14}$$
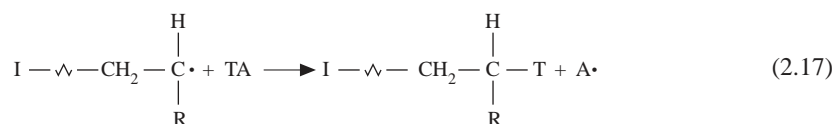
The termination reactions that are more important in polymer production are combination (or coupling) and disproportionation. In termination by combination, two growing polymer chains react with the mutual destruction of growth activity (Equation 2.15), while in disproportionation a labile atom (usually hydrogen) is transferred from one polymer radical to another (Equation 2.16).

$$I -\!\!\wedge\!\!\!\wedge\!\!- CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \cdot + \cdot \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - CH_2 -\!\!\wedge\!\!\!\wedge\!\!- I \longrightarrow I -\!\!\wedge\!\!\!\wedge\!\!- CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - CH_2 -\!\!\wedge\!\!\!\wedge\!\!- I \tag{2.15}$$

$$I -\!\!\wedge\!\!\!\wedge\!\!- CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \cdot + \cdot \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - CH_2 -\!\!\wedge\!\!\!\wedge\!\!- I \longrightarrow I -\!\!\wedge\!\!\!\wedge\!\!- CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - H + \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} = CH -\!\!\wedge\!\!\!\wedge\!\!- I \tag{2.16}$$

Coupling reactions produce a single polymer, while disproportionation results in two polymers from the two reacting polymer chain radicals. The predominant termination reaction depends on the nature of the reacting monomer and the temperature. Since disproportionation requires energy for breaking of chemical bonds, it should become more pronounced at high reaction temperatures; combination of growing polymer radicals predominates at low temperatures.
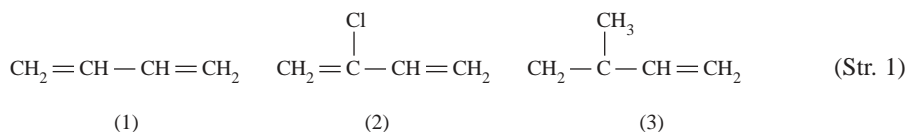
D. CHAIN TRANSFER

Ideally, free-radical polymerization involves three basic steps: initiation, propagation, and termination, as discussed above. However, a fourth step, called chain transfer, is usually involved. In chain-transfer reactions, a growing polymer chain is deactivated or terminated by transferring its growth activity to a previously inactive species, as illustrated in Equation 2.17.

$$I - \wedge - CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \cdot + TA \longrightarrow I - \wedge - CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - T + A \cdot \tag{2.17}$$

The species, TA, could be a monomer, polymer, solvent molecule, or other molecules deliberately or inadvertently introduced into the reaction mixture. Depending on its reactivity, the new radical, A·, may or may not initiate the growth of another polymer chain. If the reactivity of A· is comparable to that of the propagating chain radical, then a new chain may be initiated. If its reactivity toward a monomer is less than that of the propagating radical, then the overall reaction rate is retarded. If A· is unreactive toward the monomer, the entire reaction could be inhibited. Transfer reactions do not result in the creation or destruction of radicals; at any instant, the overall number of growing radicals remains unchanged. However, the occurrence of transfer reactions results in the reduction of the average polymer chain length, and in the case of transfer to a polymer it may result in branching.

E. DIENE POLYMERIZATION

Conjugated dienes such as butadiene (1), chloroprene (2), and isoprene (3) constitute a second group of unsaturated compounds that can undergo polymerization through their double bonds.
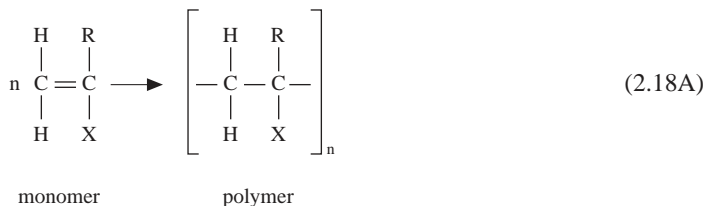
$$CH_2=CH-CH=CH_2 \qquad CH_2=\overset{\overset{\displaystyle Cl}{|}}{C}-CH=CH_2 \qquad CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2 \qquad \text{(Str. 1)}$$

$$(1) \qquad\qquad\qquad (2) \qquad\qquad\qquad (3)$$

These structures contain double bonds in the 1,2 and 3,4 positions, each of which may participate independently in polymerization giving rise to 1,2 and 3,4 units. A further possibility is that both bonds are involved in polymerization through conjugate reactions, resulting in 1,4 units. These structures are shown in Equation 2.18.

$$(2.18)$$
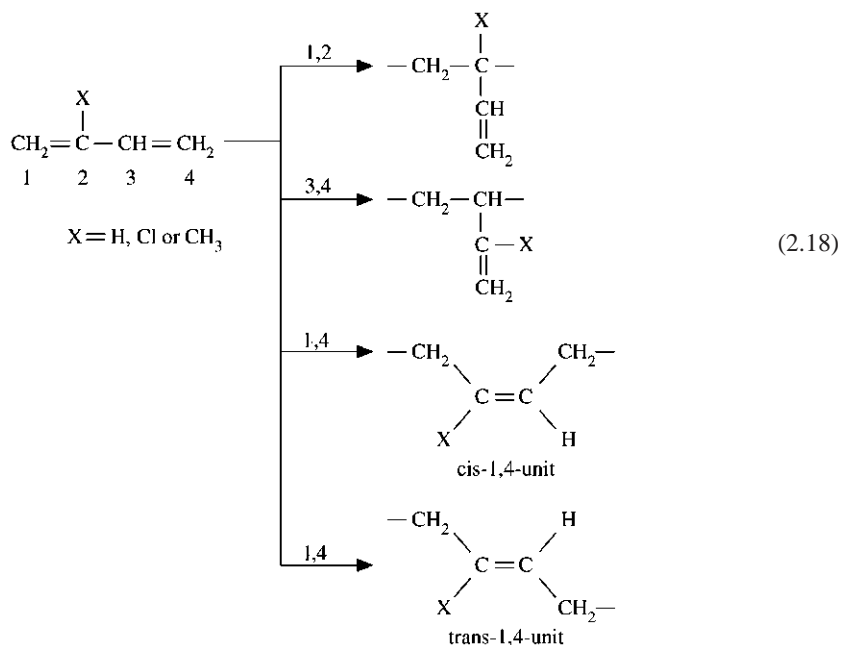
Diene polymerization thus gives rise to polymers that contain various isomeric units. With symmetrical dienes such as butadiene, the 1,2 and 3,4 units are identical. The 1,4 unit may occur in the *cis* or *trans* configuration. A diene polymer contains more than one of these structural units. The relative abundance of each unit in the polymer molecule depends on the nature of the initiator, experimental conditions, and the structure of the diene. The proportion of each type of structure incorporated into the polymer chain influences both thermal and physical properties. For example, butadiene can be polymerized by free-radical addition at low temperature to produce a polymer that consists almost entirely of *trans*-1,4 units and only about 20% 1,2 units. As the temperature is increased, the relative proportion of *cis*-1,4 units increases while the proportion of 1,2 structure remains fairly constant. Anionic diene polymerization with lithium or organolithium initiators like *n*-butyllithium in nonpolar solvents such as pentane or hexane yields polymers with high *cis*-1,4 content. When higher alkali metal initiators or more polar solvents are used, the relative amount of *cis*-1,4 units decreases. Stereoregularity can also be controlled by the use of coordination catalysts like Ziegler–Natta catalysts. Heterogeneous Alfin catalysts — which are combinations of alkenyl sodium compounds, alkali metal halides, and an alkoxide — give high-molecular-weight polymers with high content of *trans*-1,4 units.

As noted above, all chain-reaction polymerizations involve essentially the same number of steps. The main distinguishing feature between chain-reaction polymerizations, however, is by the initiation mechanism, which may be a free-radical, ionic (cationic or anionic), or coordination. The time between initiation and termination of a given chain is typically from a few tenths of a second to a few seconds. During this time thousands or tens of thousands of monomers add to the growing chain.

The structural unit in addition polymers is chemically identical to the monomer employed in the polymerization reaction, as exemplified by the following reaction of a generalized vinyl monomer:

$$
n \;
\begin{array}{c}
\text{H} \quad \text{R} \\
| \quad\quad | \\
\text{C}=\text{C} \\
| \quad\quad | \\
\text{H} \quad \text{X}
\end{array}
\longrightarrow
\left[
\begin{array}{c}
\text{H} \quad \text{R} \\
| \quad\quad | \\
-\text{C}-\text{C}- \\
| \quad\quad | \\
\text{H} \quad \text{X}
\end{array}
\right]_n
\tag{2.18A}
$$

monomer   polymer

Here R and X are monofunctional groups, R may be a hydrogen atom (H), or an alkyl group (e.g., –CH$_3$), while X may be any group (e.g., –Cl, –CN). The structural unit is evidently structurally identical to the starting monomer. Monomers generally employed in addition polymerizations are unsaturated (usually with double bonds). Because of the identical nature of the chemical formulas of monomers and the polymers derived from them, addition polymers generally take their names from the starting monomer — ethylene → polyethlene, propylene → polypropylene, etc. (Table 2.1). The backbone of addition polymer chains is usually composed of carbon atoms.

**Table 2.1**   *Some Representation Addition Polymers*

$$
n \;
\begin{array}{c}
\text{H} \quad \text{H} \\
| \quad\quad | \\
\text{C}=\text{C} \\
| \quad\quad | \\
\text{H} \quad \text{R}
\end{array}
\longrightarrow
\left[
\begin{array}{c}
\text{H} \quad \text{H} \\
| \quad\quad | \\
-\text{C}-\text{C}- \\
| \quad\quad | \\
\text{H} \quad \text{R}
\end{array}
\right]_n
$$

monomer   polymer

R	Monomer	Polymer
H	Ethylene	Polyethylene
CH$_3$	Propylene	Polypropylene
Cl	Vinyl chloride	Poly(vinyl chloride)
CN	Acrylonitrile	Polyacrylonitrile
(phenyl ring)	Styrene	Polystyrene
O | C=O | CH$_3$	Vinyl acetate	Poly(vinyl acetate)
C=O | O | CH$_3$	Methyl acrylate	Poly(methyl acrylate)

Table 2.1 (continued)   *Some Representation Addition Polymers*

$$
n \underset{\underset{R_2}{\overset{\overset{R_1}{|}}{C}}}{} = \underset{\underset{R_4}{\overset{\overset{R_3}{|}}{C}}}{} \longrightarrow \left[-\underset{\underset{R_2}{\overset{\overset{R_1}{|}}{C}}}{} - \underset{\underset{R_4}{\overset{\overset{R_3}{|}}{C}}}{} - \right]_n
$$

R_1	R_2	R_3	R_4	Monomer	Polymer
H	H	CH_3	$C=O$, O, CH_3 (see structure)	Methyl methacrylate	Poly(methyl methacrylate)
H	H	Cl	Cl	Vinylidene chloride	Poly(vinylidene chloride)
H	H	F	F	Vinylidene fluoride	Poly(vinylidene fluoride)
F	F	F	F	Tetrafluoro-ethylene	Polytetrafluoroethylene

Example 2.1: Explain the following observations.

a. α-Methylstyrene polymerizes much less readily than styrene.
b. Chain-transfer reactions reduce the average chain length of the polymer.

Solutions:

a. The reactivity of a vinyl monomer depends on the nature of the substituents on the monomer double bond. Substituents may either enhance the monomer reactivity by activating the double bond, depress the reactivity of the resulting radical by resonance stabilization, or provide steric hindrance at the reaction site.

Monomer   Radical

α - methylstyrene   (Str. 2)
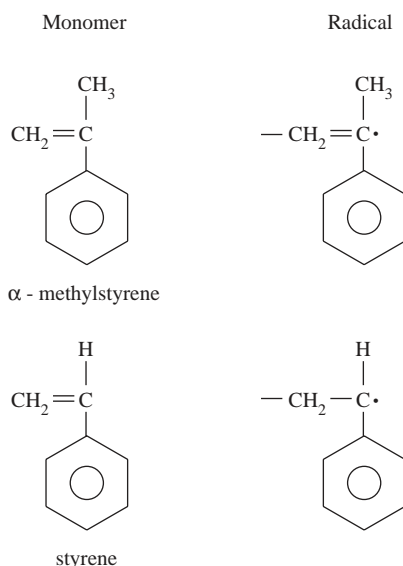
styrene

The reactivities of α-methylstyrene and styrene radicals are essentially the same due to their similar resonance stabilization. However, the activation of the double bond by the phenyl group is compensated somewhat by the presence of the electron-donating methyl group in α-methylstyrene. The methyl group also provides steric hindrance at the reactive site. Consequently, α-methylstyrene is less reactive than styrene.

b. Chain transfer may be to a solvent, initiator or monomer. During chain-transfer reactions, for each radical chain initiated, the number of polymer molecules increases except in the case of transfer to a polymer. In other words, the average number of monomer molecules consumed by each chain radical (DP) or the average polymer chain length decreases with chain-transfer reactions.
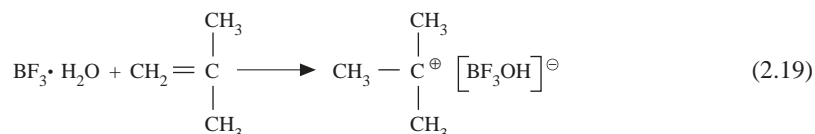
III. IONIC AND COORDINATION POLYMERIZATIONS

As noted earlier, chain-reaction polymerization may be classified as free-radical, cationic, anionic, or coordination polymerization depending on the nature of the reactive center. The growing polymer molecule is associated with counterions in ionic (cationic and anionic) polymerization or with a coordination complex in coordination polymerization. Ionic polymerizations involve chain carriers or reactive centers that are organic ions or charged organic groups. In anionic polymerization, the growing chain end carries a negative charge or carbanions, while cationic polymerization involves a growing chain end with a positive charge or carbonium (carbenium) ion. Coordination polymerization is thought to involve the formation of a coordination compound between the catalyst, monomer, and growing chain.

The mechanisms of ionic and coordination polymerizations are more complex and are not as clearly understood as those of free radical polymerization. Here, we will briefly highlight the essential features of these mechanisms, and more details will be given in Chapter 7. Initiation of ionic polymerization usually involves the transfer of an ion or an electron to or from the monomer. Many monomers can polymerize by more than one mechanism, but the most appropriate polymerization mechanism for each monomer is related to the polarity of the monomers and the Lewis acid–base strength of the ion formed.

A. CATIONIC POLYMERIZATION

Monomers with electron-donating groups like isobutylene form stable positive charges and are readily converted to polymers by cationic catalysts. Any strong Lewis acid like boron trifluoride (BF_3) or Friedel–Crafts catalysts such as $AlCl_3$ can readily initiate cationic polymerization in the presence of a cocatalyst like water, which serves as a Lewis base or source of protons. During initiation, a proton adds to the monomer to form a carbonium ion, which forms an association with the counterion. This is illustrated for isobutylene and boron trifluoride in Equation 2.19:

$$BF_3 \cdot H_2O + CH_2 = \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{\oplus}{C}}} \left[BF_3OH \right]^{\ominus} \tag{2.19}$$

Propagation involves the consecutive additions of monomer molecules to the carbonium ion at the growing chain end. Termination in cationic polymerization usually involves rearrangement to produce a polymer with an unsaturated terminal unit and the original complex or chain transfer to a monomer and possibly to the polymer or solvent molecule. Unlike free-radical polymerization, termination by combination of two cationic polymer growing chains does not occur.

Cationic polymerizations are usually conducted in solutions and frequently at temperatures as low as –80 to –100°C. Polymerization rates at these low temperature conditions are usually fast. The cation and the counterion in cationic polymerization remain in close proximity. If the intimate association between the ion pair is too strong, however, monomer insertion during propagation will be prevented. Therefore the choice of solvent in cationic polymerization has to be made carefully; a linear increase in polymer chain length and an exponential increase in the reaction rate usually occur as the dielectric strength of the solvent increases.

B. ANIONIC POLYMERIZATION

Monomers that are suitable for anionic polymerization generally contain electron-withdrawing substituent groups. Typical monomers include styrene, acrylonitrile, butadiene, methacrylates, acrylates, ethylene oxide, and lactones. The initiator in anionic polymerization may be any compound providing a strong nucleophile, including Grignard reagents and other organometallic compounds. Initiation involves

the addition of the initiator to the double bond of the monomer, as illustrated for styrene and butyllithium in Equation 2.20.

$$n - C_4H_9^-\ Li^+ + CH_2 = CH_2 \longrightarrow n - C_4H_9 - CH_2 - CH^-\ Li^+ \qquad (2.20)$$
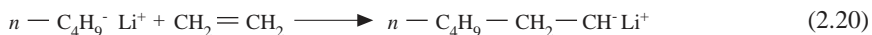
The reaction produces a carbanion at the head end to which is associated the positively charged lithium counterion. Propagation occurs by the successive insertion of monomer molecules by anionic attack of the carbanion. No chain transfer or branching occurs in anionic polymerization, particularly if reactions are carried out at low temperatures. Termination of the growth activity of the polymer chain takes place either by the deliberate or accidental introduction into the system of oxygen, carbon dioxide, methanol, water, or other molecules that are capable of reacting with the active chain ends. We note that in anionic polymerization as well as free-radical polymerization, the initiator or part of it becomes part of the resulting polymer molecule, attached to the nongrowing chain end. This contrasts with cationic polymerization where the catalyst is necessary for initiation and propagation, but is regenerated at the termination step.

In some systems, termination can be avoided if the starting reagents are pure and the polymerization reactor is purged of all oxygen and traces of water. This produces polymer molecules that can remain active even after all the monomer molecules are consumed. When fresh monomer is added, polymerization resumes. Such polymeric molecules are referred to as "living polymers" because of the absence of termination. Since the chain ends grow at the same rate, the molecular weight of living polymers is determined simply by the ratio of monomer concentration to that of the initiator (Equation 2.21).

$$\text{Degree of Polymerization (DP)} = \frac{[\text{monomer}]}{[\text{initiator}]} \qquad (2.21)$$

Polymers produced by living polymerization are characterized by very narrow molecular weight distribution (Poisson distribution). The polydispersity D is given by Equation 2.22

$$D = \overline{M}_w / \overline{M}_n = 1 + 1/DP \qquad (2.22)$$

where $\overline{M}_w$ and $\overline{M}_n$ are the weight-average molecular weight and number-average molecular weight, respectively.

As discussed in Chapter 7, the absence of termination in living polymerization permits the synthesis of unusual and unique block polymers — star- and comb-shaped polymers. Living polymerization can also be employed to introduce a variety of desired functional groups at one or both ends of polymeric chains both in homo- and block polymers. In particular, living polymerization techniques provide the synthetic polymer chemist with a vital and versatile tool to control the architecture of a polymer; complicated macromolecules can be synthesized to meet the rigid specification imposed by a scientific or technological demand.
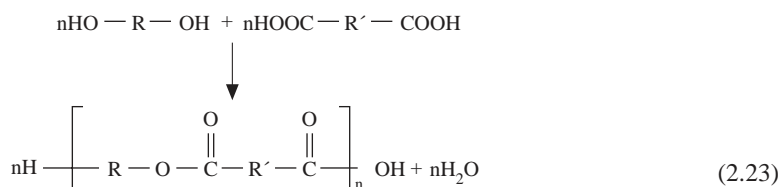
C. COORDINATION POLYMERIZATION

As we shall see in Chapter 4, monomers with side groups asymmetrically disposed with respect to the double bond are capable of producing polymers in which the side groups have a specific stereochemical or spatial arrangement (isotactic or syndiotactic). In both cationic and anionic polymerizations, the association of initiating ion and counterion permits a preferential placement of asymmetric substituted monomers, the extent of which depends on the polymerization conditions. Unbranched and stereospecific polymers are also produced by the use of Ziegler–Natta catalysts. These are complex catalyst systems derived from a transition metal compound from groups IVB to VIIIB of the periodic table and an organometallic compound usually from a group IA or IIIA metal. A typical catalyst complex is that formed by trialkyl aluminum and titanium trichloride as shown below:

(Str. 3)
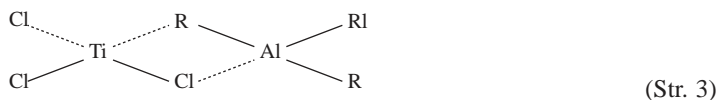
Monoolefins such as propylene and dienes such as butadiene and isoprene can be polymerized using Ziegler–Natta coordination catalysts. The catalysts function by forming transient π-complexes between the monomers and the transition metal species. The initiating species is a metal–alkyl complex and propagation involves the consecutive insertion of monomer molecules into a polarized titanium–carbon bond. Coordination polymerizations may be terminated by introducing poisons such as water, hydrogen, aromatic alcohols, or metals like zinc into the reacting system.

IV.   STEP-GROWTH POLYMERIZATION

Step-growth polymerization involves a series of reactions in which any two species (monomers, dimers, trimers, etc.) can react at any time, leading to a larger molecule. Most step-growth polymerizations, as we shall see presently, involve a classical condensation reaction such as esterification, ester interchange, or amidization. In step-growth polymerization, the stepwise reaction occurs between pairs of chemically reactive or functional groups on the reacting molecules. In most cases, step-growth polymerization is accompanied by the elimination of a small molecule such as water as a by-product. A typical step-growth polymerization of the condensation type is the formation of a polyester through the reaction of a glycol and a dicarboxylic acid, as shown in Equation 2.23
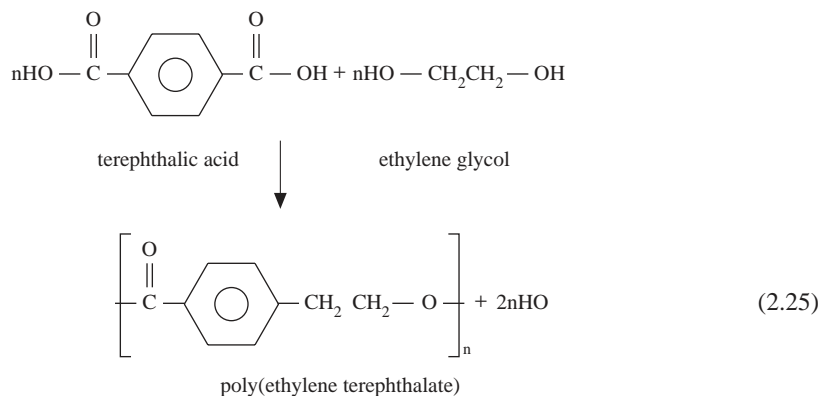
$$nHO - R - OH + nHOOC - R' - COOH$$

$$nH \left[R - O - \overset{\overset{\displaystyle O}{\|}}{C} - R' - \overset{\overset{\displaystyle O}{\|}}{C} \right]_n OH + nH_2O \qquad (2.23)$$

where R and R′ are the unreactive part of the molecules.

Step-growth polymerizations generally involve either one or more types of monomers. In either case, each monomer has at least two reactive (functional) groups. In cases where only one type of monomer is involved, which is known as A-B step-growth polymerization, the functional groups on the monomer are different and capable of intramolecular reactions. An example is the formation of an aliphatic polyester by the self-condensation of ω-hydroxycaproic acid (Equation 2.24).

$$nHO - (CH_2)_5 - \overset{\overset{\displaystyle O}{\|}}{C} - OH \longrightarrow \left[- (CH_2)_5 - \overset{\overset{\displaystyle O}{\|}}{C} - O - \right]_n + 2nH_2O \qquad (2.24)$$

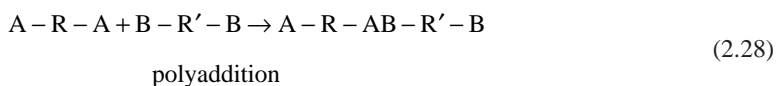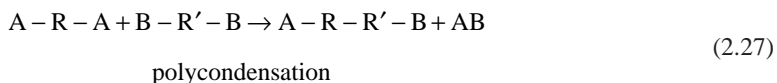ω-hydroxycproic acid   polycaprolactone
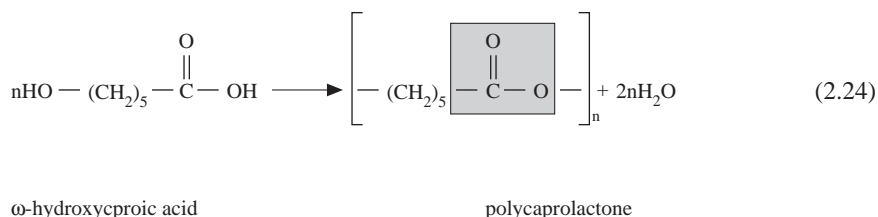
Here, each molecule contains two different functional groups: a hydroxyl group (–OH) and a carboxylic acid group (–COOH). These react to form a series of ester linkages ($-\overset{\overset{\displaystyle O}{\|}}{C}-O-$) shown in the shaded box. In those cases where more than one type of molecule is involved, the functional groups on each type of monomer are the same, but capable of intermolecular reaction with the other type of monomer. This is known as the A–A/B–B step-growth polymerization and is exemplified by the preparation of poly(ethylene terephthalate) and nylon 6,6 (Equations 2.25 and 2.26).
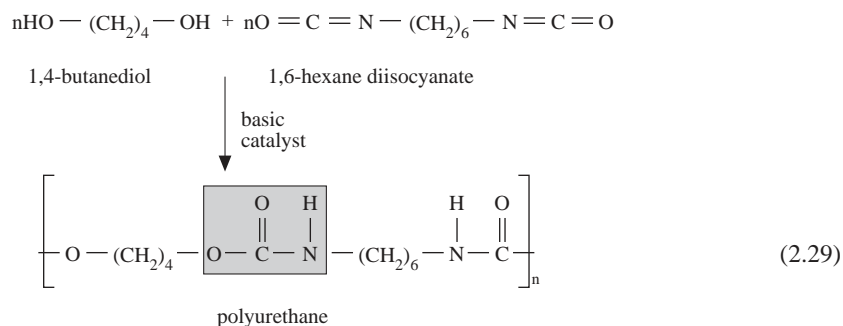
$$\text{nHO} - \underset{\underset{\text{terephthalic acid}}{}}{\overset{\overset{O}{\|}}{C}} - \text{C} - \text{OH} + \text{nHO} - \text{CH}_2\text{CH}_2 - \text{OH}$$

terephthalic acid   ethylene glycol

$$\left[\underset{}{\overset{\overset{O}{\|}}{C}} - \text{CH}_2\ \text{CH}_2 - \text{O} \right]_n + 2\text{nHO} \tag{2.25}$$

poly(ethylene terephthalate)

$$\text{nH}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2 \ + \ \text{nHO} - \overset{\overset{O}{\|}}{C} - (\text{CH}_2)_4 - \overset{\overset{O}{\|}}{C} - \text{OH} \longrightarrow$$

Hexamethylenediamine   **adipic acid**

$$\left[\overset{\overset{H}{|}}{N} - (\text{CH}_2)_6\ (\text{CH}_2)_4 - \overset{\overset{O}{\|}}{C} \right]_n + \ 2\,\text{nH}_2\text{O} \tag{2.26}$$

Nylon 6/6
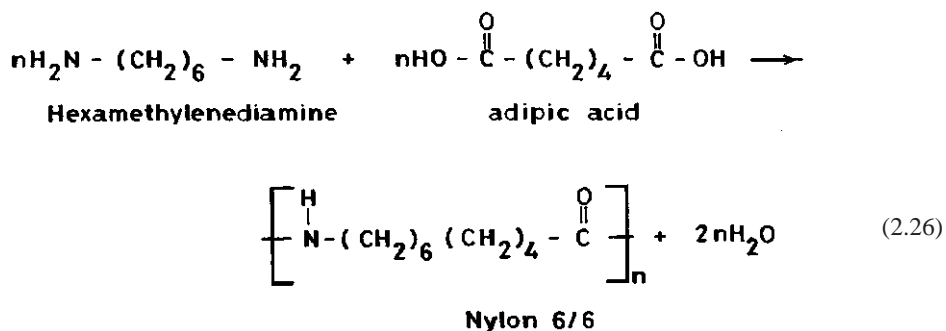
In Equation 2.25, for example, poly(ethylene terephthalate) is formed from the condensation of a dicarboxylic acid and a diol.

Step-growth polymerizations can be divided into two main categories: polycondensation, in which a small molecule is eliminated at each step, as discussed above; and polyaddition, in which, as the name suggests, monomers react without the elimination of a small molecule. These are shown in Equations 2.27 and 2.28, respectively, where R and R$'$ are the nonreactive portions of the molecules.

$$A - R - A + B - R' - B \rightarrow A - R - R' - B + AB \tag{2.27}$$

polycondensation

$$A - R - A + B - R' - B \rightarrow A - R - AB - R' - B \tag{2.28}$$

polyaddition

An example of polyaddition-type step-growth polymerization is the preparation of polyurethane by the ionic addition of diol (1,4 butanediol) to a diisocyanate (1,6 hexane diisocyanate) (Equation 2.29).

$$nHO - (CH_2)_4 - OH + nO = C = N - (CH_2)_6 - N = C = O$$

1,4-butanediol   1,6-hexane diisocyanate

basic catalyst

$$\left[-O - (CH_2)_4 - \boxed{O - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{N}} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - \right]_n \qquad (2.29)$$

polyurethane

Another example of polyaddition-type step-growth polymerization is the preparation of polyurea from the reaction of diisocyanate and diamine, as shown in Equation 2.30.

$$nH_2N - (CH_2)_6 - NH_2 + nO = C = N - (CH_2)_6 - N = C = O$$

hexamethylenediamine   hexamethylene diisocyanate

basic catalyst

$$\left[-\overset{\overset{H}{|}}{N} - (CH_2)_6 - \boxed{\overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{N}} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - \right]_n \qquad (2.30)$$

polyurea
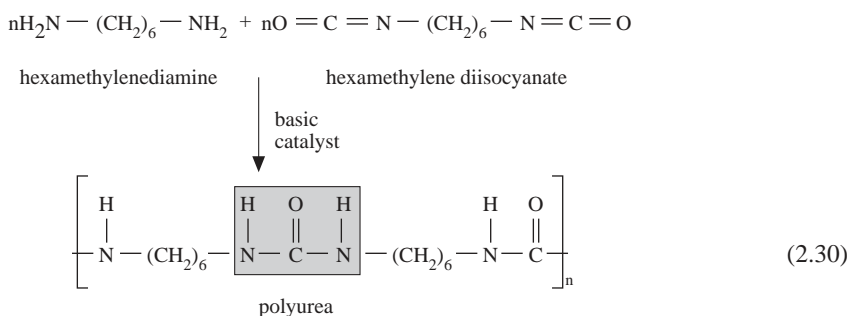
The characteristic linkage (group) in each of the above classes of polymers shown in the boxes has been summarized in Table 2.2.

In contrast to addition polymers, the structural unit in step-growth polymers is not identical chemically to the structure of the starting monomer(s). Consequently, step-growth polymers derive their names from the reactive type (characteristic interunit linkage) involved in the polymerization process. In the reaction between the glycol and dicarboxylic acid, for instance, the resulting polymer is a polyester, in consonance with the general name of reactions between hydroxyl groups (–OH) and carboxylic acid groups (–COOH) (Table 2.2).

By extension of this argument, the chemical structures of condensation polymers are not readily derived from the names of the polymers. Furthermore, the backbone of condensation polymers is heterogeneous, being generally composed of carbon plus other atoms, usually nitrogen and oxygen (Table 2.3) and sometimes sulfur and silicon. As we shall see later, this has serious implications for the resultant polymer properties. The main distinguishing features between addition and condensation polymerizations are summarized in Table 2.3.

Example 2.2: Unsaturated polyester resins, which are used as the matrix component of glass–fiber composites, may be obtained by the copolymerization of maleic anhydride and diethylene glycol. The low-molecular-weight product is soluble in styrene. Describe, with the aid of equations, the possible structures of the prepolymer and that of the polymer resulting from benzoyl peroxide-initiated polymerization of a solution of the prepolymer in styrene.

**TABLE 2.2** *Some Functional Groups and Their Characteristic Interunit Linkage in Polymers*

Reactants Functional Group	Characteristic Interunit Linkage	Polymer Type
$-OH \ + \ -COOH$	$\begin{matrix} O \\ \| \\ -C-O- \end{matrix}$	Polyester
$-NH_2 + \ -COOH$	$\begin{matrix} O \ \ H \\ \| \ \ \| \\ -C-N \end{matrix}$	Polyamide
$-OH \ + \ -NCO$	$\begin{matrix} O \ \ H \\ \| \ \ \| \\ -O-C-N \end{matrix}$	Polyurethane
$-NH_2 + \ -NCO$	$\begin{matrix} H \ \ O \ \ H \\ \| \ \ \| \ \ \| \\ -N-C-N- \end{matrix}$	Polyurea
$-COOH + \ -COOH$	$\begin{matrix} O \ \ \ \ \ O \\ \| \ \ \ \ \ \| \\ -C-O-C- \end{matrix}$	Polyanhydride
$-OH \ \ + \ \ -OH$	$-O-$	Polyether
$\begin{matrix} -CH-CH \\ \backslash \ \ / \\ O \end{matrix}$	$-O-$	Polyether
$\begin{matrix} O \\ \| \\ HO-C-OH \end{matrix}$	$\begin{matrix} O \\ \| \\ -O-C-O- \end{matrix}$	Polycarbonate

TABLE 2.3 *Distinguishing Features of Chain and Step Polymerization Mechanisms*

Chain Polymerization	Step Polymerization
Only growth reaction adds repeating unit one at a time of the chain.	Any two molecular species present can react.
Monomer concentration decreases steadily throughout reaction.	Monomer disappears early in reaction: at DP 10, less than 1% monomer remains.
High polymer is formed at once; polymer molecular weight changes little throughout reaction.	Polymer molecular weight rises steadily throughout reaction.
Reaction mixture contains only monomer, high polymer, and about 10^{-5} part of growing chains.	At any stage all molecular species are present in a calculable distribution.

From Billmeyer, F. W., Jr., *Textbook of Polymer Science,* 3rd ed., Interscience, New York, 1984. With permission.

Solution:

Maleic anhydride   Diethylene glycol

(Str. 4)

prepolymer

benzoyl
peroxide
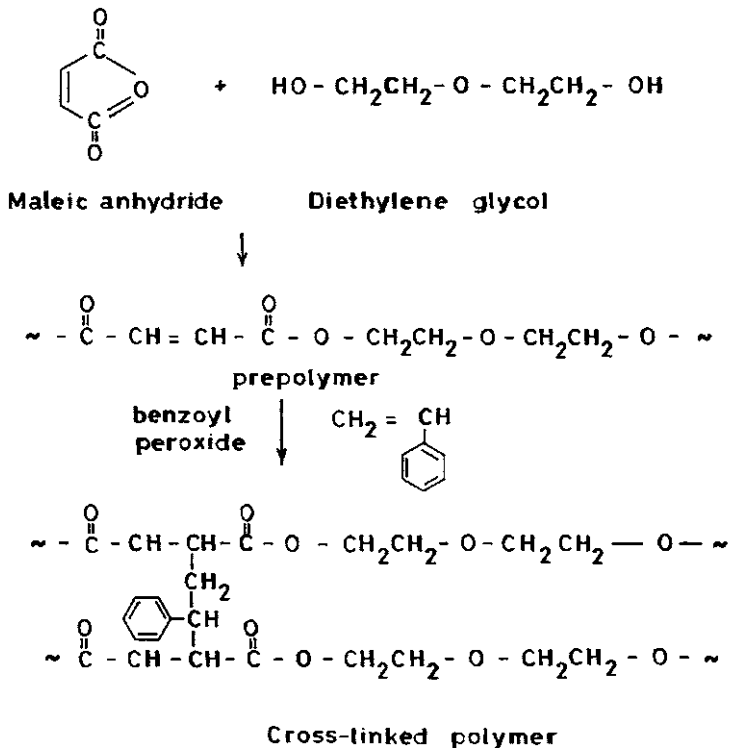
Cross-linked polymer

Maleic anhydride is unsaturated. Its reaction with diethylene glycol leads to a prepolymer with residual double bonds on the main chain. These participate in cross-linking reactions with styrene during initiation with benzoyl peroxide. The result is a network polymer.

A. TYPICAL STEP-GROWTH POLYMERIZATIONS
1. Polyesters

Polyesters form a large class of commercially important polymers. A typical polyester is poly(ethylene terephthalate) (PETP), the largest volume synthetic fiber. It is also used as film (mylar) and in bottle applications. We have already discussed in the preceding section one of the routes for the preparation of PETP. The traditional route for the production of commercial PETP is through two successive ester interchange reactions, as shown below:

$$xCH_3O-\overset{\overset{O}{\|}}{C}-\!\!\!\bigcirc\!\!\!-\overset{\overset{O}{\|}}{C}-OCH_3 + 2x \; HO-CH_2CH_2-OH$$

dimethyl terephthalate   ethylene glycol

↓ catalyst
150 - 200°C

$$nHO-CH_2CH_2-O-\left[\overset{\overset{O}{\|}}{C}-\!\!\!\bigcirc\!\!\!-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_2O\right]_x\!\!-H + 2xCH_3OH \qquad \text{(Str. 5)}$$

↓ catalyst
260 - 300°C

$$\left[-\overset{\overset{O}{\|}}{C}-\!\!\!\bigcirc\!\!\!-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2-O-\right]_{nx} + \; nx \; HO-CH_2CH_2-OH\cdot$$

poly(ethylene terephthalate)
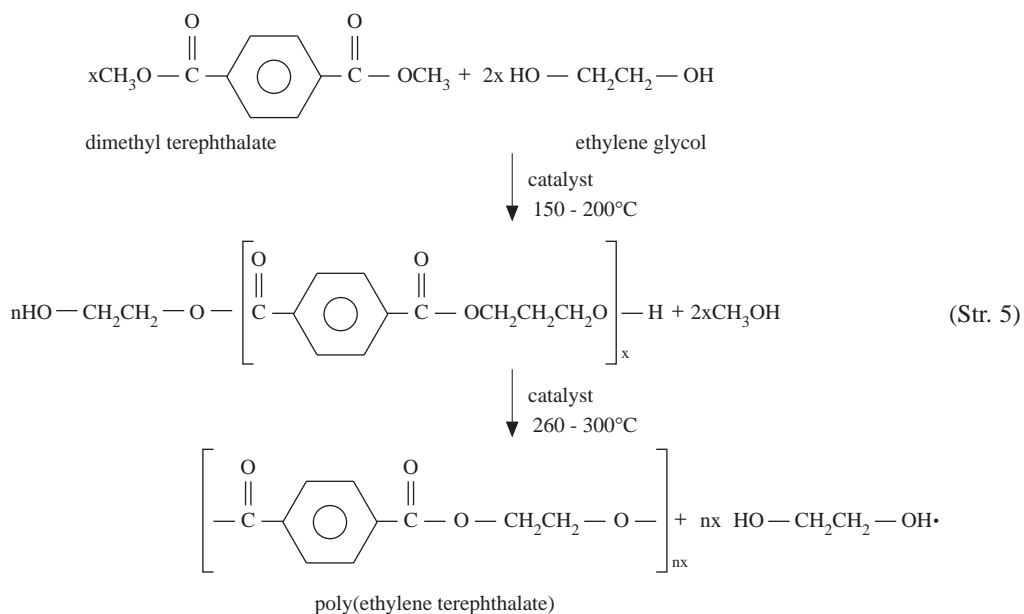
In the first step, a 1:2 molar ratio of dimethyl terephthalate to ethylene glycol is heated at temperatures near 200°C in the presence of a catalyst such as calcium acetate. During this stage, methanol is evolved and an oligomeric product (x = 1 to 4) is obtained. The second step involves a temperature increase to about 300°C. This results in the formation of high polymer with the evolution of ethylene glycol.

Poly(ethylene terephthalate) is a linear polyester obtained from the reaction of difunctional monomers. Branched or network polyesters are obtained if at least one of the reagents is tri- or multifunctional. This can be achieved either by the use of polyols such as glycerol in the case of saturated polyesters (glyptal) or by the use of unsaturated dicarboxylic acids such as maleic anhydride in the case of unsaturated polyester. In the preparation of glyptal, glycerol and phthalic anhydride react to form a viscous liquid initially, which on further reaction hardens as a result of network formation (Equation 2.31).
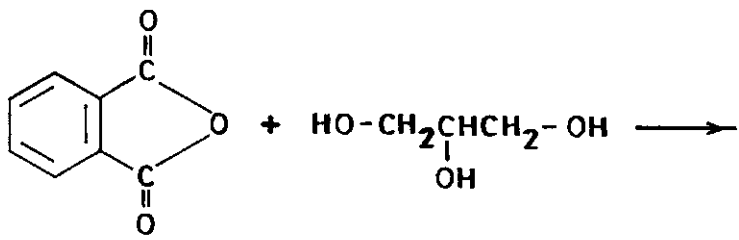
Phthalic anhydride   Glycerol
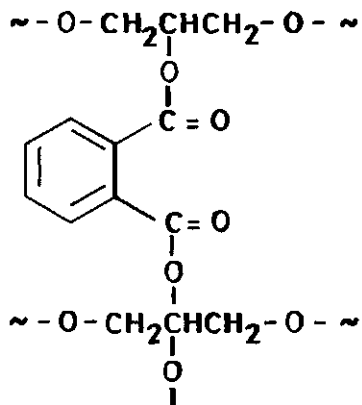
$$\sim-O-CH_2CHCH_2-O-\sim \qquad (2.31)$$

Glyptal is used mainly as an adhesive. Glyptal modified with natural or synthetic oils is known as an alkyd resin, which is a special polyester of great importance in the coatings industry. A typical alkyd resin comprises the following reagents:
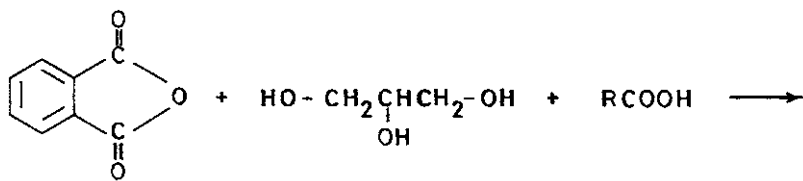
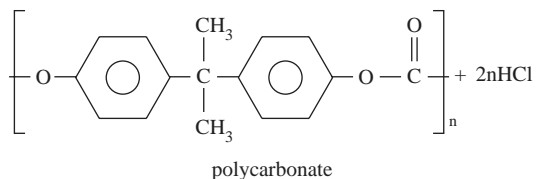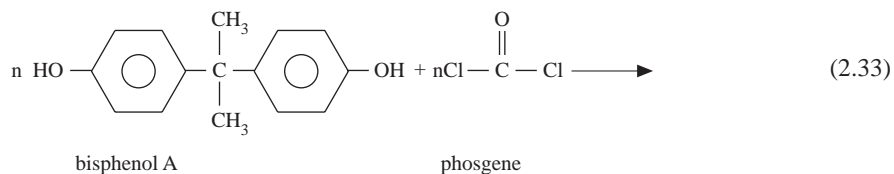Phthalic anhydride   Glycerol   Fatty acid   (2.32)
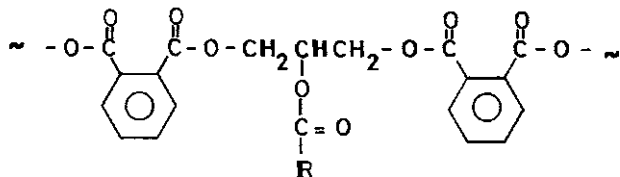
The fatty acid RCOOH may be derived from vegetable drying oils (e.g., soybean, linseed oils) or from nondrying oils (e.g., coconut oil).

2. Polycarbonates

Polycarbonates are a special class of polyesters derived from carbonic acid (HO–$\overset{\overset{\text{O}}{\|}}{\text{C}}$–OH) and have the following general structure:

$$\left[-R - O - \overset{\overset{\text{O}}{\|}}{C} - O - \right]_n \qquad \text{(Str. 6)}$$

Polycarbonates are the second largest by volume engineering thermoplastics next to polyamides. Their preparation involves the linking together of aromatic dihydroxy compounds, usually 2,2-bis(4-hydroxyphenyl) propane or bisphenol A, by reacting them with a derivative of carbonic acid such as phosgene (Equation 2.33) or diphenyl carbonate (Equation 2.34).

$$\text{n HO} - \bigcirc - \overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CH}_3}{|}}{C}} - \bigcirc - \text{OH} + \text{nCl} - \overset{\overset{\text{O}}{\|}}{C} - \text{Cl} \longrightarrow \qquad (2.33)$$

bisphenol A   phosgene

$$\left[-O - \bigcirc - \overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CH}_3}{|}}{C}} - \bigcirc - O - \overset{\overset{\text{O}}{\|}}{C} - \right]_n + \text{2nHCl}$$

polycarbonate

$$\text{n HO} - \bigcirc - \overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CH}_3}{|}}{C}} - \bigcirc - \text{OH} + \text{PhO} - \overset{\overset{\text{O}}{\|}}{C} - \text{OPH} \longrightarrow \qquad (2.34)$$

bisphenol A   diphenyl carbonate

$$\left[-O - \bigcirc - \overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CH}_3}{|}}{C}} - \bigcirc - O - \overset{\overset{\text{O}}{\|}}{C} - \right]_n + \text{2nPhOH}$$

polycarbonate
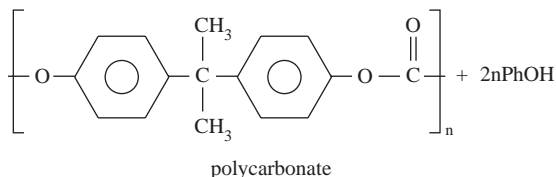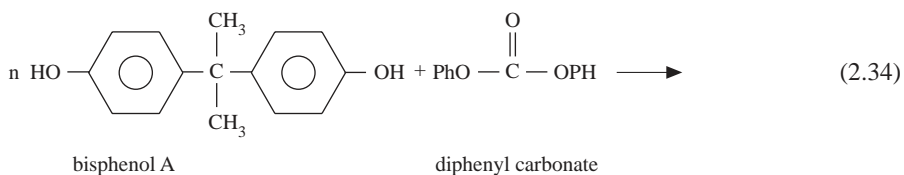
The reaction of bisphenol A with phosgene involves bubbling the phosgene into a solution of bisphenol A in pyridine at 20 to 35°C and isolation of the resulting polymer by precipitation in water or methanol. In the reaction of Bisphenol A with diphenyl carbonate, a prepolymer is formed initially by heating the mixture at 180 to 220°C in vacuum. Then the temperature is raised slowly to 280 to 300°C at reduced pressure to ensure the removal of the final traces of phenol.

3. Polyamides

Polyamides, or nylons, as they are commonly called, are characterized by the presence of amide linkages (–CONH–) on the polymer main chain. Theoretically, a large number of polyamides can be synthesized based on four main synthetic routes: (1) condensation reaction between a dicarboxylic acid and a diamine,

(2) reaction between a diacid chloride and a diamine, (3) dehydration–condensation reactions of amino acids, and (4) ring-opening polymerization of lactams. Chemically, nylons may be divided into two categories: those based on synthetic routes (1) and (2); and those based on routes (3) and (4). The commercial use of nylons is centered around two products: nylon 6,6 from the first category, and nylon 6 from the second. We now expatiate our earlier discussion of the preparation of nylon 6,6, while the preparation of nylon 6 will be deferred to a subsequent section.

As with other polyamides, the classical route for the synthesis of nylon 6,6 is the direct reaction between a dicarboxylic acid (adipic acid) and a diamine (hexamethylenediamine). In practice, however, to achieve an exact stoichiometric equivalence between the functional groups, a 1:1 salt of the two reactants is prepared initially and subsequently heated at a high temperature to form the polyamide. For nylon 6,6, an intermediate hexamethylene diammonium adipate salt is formed. A slurry of 60 to 80% of the recrystallized salt is heated rapidly. The steam that is released is purged by air. Temperature is then raised to 220°C and finally to 270 to 280°C when the monomer conversion is about 80 to 90% while maintaining the steam pressure generated during polymerization at 200 to 250 psi. The pressure is subsequently reduced to atmospheric pressure, and heating is continued until completion of polymerization:

$$HO - \underset{\substack{\|\\O}}{C} - (CH_2)_4 - \underset{\substack{\|\\O}}{C} - OH \ + \ H_2N - (CH_2)_6 - NH_2$$

adipic acid   hexamethylenediamine

heat

$$\left[\overset{\ominus}{O} - \underset{\substack{\|\\O}}{C} - (CH_2)_4 - \underset{\substack{\|\\O}}{C} - \overset{\ominus}{O}\right]\left[\overset{\oplus}{H_3N} - (CH_2)_6 - \overset{\oplus}{NH_3}\right] \qquad \text{(Str. 7)}$$

hexamethylene diammonium adipate salt

heat

$$\left[- \underset{\substack{\|\\O}}{C} - (CH_2)_4 - \underset{\substack{\|\\O}}{C} - \underset{\substack{|\\H}}{N} - (CH_2)_6 - \underset{\substack{|\\H}}{N} -\right] + \ 2H_2O$$

nylon 6,6
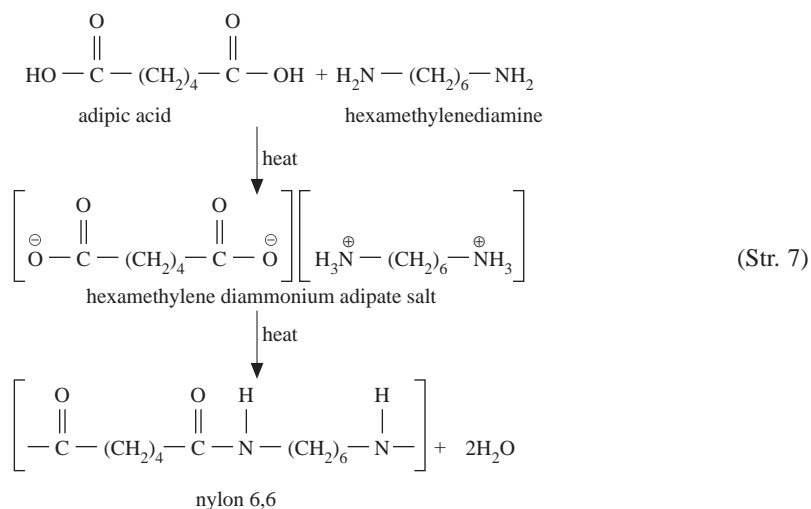
Since the polymerization reaction occurs above the melting points of both reactants and the polymer, the polymerization process is known as melt polymerization.

Other polyamides of commercial importance are nylons that are higher analogs of the more common types: nylons 11; 12; 6,10; and 6,12. The numerals in the trivial names refer to the number of carbon atoms in the monomer(s). In designating A–A/B–B nylons, the first number refers to the number of carbon atoms in the diamine while the second number refers to the total number of carbon atoms in the acid. For example, nylon 6,10 is poly(hexamethylene sebacamide) (Equation 2.35).

$$nH_2N-(CH_2)_6-NH_2 \; + \; nHO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_8-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

<div align="center">hexamethylenediamine   sebacic acid</div>

$$\left[-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_8-\overset{\overset{\displaystyle O}{\|}}{C}-\right]_n \; + \; 2nH_2O$$

<div align="center">poly(hexamethylene sebacamide)
(nylon 6,10)</div>

<div align="right">(2.35)</div>
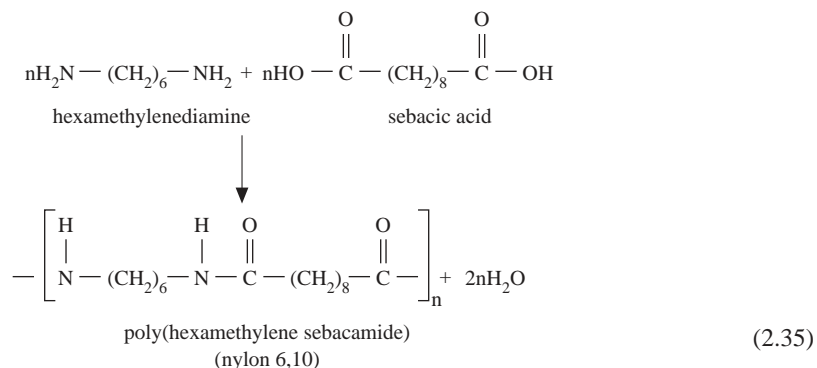
In the 1960s aromatic polyamides were developed to improve the flammability and heat resistance of nylons. Poly(*m*-phenyleneisophthalamide), or Nomex, is a highly heat resistant nylon obtained from the solution or interfacial polymerization of a metasubstituted diacid chloride and a diamine (Equation 2.36).

<div align="center">poly(<i>m</i>-phenyleneisophthalamide)
(Nomex)</div>

<div align="right">(2.36)</div>
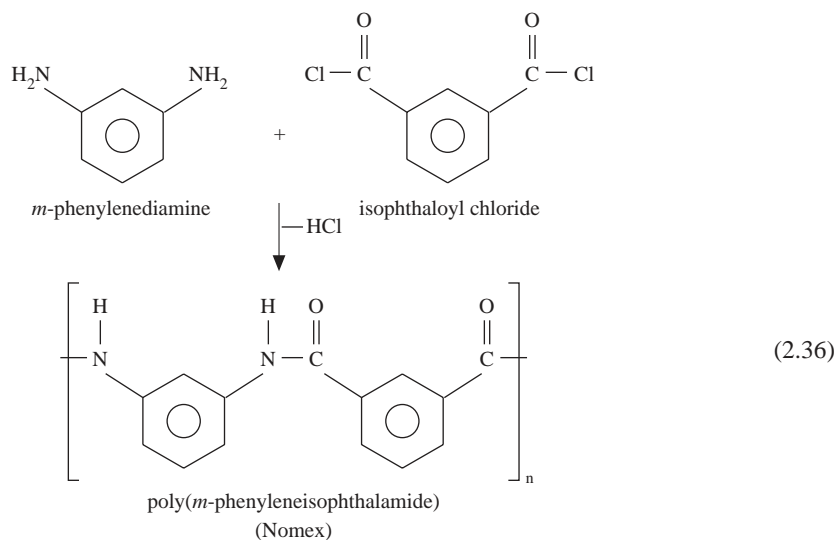
The corresponding linear aromatic polyamide is Kevlar aramid which decomposes only above 500°C (Equation 2.37).

$$\text{H}_2\text{N}-\underset{p\text{-phenylenediamine}}{\boxed{\bigcirc}}-\text{NH}_2 \quad + \quad \text{Cl}-\overset{\text{O}}{\underset{}{\text{C}}}-\underset{\text{terephthaloyl chloride}}{\boxed{\bigcirc}}-\overset{\text{O}}{\underset{}{\text{C}}}-\text{Cl} \quad \xrightarrow{-\text{HCl}}$$
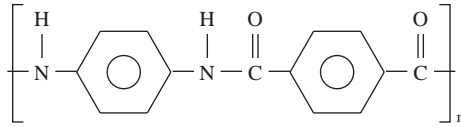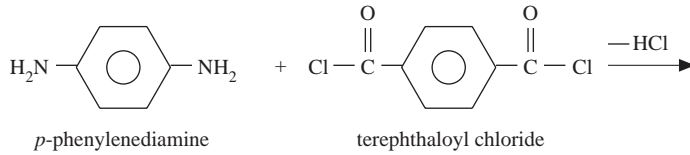
$$\left[\ \overset{\text{H}}{\underset{}{\text{N}}}-\boxed{\bigcirc}-\overset{\text{H}}{\underset{}{\text{N}}}-\overset{\text{O}}{\underset{}{\text{C}}}-\boxed{\bigcirc}-\overset{\text{O}}{\underset{}{\text{C}}}\ \right]_n \tag{2.37}$$

poly(p-phenyleneterephthalamide)
(Kevlar)

The high thermooxidative stability of Kevlar is due to the absence of aliphatic units in its main chain. The material is highly crystalline and forms a fiber whose strength and modulus are higher than that of steel on an equal weight basis.

4. Polyimides

Polyimides are condensation polymers obtained from the reaction of dianhydrides with diamines. Polyimides are synthesized generally from aromatic dianhydrides and aliphatic diamines or, in the case of aromatic polyimides, from the reaction of aromatic dianhydrides with aromatic diamines. Aromatic polyimides are formed by a general two-stage process. The first step involves the condensation of aromatic dianhydrides and aromatic diamines in a suitable solvent, such as dimethylacetamide, to form a soluble precursor or poly(amic acid). This is followed by the dehydration of the intermediate poly(amic acid) at elevated temperature:

pyromellitic dianhydride   *m*-phenyldiamine

$30 - 40°C$

poly(amic acid)   (2.38)

$150 - 250°C$

$+ \quad 2nH_2O$

poly(*m*-phenylpyromellitimide)

(4)
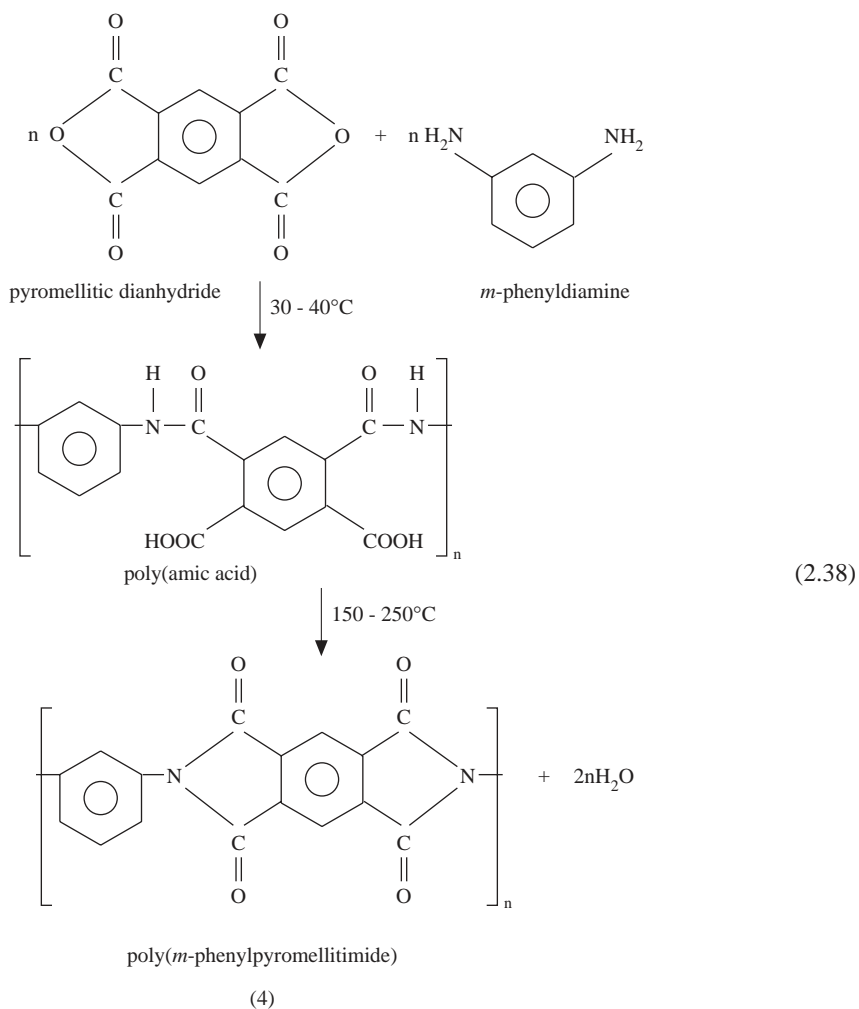
The cured or fully imidized polyimide, unlike the poly(amic acid), is insoluble and infusible with high thermooxidative stability and good electrical-insulation properties. Thermoplastic polyimides that can be melt processed at high temperatures or cast in solution are now also available. Through an appropriate choice of the aromatic diamine, phenyl or alkyl pendant groups or main-chain aromatic polyether linkages can be introduced into the polymer. The resulting polyimides are soluble in relatively nonpolar solvents.

For polyimides to be useful polymers, they must be processable, which means that they have to be meltable. Melt processability of polyimides can be improved by combining the basic imide structure with more flexible aromatic groups. This can be achieved by the use of diamines that can introduce flexible linkages like aromatic ethers and amides into the backbone. Polyamide-imides (5) are obtained by condensing trimellitic anhydrides and aromatic diamines, while polyetherimides (6) are produced by nitro displacement reaction involving bisphenol A, 4,4′-methylenedianiline, and 3-nitrophthalic anhydride.

(Str. 8)

(5)

(6)
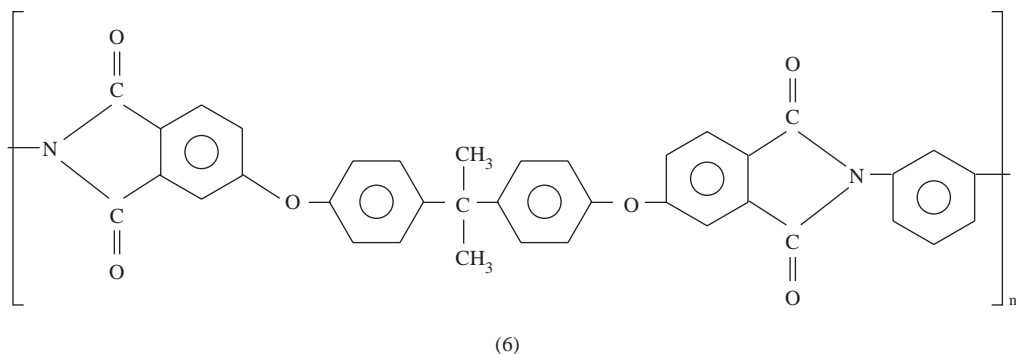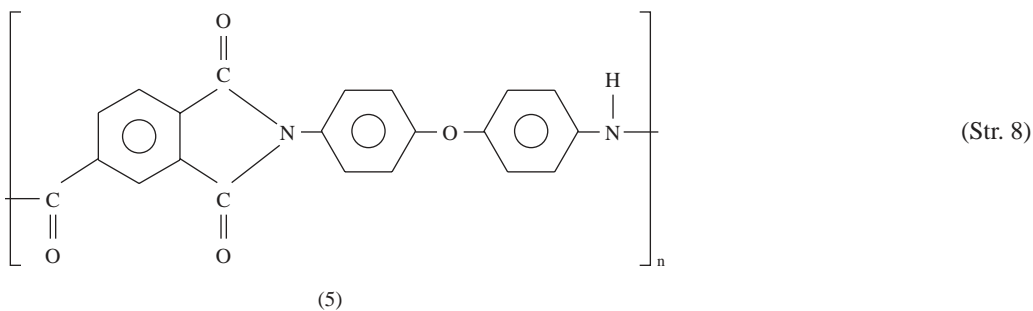
5. Polybenzimidazoles and Polybenzoxazoles

Aromatic substituents at the chains of vinyl polymers influence the behavior of these materials. Aromatic units as part of the main chain exert a profound influence on virtually all important properties of the resulting polymer. Aromatic polyamides are formed by the repetitive reaction of aromatic amino group and carboxyl group in the molar ratio of 1:1. In aromatic polyamides as well as aromatic polyesters, the chain-stiffening aromatic rings are separated from each other by three consecutive single bonds:

polyamide   polyester
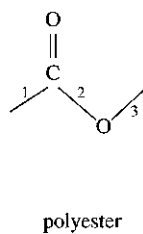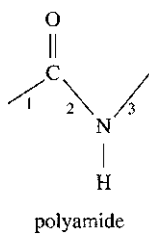
(Str. 9)

The two tetrahedral angles associated with these bonds permit some degree of chain flexibility, which limits the mechanical and thermal properties of the resulting polymers. One way of reducing flexibility and enhancing these properties is to reduce the number of consecutive single bonds between two aromatic units to two, one, or even zero. In polyethers, polysulfides, and polysulfones, as we shall see shortly, the number of consecutive single bonds has been reduced to two, and these are separated by only one tetrahedral angle:

polyether   polysulfide   polysulfone
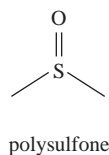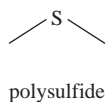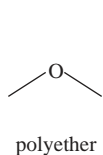
(Str. 10)

Polyimides, polybenzimidazole, and polybenzoxazoles are polymers where the number of these bonds has been reduced to one. Ladder polymers typify cases where there are no consecutive single bonds between aromatic moities in the main chain.

In aromatic polyimides (4), two of the three consecutive single bonds between aromatic groups in polyamides are eliminated by the formation of a new ring. This is achieved by employing a 2:1 molar ratio of aromatic carboxyl and amino groups. When the molar ratio of carboxyl groups (e.g., terephthalic acid) to amino groups (e.g., 3,3′ diaminobenzidine) is 1:2, polybenzimidazoles (7) are formed; whereas where the molar ratio of carboxyl, amino, and hydroxyl groups is 1:1:1, polybenzoxazoles (8) are formed.

terephthalic acid   3,3′ diaminobenzidine

(2.39)

polybenzimidazole

(7)

terephthalic acid   4,6-diamino-1,3-benzenediol dihydrochloride

(2.40)

polybenzoxazole

(8)
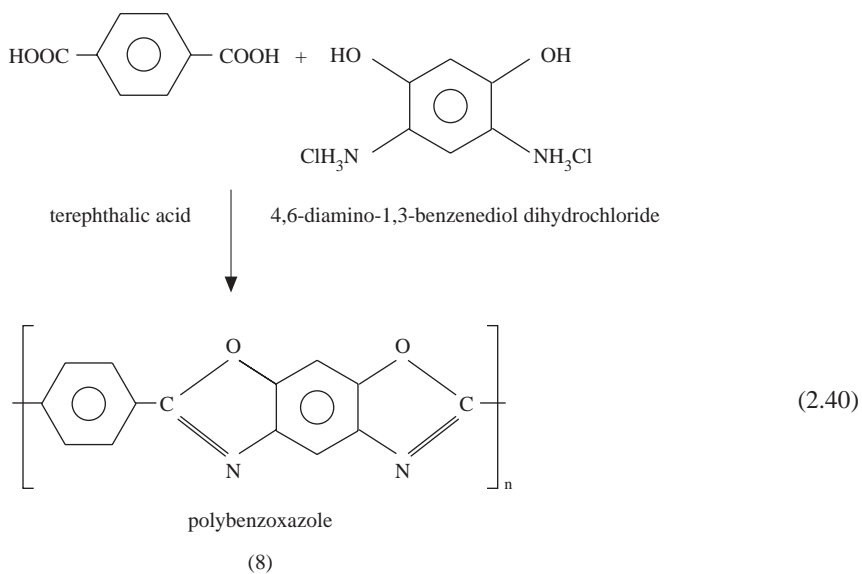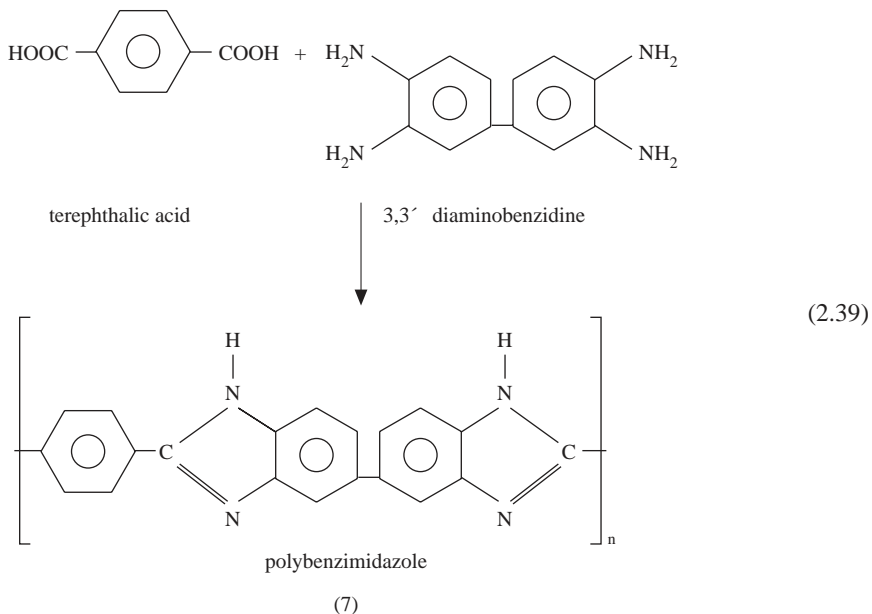
6. Aromatic Ladder Polymers

As evident from the preceding discussion, the next logical step to increase the rigidity of linear macromolecules is the elimination of single bonds in the main chain so that it is composed of only condensed cyclic units. The resulting polymer has the following generalized structure (9)
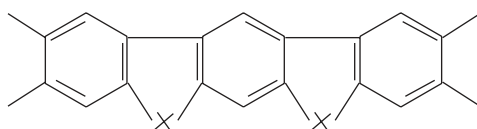
(Str. 11)

(9)

where the individual cyclic units may be either aromatic or cycloaliphatic, homocyclic or heterocyclic. Polymers of this type are known as ladder polymers. Polybenzimidazoles discussed previously are typical aromatic ladder polymers. Longer segments of ladder are present in polyimidazopyrrolones (10) prepared by polymerization of aromatic dianhydrides or aromatic tetracarboxylic acids with *ortho*-aromatic tetramines according to the following scheme:
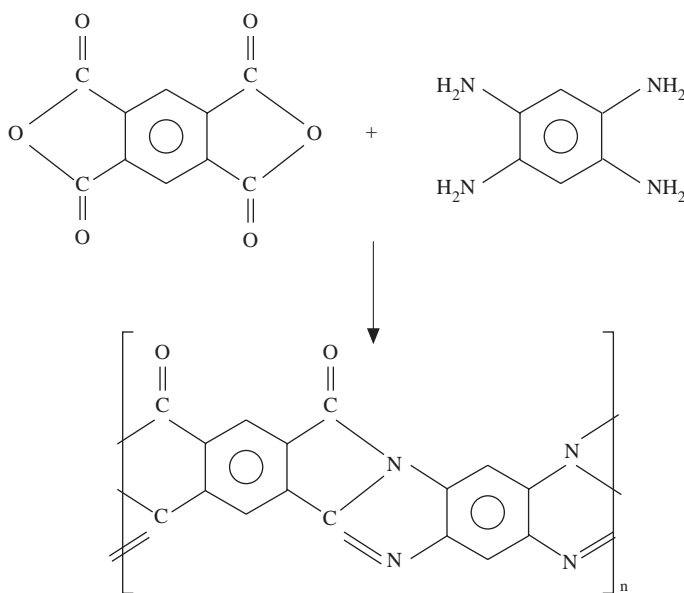
(2.41)

(10)

Polyquinoxalines (11) are another group of ladder polymers. They differ from polyimidazopyrrolones by the presence of a fused six-membered cyclic diimide structure. A possible synthetic route for polyquinoxalines involves the reaction of 1,4,5,8-naphthalene tetracarboxylic acid with aromatic tetraamines in polyphosphoric acid (PPA) at temperatures up to 220°C.

(11)

(2.42)
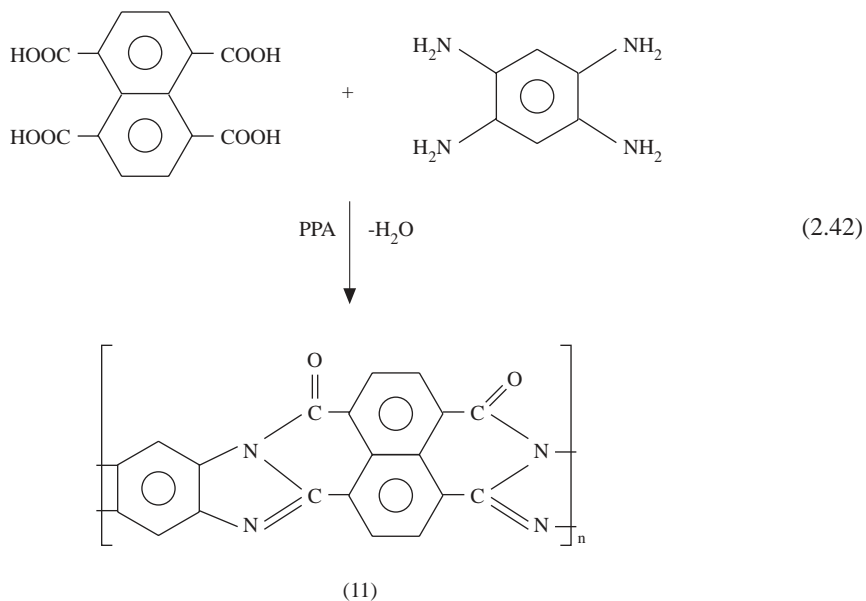
Ladder polymers are also referred to as "double-chain" or "double-strand" polymers because, unlike other polymers, the backbone consists of two chains. Cleavage reactions in single-chain polymers cause a reduction in molecular weight that ultimately results in a deterioration in the properties of the polymer. For this to happen in a ladder polymer, two bonds will have to be broken in the same chain residue, which is a very unlikely occurrence. Therefore, ladder polymers usually have exceptional thermal, mechanical, and electrical properties.

Example 2.3: Polyimides have been prepared from aromatic anhydrides and aliphatic diamines by melt fusion of salt from the diamine and tetracid (dianhydride). Aliphatic polypyromellitimide derived from straight-chain aliphatic diamines containing more than nine carbon atoms gave thin, flexible films, whereas those from shorter chain aliphatic diamines allowed the preparation of only thick, brittle moldings. Explain this observation.

Solution: The general structure of aliphatic polypyromellitimide is represented as follows:

(Str. 12)
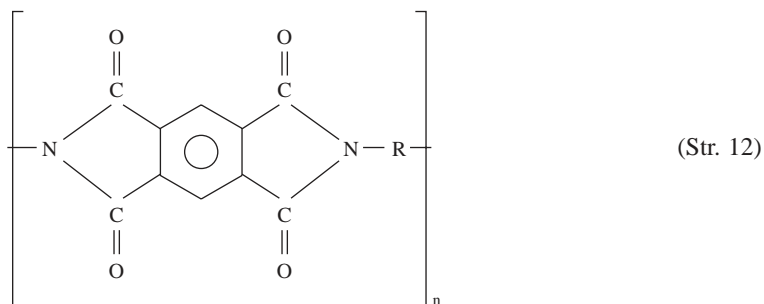
where R is an alkylene group. Polyimides are usually rigid polymers. Some flexibility can be introduced into the polymer structure by incorporating flexible groups in the backbone of the polymer such as flexible diamines. The longer the alkylene group the more flexible the diamine. It is apparent from the observation that straight-chain alkylenes with nine or more carbon atoms introduced sufficient flexibility into the resulting polymer that films made from this polymer were flexible. On the other hand, when R was less than nine carbon atoms, the resulting polymers were still too rigid and, consequently, brittle.

7. Formaldehyde Resins

Formaldehyde is employed in the production of aminoplasts and phenoplasts, which are two different but related classes of thermoset polymers. Aminoplasts are products of the condensation reaction between either urea (urea–formaldehyde or UF resins) or melamine (melamine–formaldehyde or MF resins) with formaldehyde. Phenoplasts or phenolic (phenol–formaldehyde or PF) resins are prepared from the condensation products of phenol or resorcinol and formaldehyde.

a. Urea–Formaldehyde Resins

Urea–formaldehyde resin synthesis consists basically of two steps. In the first step, urea reacts with aqueous formaldehyde under slightly alkaline conditions to produce methylol derivatives of urea (12, 13).


(2.43)
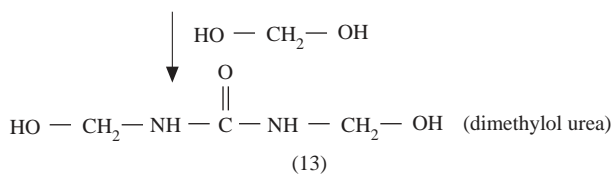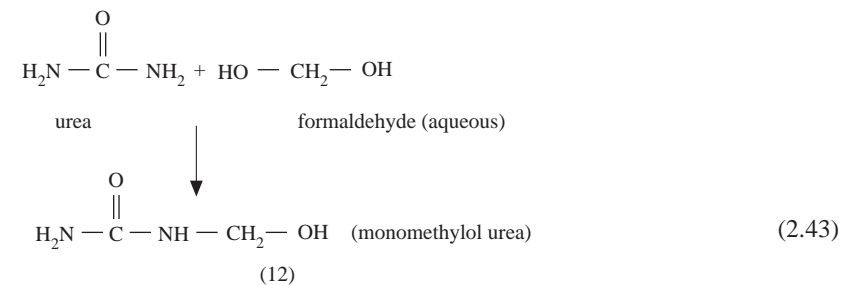
In the second step, condensation reactions between the methylol groups occur under acidic conditions, leading ultimately to the formation of a network structure (14):

$$-N-\overset{\overset{\displaystyle O}{\parallel}}{C}-NH-CH_2OH \; + \; HOCH_2-NH-\overset{\overset{\displaystyle O}{\parallel}}{C}-N-$$

$$\downarrow$$

$$-N-\overset{\overset{\displaystyle O}{\parallel}}{C}-NH-CH_2-O-CH_2-NH-\overset{\overset{\displaystyle O}{\parallel}}{C}-N- \qquad (2.44)$$

$$\downarrow$$

$$-\overset{\displaystyle |}{N}-\overset{\overset{\displaystyle O}{\parallel}}{C}-NH-CH_2-NH-\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{\displaystyle |}{N}-$$

(14)
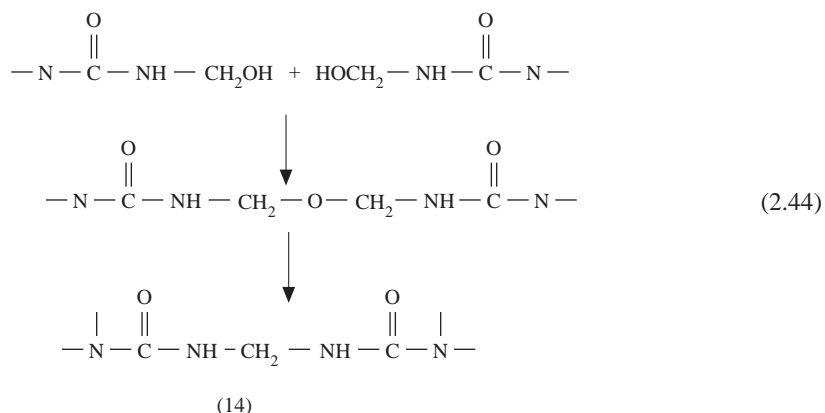
b. Melamine–Formaldehyde Resins

Production of melamine–formaldehyde polymers involves reactions essentially similar to those of UF resins, that is, initial production of methylol derivatives of melamine, which on subsequent condensation, ultimately form methylene bridges between melamine groups in a rigid network structure (15).

(2.45)

15
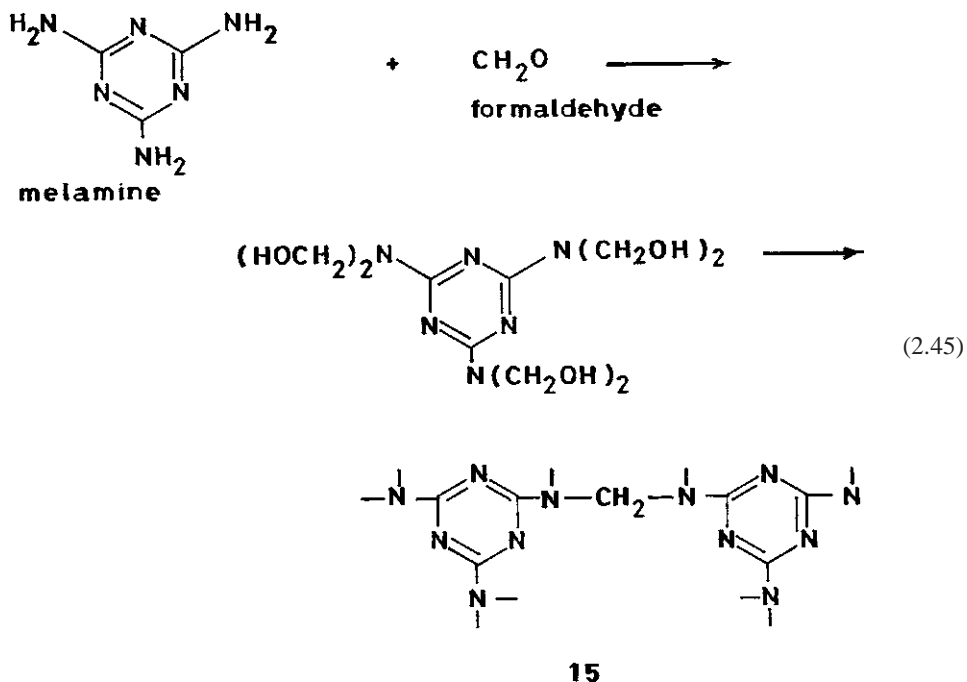
c. Phenol–Formaldehyde Resins

Phenolic resins are prepared by either base-catalyzed (resoles) or acid-catalyzed (novolacs) addition of formaldehyde to phenol. In the preparation of resoles, phenol and excess formaldehyde react to produce a mixture of methylol phenols. These condense on heating to yield soluble, low-molecular-weight prepolymers or resoles (16). On heating of resoles at elevated temperature under basic, neutral, or slightly acidic conditions, a high-molecular-weight network structure or phenolic rings linked by methylene bridges (17) is produced.

(2.46)

16

17
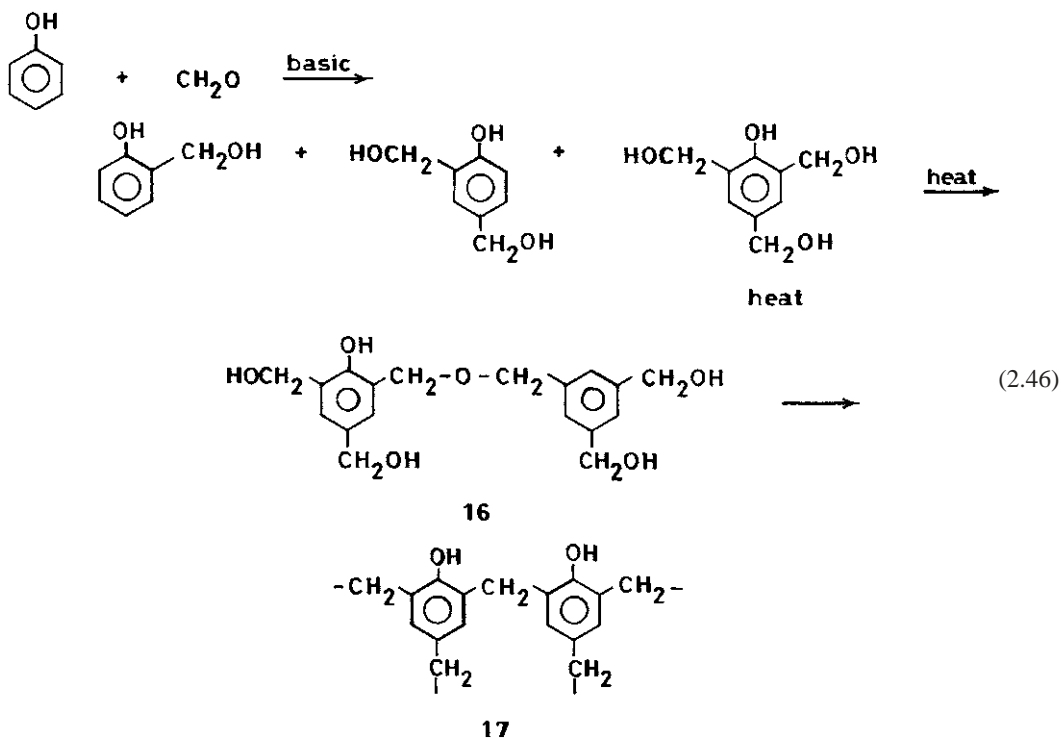
Novolacs are low-molecular-weight, fusible but insoluble prepolymers (18) prepared by reaction of formaldehyde with molar excess of phenol. Novolacs, unlike resoles, do not contain residual methylol groups. A high-molecular-weight network polymer similar to that of resoles is formed by heating novolac with additional formaldehyde, paraformaldehyde, or hexamethylenetetramine.


(Str. 13)

(18)
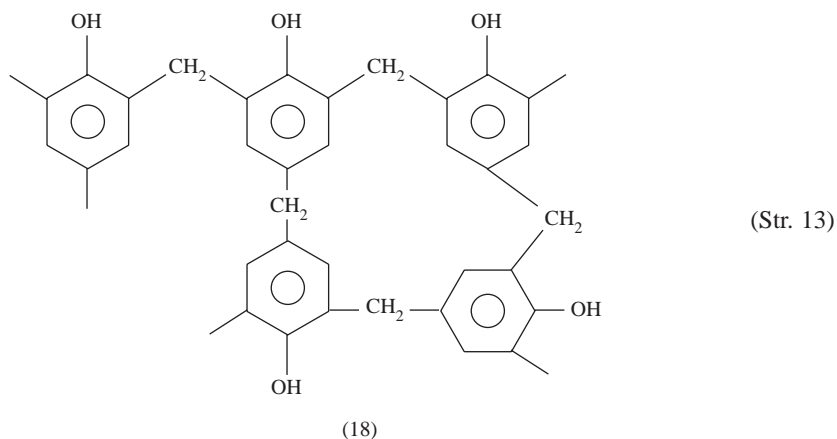
We now discuss a number of polymerization reactions that are of the step-reaction type but which may not necessarily involve condensation reactions.

8. Polyethers

As we said earlier, the introduction of aromatic units into the main chain results in polymers with better thermal stability than their aliphatic analogs. One such polymer is poly(phenylene oxide), PPO, which has many attractive properties, including high-impact strength, resistance to attack by mineral and organic acids, and low water absorption. It is used, usually blended with high-impact polystyrene (HIPS), to ease processability in the manufacture of machined parts and business machine enclosures.

Poly(phenylene oxide) (19) is obtained from free-radical, step-growth, oxidative coupling of 2,6-dimethylphenol (2,6-xylenol). This involves passing oxygen into a reaction mixture containing 2,6-xylenol, cuprous chloride, and pyridine.

$$
n \; \text{2,6-xylenol} \; + \; \frac{n}{2} \, O_2 \longrightarrow \text{(19)} + nH_2O \tag{2.47}
$$

(19)
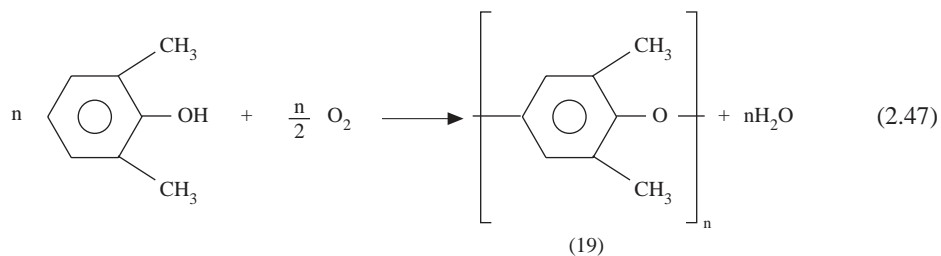
9. Polysulfides

Aromatic polythioethers or polysulfides are closely related to polyethers in structure and properties. A typical aromatic polysulfide is poly(phenylene sulfide) (PPS) (20), which is used as electrical insulators and structural parts in the building of engines and vehicles. Poly(phenylene sulfide) is prepared by the condensation reaction between *p*-dichlorobenzene and sodium sulfide:

$$
n \; Cl \text{---} \bigcirc \text{---} Cl + nNa_2S \longrightarrow \text{(20)} + 2nNaCl \tag{2.48}
$$

(20)
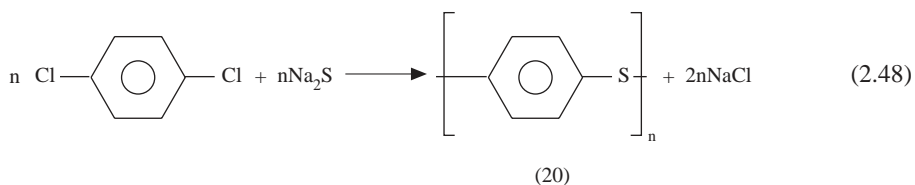
10. Polysulfones

Another family of linear aromatic polymers is the polysulfones. They are tough, high-temperature-resistant engineering thermoplastics. Polysulfones may be synthesized by the nucleophilic substitution of alkali salts of biphenates with activated aromatic dihalides. A typical example is the preparation of bisphenol A polysulfone (21) from the reaction of disodium salt of bisphenol A with dichlorodiphenyl sulfone:

disodium salt of bisphenol A   4,4′-dichlorodiphenyl sulfone

(2.49)

(21)
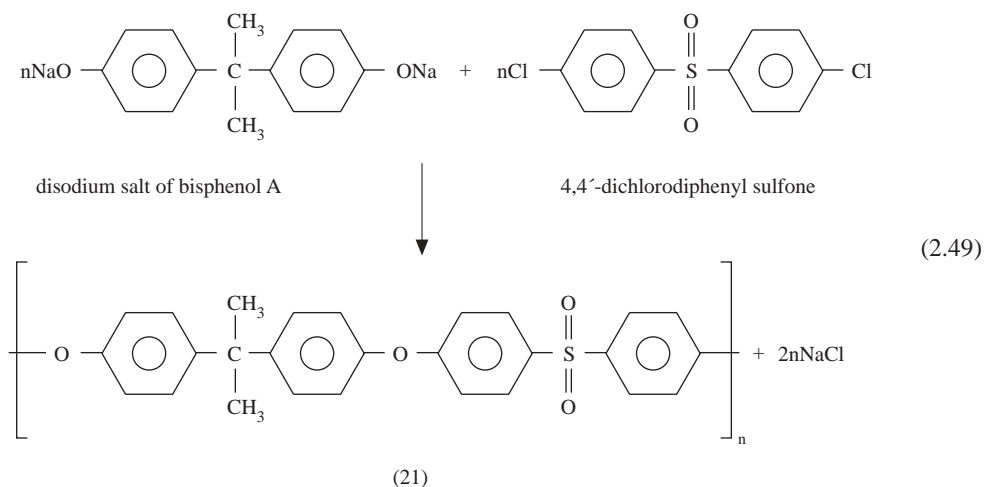
The polymerization reaction involves the initial preparation of the disodium salt of bisphenol A by the addition of aqueous NaOH to bisphenol A in dimethyl sulfoxide (DMSO). A solution of dichlorodiphenyl sulfone is added, and polymerization is carried out at 160°C.

V. RING-OPENING POLYMERIZATION

While ring-opening polymerization shares certain features with condensation and addition polymerization mechanisms, it differs from each of them in at least one important respect. In the first place, in contrast to condensation polymerization, no small molecule is split off in ring-opening polymerization. Second, unlike olefin polymerization, the driving force for ring-opening polymerization is not derived from the loss of unsaturation.

A significant number of polymers has been produced from the ring-opening of cyclic organic compounds, including epoxides such as ethylene and propylene oxides and epichlorohydrin and other cyclic ethers like trioxane and tetrahydrofuran. Other important systems include cyclic esters (lactones), cyclic amides (lactams), cycloolefins, and siloxane. Ring-opening polymerization involves essentially an initial ring-opening of the cyclic monomer followed by polyaddition. The resulting polymers are normally linear. Their structural units usually have the same composition as the monomer. Major applications of polymers obtained from ring-opening polymerization are in coatings, fibers, elastomers, adhesives, and thermoplastics- and thermoset-based composite systems.

Ring-opening polymerizations may be represented broadly by Equation 2.50

$$\left(\text{(CH}_2)_y \quad X\right) \quad \longrightarrow \quad \left[-\text{(CH}_2)_y-X-\right]_n \tag{2.50}$$
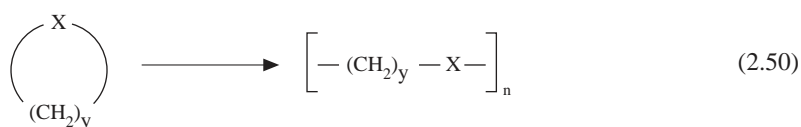
where X may be a heteroatom such as O, S, or a group like NH, –O–CO–, –NH–CO, or –C› C–. Not all cyclic compounds can undergo ring-opening polymerization. It is therefore understood from Equation 2.50 that the cyclic structure is capable of ring-opening polymerization to produce a linear chain of degree of polymerization, n. The nature of X is such that it provides a mechanism for a catalyst or initiator to form the initiating coordination intermediate with the cyclic ring. Table 2.4 shows a number of commercially important polymers produced by ring-opening polymerization together with the associated polymerization initiation mechanism.
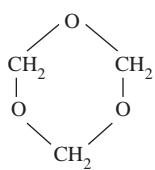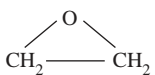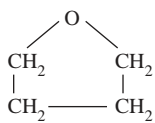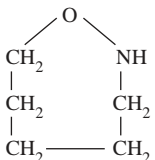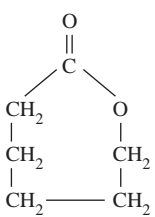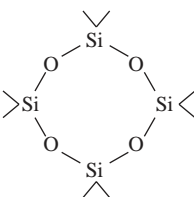
A. POLY(PROPYLENE OXIDE)

The polymerization of propylene oxide represents an important example of industrial ring-opening polymerization. It involves an attack of the least sterically hindered carbon by the hydroxyl anion to produce the alkoxide (Equation 2.51). This produces essentially linear polymer molecules.

$$\text{KOH} + \text{CH}_2\underset{\text{O}}{-}\text{CH}-\text{CH}_3 \xrightarrow{\Delta}$$

$$\text{HO}-\text{CH}_2-\underset{\underset{\text{CH}_3}{|}}{\text{CH}}-\text{O} \ominus \text{K} \oplus \xrightarrow[\text{then H}^+]{\text{Propagation}} \left[\text{CH}_2-\text{CH}-\text{O}\right]_n \tag{2.51}$$
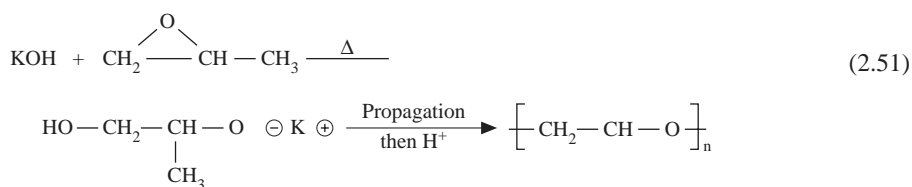
Poly(propylene oxide) glycols are utilized extensively as soft segments in urethane foams, which, among other applications, are used as automobile seats. It is frequently necessary to modify the growing species in propylene oxide polymerization with ethylene oxide in order to produce a polymer with acceptable reactivity with isocyanates and urethane product with desirable properties.

Table 2.4 *Examples of Commercially Important Ring-Opening Polymerizations*

Monomer	Polymer	Mechanism
trioxane	$[-CH_2-O-]_n$ polyoxymethylene	Cationic
ethylene oxide	$-[CH_2-CH_2-O-]_n$ poly(ethylene oxide)	Anionic, cationic, coordination
tetrahydrofuran	$-[(CH_2)_4-O-]_n$ poly(tetramethylene oxide)	Cationic
Caprolactam	Polycaprolactam (nylon 6)	Hydrolytic, anionic
caprolactone	polycaprolactone	Anionic, cationic
Dimethysiloxane (cyclic tetramer)	poly(dimethylsiloxane)	Anionic, cationic

B. EPOXY RESINS

Epoxy resins are normally prepared by the base-catalyzed reaction between an epoxide such as epichlorohydrin and a polyhydroxy compound such as bisphenol A:

bisphenol A   epichlorohydrin


$$\text{(2.52)}$$
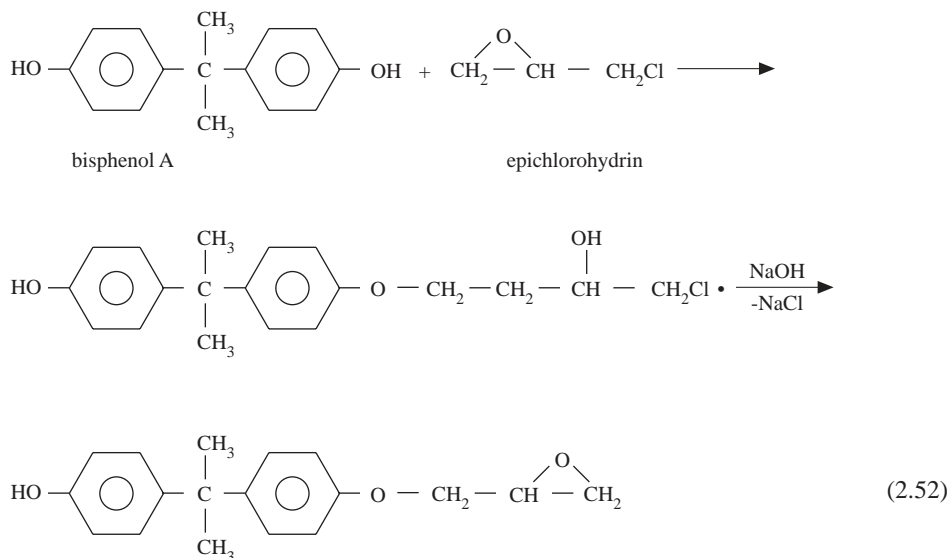
The molar ratio of epichlorohydrin to bisphenol A can range from as high as 10:1 to as low as 1.2:1. This produces resins ranging from liquid to semisolid to solid and varying molecular weights and softening points. The products are oligomers or prepolymers, which are hardly used as such; they have pendant hydroxyl groups and terminal epoxy groups. The epoxy prepolymer can be cross-linked or cured by reaction with a number of reagents, including primary and secondary amines.

C. POLYCAPROLACTAM (NYLON 6)

The industrial manufacture of nylons involves either water-initiated (hydrolytic) or a strong base-initiated (anionic) polymerization of caprolactam. Polymerization by cationic initiation is also known, but monomer conversion and attainable molecular weights are inadequate for practical purposes and as such there is no commercial practice of this process.

Hydrolytic polymerization of caprolactam is the most important commercial process for the production of nylon 6. The following synthetic scheme outlines hydrolytic polymerization of caprolactam:

$$\text{(2.53)}$$

$$\text{(2.54)}$$
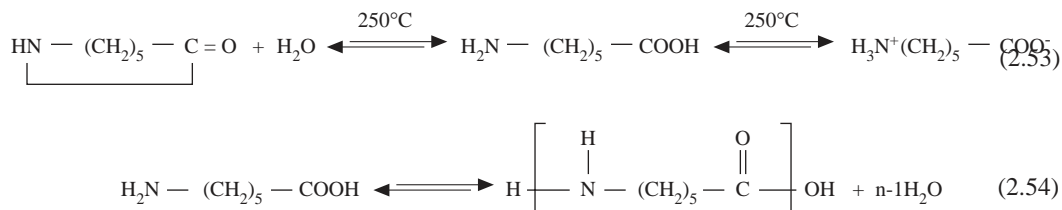
Water opens the caprolactam ring producing aminocaproic acid, which is believed to exist as the zwitterion. The zwitterion interacts with and initiates the step polymerization of the monomer, with the ultimate generation of linear polymer molecules. In other words, the polymerization process involves an initial ring-opening of the monomer that is followed by the step polymerization.
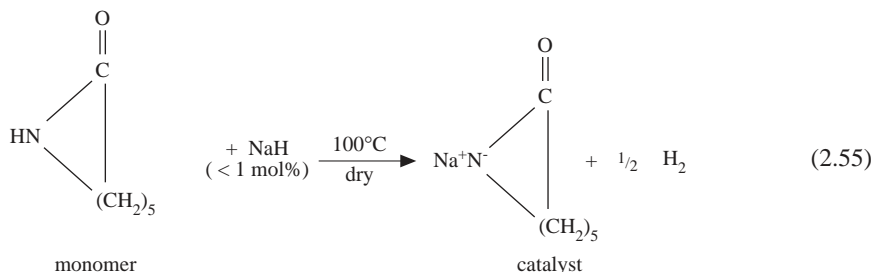
The hydrolytic polymerization process may be carried out as a continuous operation or it may be operated batchwise. It involves heating caprolactam in an essentially oxygen-free atmosphere in the presence of water to temperatures in the range 250 to 270°C for periods ranging from 12 h to more than 24 h. Most of the water used to initiate the reaction is removed during the process after about 80 to 90%

conversion. The overall polymerization involves various equilibria and does not result in complete conversion of the caprolactam. The quantity of the residual monomer depends on the reaction temperature, which under industrial conditions amounts to 8 to 10%. In addition, there are about 3% of predominantly cyclic low-molecular-weight oligomers. These impurities adversely affect the subsequent processing and end-use performance of the polymer and must, therefore, be removed from it. This is achieved either by hot-water extraction or by vacuum evaporation.
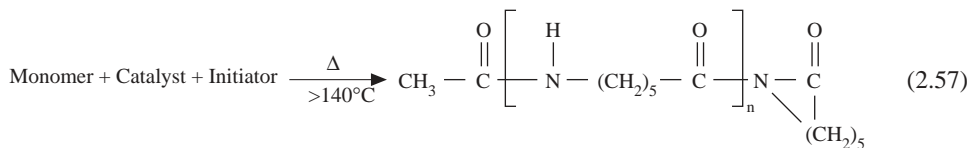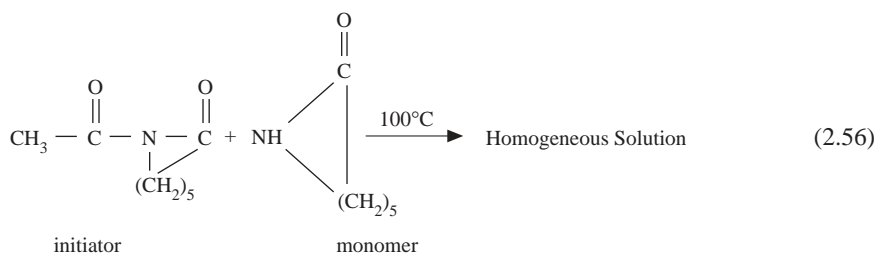
The second approach for the commercial synthesis of nylon 6, which accounts for up to 10% of the volume of the polymer, is the base-initiated anionic polymerization of caprolactam. A small but important number of applications utilize this process, which is characterized by high conversion rates. It involves two techniques: "high-temperature" and "low-temperature" polymerizations. The high-temperature polymerization is carried out at temperatures above the melting point of nylon 6 (i.e., 220°C); whereas the low temperature polymerization involves temperatures in the range 140 to 180°C, which are above the melting point of caprolactam but below the melting point of the resulting polycaprolactam. The polymerization catalysts are strong bases such as sodium hydride or a Grignard reagent. To obtain satisfactory low-temperature polymerization, a coinitiator such as N-acyl caprolactam or acyl-urea is employed in addition to the strong base.

Sodium or magnesium caprolactam salt is produced by reaction of sodium hydride or a Grignard reagent with caprolactam. A rapid polymerization occurs when the acylated lactam, the catalyst, and monomer are mixed at temperature at or greater than 140°C. This polymerization is usually carried out in a two-stream reactor in which one stream contains the catalyst dissolved in the monomer and the second stream contains the initiator dissolved separately in the monomer:

Stream 1:

$$\text{monomer} \quad + \text{ NaH} \atop (<1 \text{ mol\%}) \quad \xrightarrow[\text{dry}]{100°C} \quad \text{catalyst} \quad + \quad {}^{1}/_{2} \ H_2 \tag{2.55}$$

Stream 2:

$$\text{initiator} \quad + \quad \text{monomer} \quad \xrightarrow{100°C} \quad \text{Homogeneous Solution} \tag{2.56}$$

$$\text{Monomer + Catalyst + Initiator} \quad \xrightarrow[>140°C]{\Delta} \quad CH_3 - \overset{O}{\overset{\|}{C}} \left[N - (CH_2)_5 - \overset{O}{\overset{\|}{C}} \right]_n N - \overset{O}{\overset{\|}{C}} \atop (CH_2)_5 \tag{2.57}$$

Unlike the high-temperature process where about 8 to 10% cyclics are generated, the equilibrium monomer content of nylon 6 resulting from polymerization at temperature lower than 200°C (i.e., low-temperature polymerization) can be less than 2%. The polymer therefore does not usually require any additional purification. Also, the maximum rate of crystallization of nylon 6 falls within the range of

temperature employed in low-temperature polymerization. Consequently, the resulting polymers are characterized by a high degree of crystallinity. Nylon 6 objects of any desired shape are obtainable in essentially a single-stage polymerization. Therefore, this process is frequently referred to as "cast nylon 6" or, in current usage, Reaction Injection-Molded (RIM) Nylon 6.

Example 2.4: Ethylene oxide polymerizes readily to high conversions under either anionic or cationic conditions. Tetrahydrofuran can be induced to polymerize in the presence of phosphorous or antimony pentafluorides as catalysts. Tetrahydropyran is unreactive under polymerization conditions. Explain these observations.

Solution:

(Str. 14)

ethylene oxide   tetrahydrofuran   tetrahydropyran
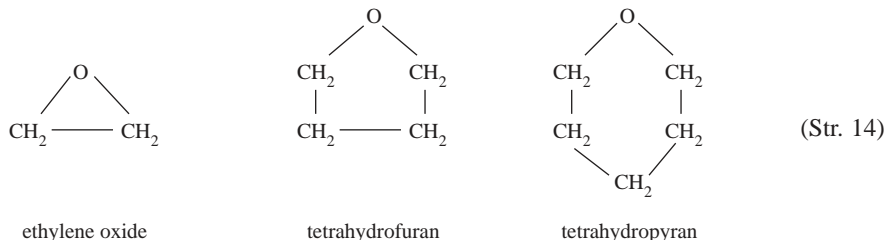
From the structures of these compounds, it is apparent that the ease of polymerization is related to the degree of ring strain. Ethylene oxide is a highly strained three-membered ring. The need to release this strain provides the driving force for polymerization and is reflected in the ease with which ethylene oxide undergoes polymerization. The ring strain decreases in the five-membered tetrahydrofuran and is absent in the six-membered tetrahydropyran.

VI. PROBLEMS

2.1.   Explain the following observations:

  a. Butadiene polymerizes much less readily than vinyl acetate.
  b. Increasing initiator concentration usually leads to lower average molecular weight.

2.2.   The use of phthalic anhydride along with maleic anhydride reduces the brittleness of resin described in Example 2.2 in the text. Why?

2.3.   Melt polymerization of useful aliphatic polypyromellitimides is limited to those polyimides with melting points sufficiently low that they remain molten under the polymerization conditions. Which of the two diamines (ethylenediamine or decamethylenediamine) is more likely to form a useful polymer?

2.4.   Polyheteroaromatics can be produced from aromatic amino carboxylic acids with the following general structure:

(Str. 15)

Comment on the relative thermal stabilities of the polymers made from compounds where Ar is either A, B, or C.

(Str. 16)

(A)   (B)   (C)
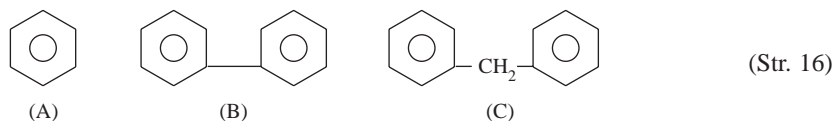
2.5.   Several higher homologs of phenol such as *p*-tertiary butyl phenol, *p*-tertiary amyl phenol and *p*-tertiary octyl-phenol are used to make oil-soluble phenolic resins for varnishes and other coatings systems. What structural features of these compounds make oil solubility of the resins possible?

2.6.   Sketch, on the same graph, the molecular weight conversion curves for A, free-radical polymerization; B, condensation polymerization; and C, living polymerization. Explain the basis of your sketch.

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