

## CHAPTER 2

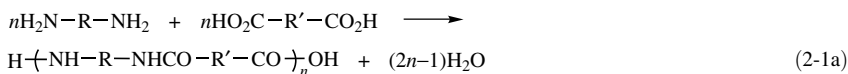
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# STEP POLYMERIZATION

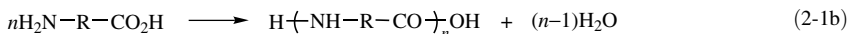
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Many of the common condensation polymers are listed in Table 1-1. In all instances the polymerization reactions shown are those proceeding by the step polymerization mechanism. This chapter will consider the characteristics of step polymerization in detail. The synthesis of condensation polymers by ring-opening polymerization will be subsequently treated in Chap. 7. A number of different chemical reactions may be used to synthesize polymeric materials by step polymerization. These include esterification, amidation, the formation of urethanes, aromatic substitution, and others. Polymerization usually proceeds by the reactions between two different functional groups, for example, hydroxyl and carboxyl groups, or isocyanate and hydroxyl groups.

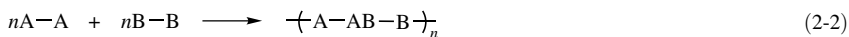
All step polymerizations fall into two groups depending on the type of monomer(s) employed. The first involves two different bifunctional and/or polyfunctional monomers in which each monomer possesses only one type of functional group. (A polyfunctional monomer is a monomer with more than one functional group per molecule. A *bifunctional monomer* is one with two functional groups per molecule.) The second involves a single monomer containing both types of functional groups. The synthesis of polyamides illustrates both groups of polymerization reactions. Thus polyamides can be obtained from the reaction of diamines with diacids



or from the reaction of amino acids with themselves:



The two groups of reactions can be represented in a general manner by the equations



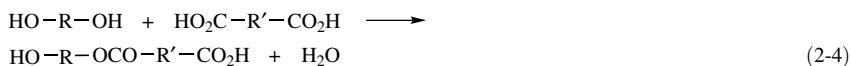
where A and B are the two different types of functional groups. The characteristics of these two polymerization reactions are very similar. The successful synthesis of high polymers (i.e., polymer of sufficiently high molecular weight to be useful from the practical viewpoint) using any step polymerization reaction generally is more difficult than the corresponding small molecule reaction, since high polymers can be achieved only at very high conversions (>98–99%). A conversion of 90%, which would be considered excellent for the synthesis of ethyl acetate or methyl benzamide, is a disaster for the synthesis of the corresponding polyester or polyamide. The need for very high conversions to synthesize high polymer places several stringent requirements on any reaction to be used for polymerization—a favorable equilibrium and the absence of cyclization and other side reactions. These stringent requirements are met by a relatively small fraction of the reactions familiar to and used by chemists to synthesize small molecules. An additional requirement for achieving high molecular weights is the need for the A and B functional groups to be present at very close to stoichiometric amounts.

## 2-1 REACTIVITY OF FUNCTIONAL GROUPS

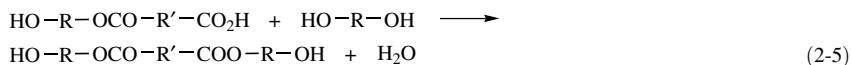
### 2-1a Basis for Analysis of Polymerization Kinetics

The kinetics of polymerization are of prime interest from two viewpoints. The practical synthesis of high polymers requires a knowledge of the kinetics of the polymerization reaction. From the theoretical viewpoint the significant differences between step and chain polymerizations reside in large part in their respective kinetic features.

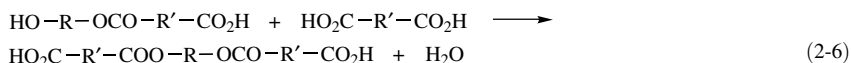
Step polymerization proceeds by a relatively slow increase in molecular weight of the polymer. Consider the synthesis of a polyester from a diol and a diacid. The first step is the reaction of the diol and diacid monomers to form dimer:



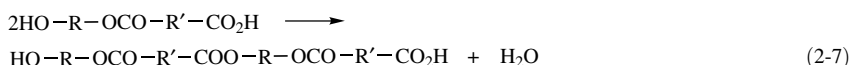
The dimer then forms trimer by reaction with diol monomer



and also with diacid monomer:

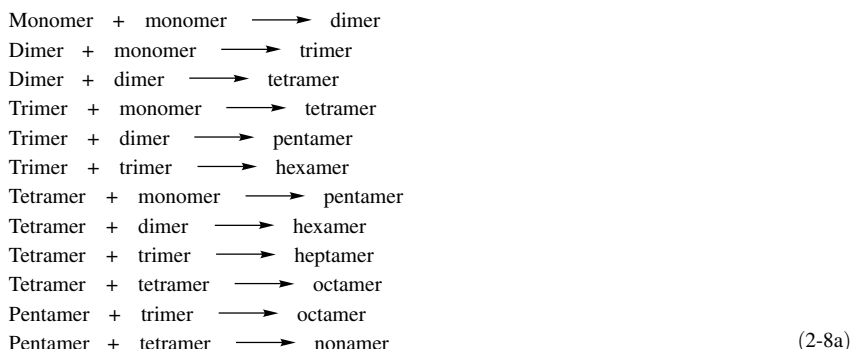


Dimer reacts with itself to form tetramer:



The tetramer and trimer proceed to react with themselves, with each other, and with monomer and dimer. The polymerization proceeds in this stepwise manner with the molecular weight of the polymer continuously increasing with time (conversion). Step polymerizations are characterized by the disappearance of monomer early in the reaction far before the production of any polymer of sufficiently high molecular weight (approximately  $>5000$ – $10,000$ ) to be of practical utility. Thus for most step polymerizations there is less than 1% of the original monomer remaining at a point where the average polymer chain contains only  $\sim 10$  monomer units. As will be seen in Chap. 3, the situation is quite different in the case of chain polymerization.

The rate of a step polymerization is, therefore, the sum of the rates of reaction between molecules of various sizes, that is, the sum of the rates for reactions such as



which can be expressed as the general reaction



The reaction mixture at any instance consists of various-sized diol, diacid, and hydroxy acid molecules. Any HO-containing molecule can react with any COOH-containing molecule. This is a general characteristic of step polymerization.

The kinetics of such a situation with innumerable separate reactions would normally be difficult to analyze. However, kinetic analysis is greatly simplified if one assumes that the reactivities of both functional groups of a bifunctional monomer (e.g., both hydroxyls of a diol) are the same, the reactivity of one functional group of a bifunctional reactant is the same irrespective of whether the other functional group has reacted, and the reactivity of a functional group is independent of the size of the molecule to which it is attached (i.e., independent of the values of  $n$  and  $m$ ). These simplifying assumptions, often referred to as the concept of *equal reactivity of functional groups*, make the kinetics of step polymerization identical to those for the analogous small molecule reaction. As will be seen shortly, the kinetics of a polyesterification, for example, become essentially the same as that for the esterification of acetic acid with ethanol.

## 2-1b Experimental Evidence

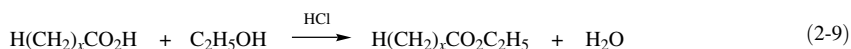
These simplifying assumptions are justified on the basis that many step polymerizations have reaction rate constants that are independent of the reaction time or polymer molecular

**TABLE 2-1 Rate Constants for Esterification (25°C) in Homologous Compounds<sup>a,b</sup>**

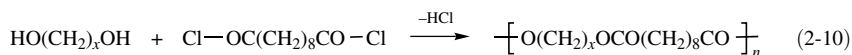
| Molecular Size ( <i>x</i> ) | $k \times 10^4$ for<br>$\text{H}(\text{CH}_2)_x\text{CO}_2\text{H}$ | $k \times 10^4$ for<br>$(\text{CH}_2)_x(\text{CO}_2\text{H})_2$ |
|-----------------------------|---------------------------------------------------------------------|-----------------------------------------------------------------|
| 1                           | 22.1                                                                |                                                                 |
| 2                           | 15.3                                                                | 6.0                                                             |
| 3                           | 7.5                                                                 | 8.7                                                             |
| 4                           | 7.5                                                                 | 8.4                                                             |
| 5                           | 7.4                                                                 | 7.8                                                             |
| 6                           |                                                                     | 7.3                                                             |
| 8                           | 7.5                                                                 |                                                                 |
| 9                           | 7.4                                                                 |                                                                 |
| 11                          | 7.6                                                                 |                                                                 |
| 13                          | 7.5                                                                 |                                                                 |
| 15                          | 7.7                                                                 |                                                                 |
| 17                          | 7.7                                                                 |                                                                 |

<sup>a</sup> Rate constants are in units of  $\text{L mol}^{-1} \text{s}^{-1}$ .<sup>b</sup> Data from Bhide and Sudborough [1925].

weight. It is, however, useful to examine in more detail the experimental and theoretical justifications for these assumptions. Studies of the reactions of certain nonpolymeric molecules are especially useful for understanding polymerization kinetics [Flory, 1953]. The independence of the reactivity of a functional group on molecular size can be observed from the reaction rates in a homologous series of compounds differing from each other only in molecular weight. Consider, for example, the rate constant data in the first column in Table 2-1 for the esterification of a series of homologous carboxylic acids [Bhide and Sudborough, 1925]:



It is evident that, although there is a decrease in reactivity with increased molecular size, the effect is significant only at a very small size. The reaction rate constant very quickly reaches a limiting value at  $x = 3$ , which remains constant and independent of molecular size. Analogous results are found for the polyesterification of sebacoyl chloride with  $\alpha,\omega$ -alkane diols [Ueberreiter and Engel, 1977]:



The rate constant for esterification is independent of  $x$  for the compounds studied (Table 2-2). Examples of similar behavior can be found for other reactions [Rand et al., 1965]. The results for sebacoyl chloride offer direct evidence of the concept of functional group reactivity being independent of molecular size, since the rate constant is independent of  $n$  as well as  $x$ .

The independence of functional group reactivity of molecular size is contrary to the general impression that was widely held in the early years of polymer science. There was a general misconception of decreased reactivity with increased molecular size. This was due

**TABLE 2-2 Rate Constants for Polyesterification (26.9°C)  
of Sebacyl Chloride with  $\alpha,\omega$ -Alkane Diols in Dioxane<sup>a,b</sup>**

| Molecular Size ( $x$ ) | $k \times 10^3$ for $\text{HO}(\text{CH}_2)_x\text{OH}$ |
|------------------------|---------------------------------------------------------|
| 5                      | 0.60                                                    |
| 6                      | 0.63                                                    |
| 7                      | 0.65                                                    |
| 8                      | 0.62                                                    |
| 9                      | 0.65                                                    |
| 10                     | 0.62                                                    |

<sup>a</sup> Rate constants are in units of  $\text{L mol}^{-1} \text{s}^{-1}$ .

<sup>b</sup> Data from Ueberreiter and Engel [1977].

in large part to the fact that reactions with the larger-sized species were often attempted without adjusting concentrations so as to have equivalent concentrations of the reacting functional groups. In many instances the low or difficult solubility of the higher-molecular-weight reactants in a homologous series was responsible for the observed, apparent low reactivity. These effects are still pitfalls to be avoided.

## 2-1c Theoretical Considerations

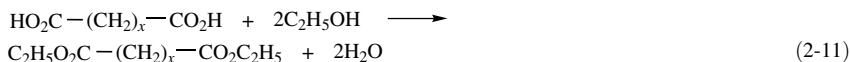
There is theoretical justification for the independence of the reactivity of a functional group of molecular size [Rabinowitch, 1937]. The common misconception regarding the alleged low reactivity of groups attached to large molecules comes from the lower diffusion rates of the latter. However, the observed reactivity of a functional group is dependent on the collision frequency of the group, not on the diffusion rate of the whole molecule. The collision frequency is the number of collisions one functional group makes with other functional groups per unit of time. A terminal functional group attached to a growing polymer has a much greater mobility than would be expected from the mobility of the polymer molecule as a whole. The functional group has appreciable mobility due to the conformational rearrangements that occur in nearby segments of the polymer chain. The collision rate of such a functional group with neighboring groups will be about the same as for small molecules.

The lowered mobility of the polymer molecule as a whole alters the time distribution of collisions. A lower diffusion rate means that any two functional groups will undergo more total collisions before diffusing apart. Thus in any particular time interval (which is long compared to the interval required for diffusion of a group from one collision partner to the next) the number of partners with which a functional group undergoes collisions is less for a group attached to a polymer chain than for one attached to a small molecule. But, most significantly, their overall collision frequencies are the same in the two cases. If the diffusion of a functional group from one collision partner to the next were too slow to maintain the concentration of the reactive pairs of functional groups at equilibrium, one would observe decreased reactivity for the functional group. The opposite is the case, since reaction between two functional groups in a step polymerization occurs only about once in every  $10^{13}$  collisions [Flory, 1953]. During the time interval required for this many collisions, sufficient diffusion of the molecule and of the functional group occurs to maintain the equilibrium concentration of collision pairs of functional groups. The net result of these

considerations is that the reactivity of a functional group will be independent of the size of the molecule to which it is attached. Exceptions to this occur when the reactivities of the groups are very high and/or the molecular weights of the polymer are very high. The polymerization becomes diffusion-controlled in these cases because mobility is too low to allow maintenance of the equilibrium concentration of reactive pairs and of their collision frequencies.

### 2-1d Equivalence of Groups in Bifunctional Reactants

The equivalence of the reactivities of the two functional groups in bifunctional reactants has also been demonstrated in many systems. The second column in Table 2-1 shows data for the esterification of a homologous series of dibasic acids:

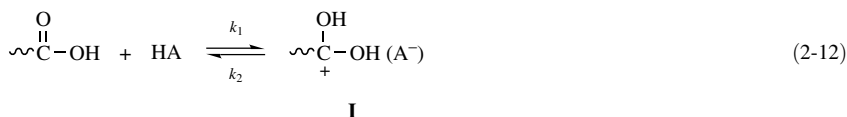


The rate constants tabulated are the averages of those for the two carboxyl groups in each dibasic acid. The rate constants for the two carboxyls were the same within experimental error. Further, a very important observation is that the reactivity of one of the functional groups is not dependent on whether the other has reacted. As in the case of the monocarboxylic acids, the reactivity of the carboxyl group quickly reaches a limiting value. Similar results were observed for the polyesterification of sebacoyl chloride (Table 2-2).

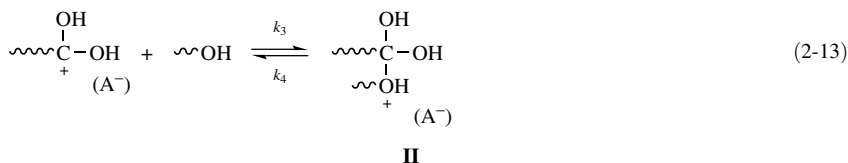
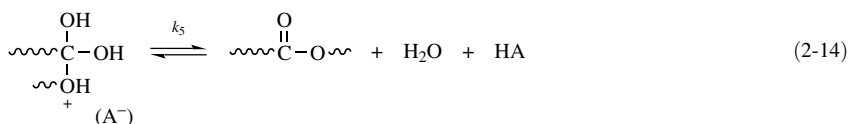
It should not be concluded that the reactivity of a functional group is not altered by the presence of a second group. The data show that at small values of  $x$  up to 4 or 5, there is an effect of the second group. In most instances the effect disappears fairly rapidly with increasing molecular size as the two functional groups become isolated from each other. Thus the rate constant for the esterification of the dibasic acid with  $x = 6$  is the same as that for the monobasic acids. It might appear at first glance that polymerizations involving bifunctional reagents with low  $x$  values would present a problem. However, the difference in reactivities of the functional groups of a bifunctional reagent compared to the functional group in a monofunctional reagent is not an important consideration in handling the kinetics of step polymerization. The most significant considerations are that the reactivity of a functional group in a bifunctional monomer is not altered by the reaction of the other group, and that the reactivities of the two functional groups are the same and do not change during the course of the polymerization.

## 2-2 KINETICS OF STEP POLYMERIZATION

Consider the polyesterification of a diacid and a diol to illustrate the general form of the kinetics of a typical step polymerization. Simple esterification is a well-known acid-catalyzed reaction and polyesterification follows the same course [Otton and Ratton, 1988; Vancso-Szmercsanyi and Makay-Bodi, 1969]. The reaction involves protonation of the carboxylic acid,



followed by reaction of the protonated species **I** with the alcohol to yield the ester



In the above equations  $\sim\sim$  and  $\sim$  are used to indicate all acid or alcohol species in the reaction mixture (i.e., monomer, dimer, trimer, . . . ,  $n$ -mer). Species **I** and **II** are shown in the form of their associated ion pairs since polymerization often takes place in organic media of low polarity. ( $\text{A}^-$ ) is the negative counterion derived from the acid HA. Polyesterifications, like many other step polymerizations, are equilibrium reactions. However, from the practical viewpoint of obtaining high yields of high-molecular-weight product such polymerizations are run in a manner so as to continuously shift the equilibrium in the direction of the polymer. In the case of a polyesterification this is easily accomplished by removal of the water that is a by-product of the reaction species **II** (Eq. 2-14). Under these conditions the kinetics of polymerization can be handled by considering the reactions in Eqs. 2-13 and 2-14 to be irreversible. (A consideration of the kinetics of a reversible step polymerization is given in Sec. 2-4c.)

The rate of a step polymerization is conveniently expressed in terms of the concentrations of the reacting functional groups. Thus the polyesterification can be experimentally followed by titrating for the unreacted carboxyl groups with a base. The rate of polymerization  $R_p$  can then be expressed as the rate of disappearance of carboxyl groups  $-d[\text{COOH}]/dt$ . For the usual polyesterification, the polymerization rate is synonymous with the rate of formation of species **II**; that is,  $k_4$  is vanishingly small (since the reaction is run under conditions that drive Eqs. 2-13 and 2-14 to the right), and  $k_1$ ,  $k_2$ , and  $k_5$  are large compared to  $k_3$ . An expression for the reaction rate can be obtained following the general procedures for handling a reaction scheme with the characteristics described [Moore and Pearson, 1981]. The rate of polymerization is given by

$$R = \frac{-d[\text{COOH}]}{dt} = k_3[\text{C}^+(\text{OH})_2][\text{OH}] \quad (2-15)$$

where  $[\text{COOH}]$ ,  $[\text{OH}]$ , and  $[\text{C}^+(\text{OH})_2]$  represent the concentrations of carboxyl, hydroxyl, and protonated carboxyl (**I**) groups, respectively. The concentration terms are in units of moles of the particular functional group per liter of solution.

Equation 2-15 is inconvenient in that the concentration of protonated carboxylic groups is not easily determined experimentally. One can obtain a more convenient expression for  $R_p$  by substituting for  $\text{C}^+(\text{OH})_2$  from the equilibrium expression

$$K = \frac{k_1}{k_2} = \frac{[\text{C}^+(\text{OH})_2]}{[\text{COOH}][\text{HA}]} \quad (2-16)$$

for the protonation reaction (Eq. 2-12). Combination of Eqs. 2-15 and 2-16 yields

$$\frac{-d[\text{COOH}]}{dt} = k_3 K [\text{COOH}][\text{OH}][\text{HA}] \quad (2-17)$$

Two quite different kinetic situations arise from Eq. 2-17 depending on the identity of HA, that is, on whether a strong acid such as sulfuric acid or *p*-toluenesulfonic acid is added as an external catalyst.

## 2-2a Self-Catalyzed Polymerization

In the absence of an externally added strong acid the diacid monomer acts as its own catalyst for the esterification reaction. For this case [HA] is replaced by [COOH] and Eq. 2-17 can be written in the usual form [Flory, 1953]

$$\frac{-d[\text{COOH}]}{dt} = k [\text{COOH}]^2 [\text{OH}] \quad (2-18)$$

where  $K$  and  $k_3$  have been combined into the experimentally determined rate constant  $k$ . Equation 2-18 shows the important characteristic of the self-catalyzed polymerization—the reaction is third-order overall with a second-order dependence on the carboxyl concentration. The second-order dependence on the carboxyl concentration is comprised of two first-order dependencies—one for the carboxyl as the reactant and one as the catalyst.

For most polymerizations the concentrations of the two functional groups are very nearly stoichiometric, and Eq. 2-18 can be written as

$$\frac{-d[\text{M}]}{dt} = k [\text{M}]^3 \quad (2-19a)$$

or

$$\frac{-d[\text{M}]}{[\text{M}]^3} = k dt \quad (2-19b)$$

where [M] is the concentration of hydroxyl groups or carboxyl groups. Integration of Eq. 2-19b yields

$$2kt = \frac{1}{[\text{M}]^2} - \frac{1}{[\text{M}]_0^2} \quad (2-20)$$

where  $[\text{M}]_0$  is the initial (at  $t = 0$ ) concentration of hydroxyl or carboxyl groups. It is convenient at this point to write Eq. 2-20 in terms of the *extent* or *fraction of reaction*  $p$  defined as the fraction of the hydroxyl or carboxyl functional groups that has reacted at time  $t$ .  $p$  is also referred to as the *extent* or *fraction of conversion*. (The value of  $p$  is calculated from a determination of the amount of unreacted carboxyl groups.) The concentration [M] at time  $t$  of either hydroxyl or carboxyl groups is then given by

$$[\text{M}] = [\text{M}]_0 - [\text{M}]_0 p = [\text{M}]_0 (1 - p) \quad (2-21)$$

Combination of Eqs. 2-20 and 2-21 yields

$$\frac{1}{(1-p)^2} = 2[M]_0^2 kt + 1 \quad (2-22)$$

### 2-2a-1 Experimental Observations

Equation 2-22 indicates that a plot of  $1/(1-p)^2$  versus  $t$  should be linear. This behavior has been generally observed in polyesterifications. Figure 2-1 shows the results for the polymerization of diethylene glycol,  $(\text{HOCH}_2\text{CH}_2)_2\text{O}$ , and adipic acid [Flory, 1939; Solomon, 1967, 1972]. The results are typical of the behavior observed for polyesterifications. Although various authors agree on the experimental data, there has been considerable disagreement on the interpretation of the results. At first glance the plot does not appear to exactly follow the relationship. The experimental points deviate from the third-order plot in the initial region below 80% conversion and in the later stages above 93% conversion. These deviations led various workers [Amass, 1979; Fradet and Marechal, 1982a,b; Solomon, 1967, 1972] to suggest alternate kinetic expressions based on either 1- or  $\frac{3}{2}$ -order dependencies of

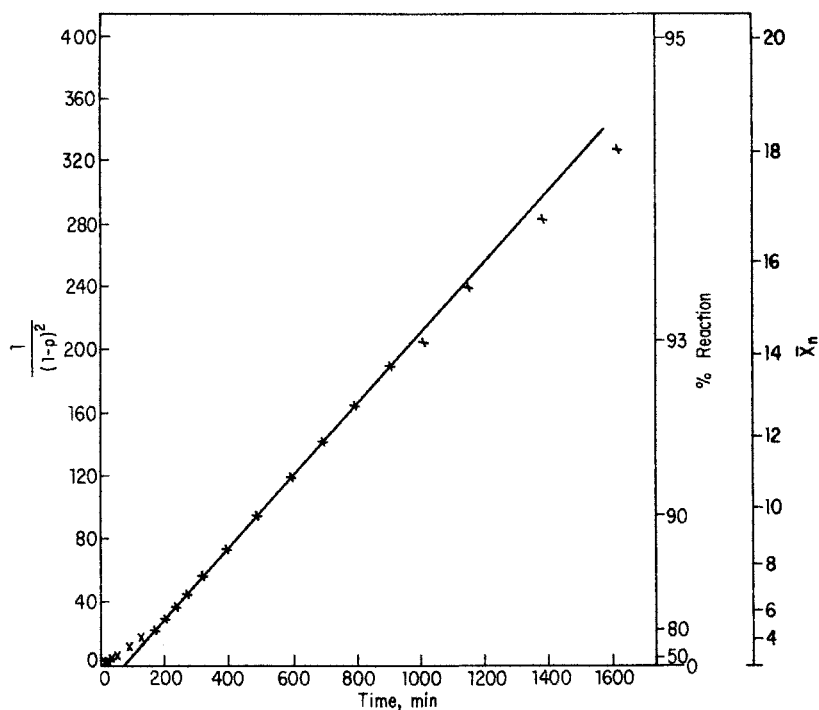


**Fig. 2-1** Third-order plot of the self-catalyzed polyesterification of adipic acid with diethylene glycol at 166°C. After Solomon [1967] (by permission of Marcel Dekker, New York) from the data of Flory [1939] (by permission of American Chemical Society, Washington, DC).

the reaction rate on the carboxyl concentration, that is, 2- and  $2\frac{1}{2}$ -order dependencies according to

$$\frac{-d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}] \quad (2-23a)$$

and

$$\frac{-d[\text{COOH}]}{dt} = k[\text{COOH}]^{3/2}[\text{OH}] \quad (2-23b)$$

However, a critical evaluation shows that both kinetic possibilities leave much to be desired. The experimental rate data fits Eq. 2-23a well only in the region between 50 and 86% conversion with an excessively poor fit above 86% conversion. On the other hand, a plot according to Eq. 2-23b fits reasonably well up to about 80% conversion but deviates badly above that point. Neither of the two alternate kinetic plots comes close to being as useful as the third-order plot in Fig. 2-1. The third-order plot fits the experimental data much better than does either of the others at the higher conversions. The fit of the data to the third-order plot is reasonably good over a much greater range of the higher conversion region. The region of high conversion is of prime importance, since, as will be shown in Sec. 2-2a-3, high-molecular-weight polymer is obtained only at high conversions. From the practical viewpoint, the low conversion region of the kinetic plot is of little significance.

### 2-2a-2 Reasons for Nonlinearity in Third-Order Plot

The failure to fit the data over the complete conversion range from 0 to 100% to a third-order plot has sometimes been ascribed to failure of the assumption of equal functional group reactivity, but this is an invalid conclusion. The nonlinearities are not inherent characteristics of the polymerization reaction. Similar nonlinearities have been observed for nonpolymerization esterification reactions such as esterifications of lauryl alcohol with lauric or adipic acid and diethylene glycol with caproic acid [Flory, 1939; Fradet and Marechal, 1982b].

**2-2a-2-a Low-Conversion Region.** Flory attributed the nonlinearity in the low conversion region to the large changes that take place in the reaction medium. The solvent for the reaction changes from an initial mixture of carboxylic acid and alcohol to an ester. There is a large decrease in the polarity of the reaction system as the polar alcohol and acid groups are replaced by the less polar ester groups with the simultaneous removal of water. This effect may exert itself in two ways—a change in the reaction rate constant or order of reaction. Either possibility is compatible with the experimental observations. The low conversion region of the third-order plot in Fig. 2-1 is approximately linear but with a smaller slope (rate constant) than in the region of higher conversion. The direction of this change corresponds to that expected for a reaction involving a charged substrate (protonated carboxyl) and neutral nucleophile (alcohol). The reaction rate constant increases with decreased solvent polarity since the transition state is less charged than the reactants [Ritchie, 1990]. It has also been suggested that extensive association of both the diol and diacid reactants in the low conversion region lowers the reaction rate by effectively decreasing the concentrations of the reactive species, that is, free, unassociated OH and COOH groups [Ueberreiter and Hager, 1979].

The low conversion region fits an overall  $2\frac{1}{2}$  reaction order better than it does 3-order. A change from  $2\frac{1}{2}$ - to 3-order as the reaction medium becomes less polar is compatible with a

change from specific acid (i.e.,  $H^+$ ) catalysis to general-acid catalysis. The proton concentration is relatively high and  $[H^+]$  is a more effective catalyst than the unionized carboxylic acid in the polar, low conversion region. HA in Eqs. 2-12, 2-16, and 2-17 is replaced by  $H^+$ . The reaction rate becomes first-order each in carboxyl and hydroxyl groups and  $H^+$ . The proton concentration is given by

$$[H^+] = (K_{HA}[HA])^{1/2} \quad (2-24)$$

where  $K_{HA}$  is the ionization constant for the carboxylic acid. Combination of Eqs. 2-17 and 2-24 yields

$$\frac{-d[COOH]}{dt} = k_3 K K_{HA}^{1/2} [COOH]^{3/2} [OH] \quad (2-25)$$

for the polymerization rate. The reaction medium becomes less polar after the low-conversion (>80%) region and the major catalyst in the reaction system is the unionized carboxylic acid—the reaction is second-order in carboxylic acid and third-order overall (Eqs. 2-18 and 2-19).

Another problem is the very high concentrations of reactants present in the low-conversion region. The correct derivation of any rate expression such as Eqs. 2-20 and 2-22 requires the use of activities instead of concentrations. The use of concentrations instead of activities assumes a direct proportionality between concentration and activity. This assumption is usually valid at the dilute and moderate concentrations where kinetic studies on small molecules are typically performed. However, the assumption often fails at high concentrations and those are the reaction conditions for the typical step polymerization that proceeds with neat reactants. A related problem is that neither concentration nor activity may be the appropriate measure of the ability of the reaction system to donate a proton to the carboxyl group. The acidity function  $h_0$  is often the more appropriate measure of acidity for nonaqueous systems or systems containing high acid concentrations [Ritchie, 1990]. Unfortunately, the appropriate  $h_0$  values are not available for polymerization systems.

Yet another possibility for the nonlinearity in the low conversion region is the decrease in the volume of the reaction mixture with conversion due to loss of one of the products of reaction (water in the case of esterification). This presents no problem if concentration is plotted against time as in Eq. 2-20. However, a plot of  $1/(1-p)^2$  against time (Eq. 2-22) has an inherent error since the formulation of Eq. 2-21 assumes a constant reaction volume (and mass) [Szabo-Rethy, 1971]. Elias [1985] derived the kinetics of step polymerization with correction for loss of water, but the results have not been tested. It is unclear whether this effect alone can account for the nonlinearity in the low conversion region of esterification and polyesterification.

**2-2a-2-b High-Conversion Region.** The nonlinearity observed in the third-order plot in the final stages of the polyesterification (Fig. 2-1) is probably not due to any of the above mentioned reasons, since the reaction system is fairly dilute and of relatively low polarity. Further, it would be difficult to conjecture that the factors responsible for nonlinearity at low conversions are present at high conversion but absent in between. It is more likely that other factors are responsible for the nonlinear region above 93% conversion.

Polyesterifications, like many step polymerizations, are carried out at moderate to high temperatures not only to achieve fast reaction rates but also to aid in removal of the small molecule by-product (often  $H_2O$ ). The polymerization is an equilibrium reaction and the

equilibrium must be displaced to the right (toward the polymer) to achieve high conversions (synonymous with high molecular weights). Partial vacuum (often coupled with purging of the reaction system by nitrogen gas) is usually also employed to drive the system toward high molecular weight. Under these conditions small amounts of one or the other or both reactants may be lost by degradation or volatilization. In the case of polyesterification, small degradative losses might arise from dehydration of the diol, decarboxylation of the diacid, or other side reactions (Sec. 2-8d). Although such losses may not be important initially, they can become very significant during the later stages of reaction. Thus a loss of only 0.3% of one reactant can lead to an error of almost 5% in the concentration of that reactant at 93% conversion. Kinetic studies on esterification and polyesterification have been performed under conditions which minimized the loss of reactants by volatilization or side reactions [Hamann et al., 1968]. An ester or polyester was synthesized in a first stage, purified, and then used as the solvent for a second-stage esterification or polyesterification. The initial reactant concentrations of the second-stage reactions corresponded to 80% conversion relative to the situation if the first-stage reaction had not been stopped but with an important difference—the reactant concentrations are accurately known. The second-stage reaction showed third-order behavior up to past 98–99% conversion (higher conversions were not studied). This compares with the loss of linearity in the third-order plot at about 93% conversion if the first-stage reactions were carried out without interruption.

Another possible reason for the observed nonlinearity is an increase in the rate of the reverse reaction. The polyesterification reaction (as well as many other step polymerizations) is an equilibrium reaction. It often becomes progressively more difficult to displace the equilibrium to the right (toward the polymer) as the conversion increases. This is due in large part to the greatly increased viscosity of the reaction medium at high conversions. The viscosity in the adipic acid–diethylene glycol polymerization increases from 0.015 to 0.30 poise during the course of the reaction [Flory, 1939]. This large viscosity increase decreases the efficiency of water removal and may lead to the observed decrease in the reaction rate with increasing conversion. High viscosity in the high-conversion region may also lead to failure of the assumption of equal reactivity of functional groups—specifically to a decrease in functional group reactivity at very large molecular size if there is too large a decrease in molecular mobility.

### 2-2a-3 Molecular Weight of Polymer

The molecular weight of a polymer is of prime concern from the practical viewpoint, for unless a polymer is of sufficiently high molecular weight (approximately >5000–10,000) it will not have the desirable strength characteristics. It is therefore important to consider the change in polymer molecular weight with reaction time. For the case of stoichiometric amounts of diol and diacid, the number of unreacted carboxyl groups  $N$  is equal to the total number of molecules present in the system at some time  $t$ . This is so because each molecule larger than a monomer will on the average have a hydroxyl at one end and a carboxyl at the other end, while each diacid monomer molecule contains two carboxyls and each diol monomer contains no carboxyls.

The residue from each diol and each diacid (separately, not together) in the polymer chain is termed a *structural unit* (or a *monomer unit*). The *repeating unit* of the chain consists of two structural units, one each of the diol and diacid. The total number of structural units in any particular system equals the total number of bifunctional monomers initially present. The *number-average degree of polymerization*  $\bar{X}_n$  is defined as the average number of structural units per polymer chain. (The symbols  $\bar{P}$  and  $\overline{DP}$  are also employed to signify

the number-average degree of polymerization.)  $\bar{X}_n$  is simply given as the total number of monomer molecules initially present divided by the total number of molecules present at time  $t$ :

$$\bar{X}_n = \frac{N_0}{N} = \frac{[M]_0}{[M]} \quad (2-26)$$

Combining Eqs. 2-21 and 2-26, one obtains

$$\bar{X}_n = \frac{1}{(1-p)} \quad (2-27)$$

This equation relating the degree of polymerization to the extent of reaction was originally set forth by Carothers [1936] and is often referred to as the *Carothers equation*.

The *number-average molecular weight*  $\bar{M}_n$ , defined as the total weight of a polymer sample divided by the total number of moles in it (Eqs. 1-15 and 1-16), is given by

$$\bar{M}_n = M_o \bar{X}_n + M_{eg} = \frac{M_o}{(1-p)} + M_{eg} \quad (2-28)$$

where  $M_o$  is the mean of the molecular weights of the two structural units, and  $M_{eg}$  is the molecular weight of the end groups. For the polyesterification of adipic acid,  $\text{HO}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H}$ , and ethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , the repeating unit is



### III

and one half of its weight or 86 is the value of  $M_o$ . The end groups are  $\text{H—}$  and  $\text{—OH}$  and  $M_{eg}$  is 18. For even a modest molecular weight polymer the contribution of  $M_{eg}$  to  $\bar{M}_n$  is negligibly small, and Eq. 2-28 becomes

$$\bar{M}_n = M_o \bar{X}_n = \frac{M_o}{(1-p)} \quad (2-29)$$

Combination of Eqs. 2-22 and 2-27 yields

$$\bar{X}_n^2 = 1 + 2[M]_0^2 kt \quad (2-30)$$

Since the reaction time and degree of polymerization appear as the first and second powers, respectively, the polymer molecular weight will increase very slowly with reaction time except in the early stages of the reaction. This means that very long reaction times are needed to obtain a high-molecular-weight polymer product. The right-hand ordinate of Fig. 2-1 shows the variation of  $\bar{X}_n$  with  $t$ . The slow increase of the molecular weight of the polymer with time is clearly apparent. The rate of increase of  $\bar{X}_n$  with time decreases as the reaction proceeds. The production of high polymers requires reaction times that are too long from the practical viewpoint.

## 2-2b External Catalysis of Polymerization

The slow increase in molecular weight was mistakenly thought originally to be due to the low reactivity of functional groups attached to large molecules. It is, however, simply a

consequence of the third-order kinetics of the direct polyesterification reaction. The realization of this kinetic situation led to the achievement of high-molecular-weight products in reasonable reaction times by employing small amounts of externally added strong acids (such as sulfuric acid or *p*-toluenesulfonic acid) as catalysts. Under these conditions, [HA] in Eq. 2-17 is the concentration of the catalyst. Since this remains constant throughout the course of the polymerization, Eq. 2-17 can be written as

$$\frac{-d[M]}{dt} = k'[M]^2 \quad (2-31)$$

where the various constant terms in Eq. 2-17 have been collected into the experimentally determinable rate constant  $k'$ . Equation 2-31 applies to reactions between stoichiometric concentrations of the diol and diacid.

Integration of Eq. 2-31 yields

$$k't = \frac{1}{[M]} - \frac{1}{[M]_0} \quad (2-32)$$

Combining Eqs. 2-32 and 2-21 yields the dependence of the degree of polymerization on reaction time as

$$[M]_0 k't = \frac{1}{(1-p)} - 1 \quad (2-33a)$$

or

$$\bar{X}_n = 1 + [M]_0 k't \quad (2-33b)$$

Data for the polymerization of diethylene glycol with adipic acid catalyzed by *p*-toluenesulfonic acid are shown in Fig. 2-2. The plot follows Eq. 2-33 with the degree of polymerization increasing linearly with reaction time. The much greater rate of increase of  $\bar{X}_n$  with reaction time in the catalyzed polyesterification (Fig. 2-2) relative to the uncatalyzed reaction (Fig. 2-1) is a general and most significant phenomenon. The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an external acid. The self-catalyzed polymerization is not a useful reaction from the practical viewpoint of producing high polymers in reasonable reaction times.

Equations 2-27 and 2-33 and Fig. 2-2 describe the much greater difficulty of performing a successful polymerization compared to the analogous small-molecule reaction (such as the synthesis of ethyl acetate from acetic acid and ethanol). Consider the case where one needs to produce a polymer with a degree of polymerization of 100, which is achieved only at 99% reaction. Running the polymerization to a lower conversion such as 98%, an excellent conversion for a small-molecule synthesis, results in no polymer of the desired molecular weight. Further, one must almost double the reaction time (from ~450 min to 850 min in Fig. 2-2) to achieve 99% reaction and the desired polymer molecular weight. For the small molecule reaction one would not expend that additional time to achieve only an additional 1% conversion. For the polymerization one has no choice other than to go to 99% conversion.

The nonlinearity in the initial region of Fig. 2-2 is, like that in Fig. 2-1, a characteristic of esterifications in general and not of the polymerization reaction. The general linearity of the plot in the higher conversion region is a strong confirmation of the concept of functional group reactivity independent of molecular size. Figure 2-2 shows that the polyesterification

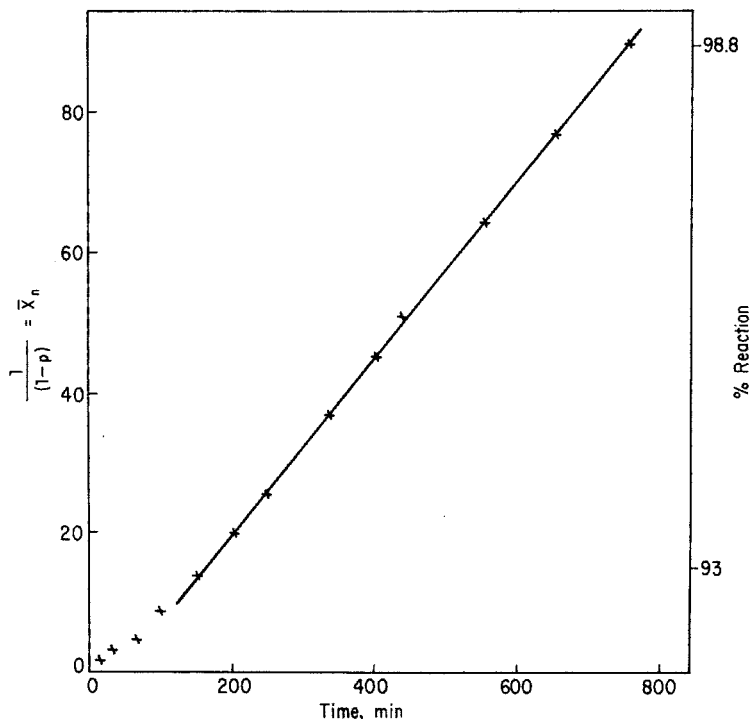


**Fig. 2-2** Polyesterification of adipic acid with diethylene glycol at 109°C catalyzed by 0.4 mol% *p*-toluenesulfonic acid. After Solomon [1967] (by permission of Marcel Dekker, New York) from the data of Flory [1939] (by permission of American Chemical Society, Washington, DC).

continues its second-order behavior at least up to a degree of polymerization of 90 corresponding to a molecular weight of  $\sim 10,000$ . There is no change in the reactivities of the hydroxyl and carboxyl groups in spite of the large increase in molecular size (and the accompanying large viscosity increase of the medium). Similar results have been observed in many other polymerizations. Data on the degradation of polymers also show the same effect. Thus in the acid hydrolysis of cellulose there is no effect of molecular size on hydrolytic reactivity up to a degree of polymerization of 1500 (molecular weight 250,000) [Flory, 1953]. The concept of functional group reactivity independent of molecular size has been highly successful in allowing the kinetic analysis of a wide range of polymerizations and reactions of polymers. Its validity, however, may not always be quite rigorous at very low or very high conversions.

## 2-2c Step Polymerizations Other than Polyesterification: Catalyzed versus Uncatalyzed

The kinetics of step polymerizations other than polyesterification follow easily from those considered for the latter. The number of different general kinetic schemes encountered in actual polymerization situations is rather small. Polymerizations by reactions between the

A and B functional groups of appropriate monomers proceed by one of the following situations [Saunders and Dobinson, 1976]:

1. Some polymerizations, such as the formation of polyamides, proceed at reasonable rates as uncatalyzed reactions.
2. Other polymerizations such as those of urea, melamine, or phenol with formaldehyde (see Table 1-1) require an externally added acid or base catalyst to achieve the desired rates of reaction.
3. A few polymerizations can be reasonably employed either in a catalyzed or an uncatalyzed process. Polyurethane formation is an example of this type of behavior. The reaction between diols and diisocyanates is subject to base catalysis. However, the polymerization is often carried out as an uncatalyzed reaction to avoid various undesirable side reactions.

Regardless of the situation into which a particular polymerization falls, the observed overall kinetic features will be the same. The polymerization rates will be dependent on both the A and B groups. For the usual case where one has stoichiometric amounts of the two functional groups, the kinetics will be governed by Eq. 2-30 or 2-33. The observed kinetics will also be the same whether the polymerization is carried by the reaction of A—A and B—B monomers or by the self-reaction of an A—B monomer.

The derivation (Sec. 2-2b) of the kinetics of catalyzed polyesterification assumes that the catalyzed reaction is much faster than the uncatalyzed reaction, that is,  $k' \gg k$ . This assumption is usually valid and therefore one can ignore the contribution by the uncatalyzed polyesterification to the total polymerization rate. For example,  $k'$  is close to two orders of magnitude larger than  $k$  for a typical polyesterification. For the atypical situation where  $k$  is not negligible relative to  $k'$ , the kinetic expression for  $[M]$  or  $\bar{X}_n$  as a function of reaction time must be derived [Hamann et al., 1968] starting with a statement of the polymerization rate as the sum of the rates of the catalyzed and uncatalyzed polymerizations:

$$\frac{-dM}{dt} = k[M]^3 + k'[M]^2 \quad (2-34)$$

Integration of Eq. 2-34 yields

$$k't = \frac{k}{k'} \ln \frac{[M](k[M]_0 + k')}{(k[M] + k')[M]_0} + \frac{1}{[M]} - \frac{1}{[M]_0} \quad (2-35)$$

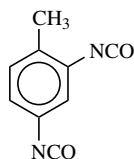
The natural log term on the right side of Eq. 2-35 is the contribution of the uncatalyzed reaction. Its relative importance increases as  $k/k'$  increases. (When  $k/k'$  is very small, Eq. 2-35 converts to Eq. 2-32.)

## 2-2d Nonequivalence of Functional Groups in Polyfunctional Reagents

### 2-2d-1 Examples of Nonequivalence

There are instances where some or all parts of the concept of equal reactivity of functional groups are invalid [Kronstadt et al., 1978; Lovering and Laidler, 1962]. The assumption of equal reactivities of all functional groups in a polyfunctional monomer may often be incorrect. The same is true for the assumption that the reactivity of a functional group is

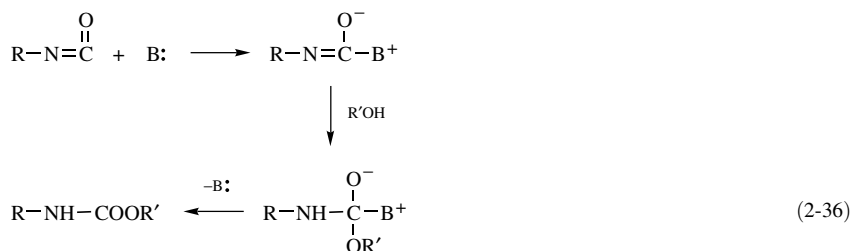
independent of whether the other functional groups in the monomer have reacted. Neither of these assumptions is valid for 2,4-tolylene diisocyanate (**IV**)



**IV**

which is one of diisocyanate monomers used in the synthesis of polyurethanes [Caraculacu and Coseri, 2001].

Urethane formation can be depicted as occurring by the sequence



where B: is a base catalyst (e.g., a tertiary amine). The reaction involves a rate-determining nucleophilic attack by the alcohol on the electrophilic carbon-nitrogen linkage of the isocyanate. This is substantiated by the observation that the reactivity of the isocyanate group increases with the electron-pulling ability of the substituent attached to it [Kaplan, 1961].

In 2,4-tolylene diisocyanate several factors cause the reactivities of the two functional groups to differ. These can be discussed by considering the data in Table 2-3 on the reactivities of various isocyanate groups compared to that in phenyl isocyanate toward reaction with

**TABLE 2-3 Reactivity of Isocyanate Group with  $n\text{-C}_4\text{H}_9\text{OH}$ <sup>a</sup>**

| Isocyanate Reactant              | Rate Constants <sup>b</sup> |       |           |
|----------------------------------|-----------------------------|-------|-----------|
|                                  | $k_1$                       | $k_2$ | $k_1/k_2$ |
| <b>Monoisocyanate</b>            |                             |       |           |
| Phenyl isocyanate                | 0.406                       |       |           |
| <i>p</i> -Tolyl isocyanate       | 0.210                       |       |           |
| <i>o</i> -Tolyl isocyanate       | 0.0655                      |       |           |
| <b>Diisocyanates</b>             |                             |       |           |
| <i>m</i> -Phenylene diisocyanate | 4.34                        | 0.517 | 8.39      |
| <i>p</i> -Phenylene diisocyanate | 3.15                        | 0.343 | 9.18      |
| 2,6-Tolylene diisocyanate        | 0.884                       | 0.143 | 6.18      |
| 2,4-Tolylene diisocyanate        | 1.98                        | 0.166 | 11.9      |

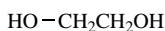
<sup>a</sup> Data from Brock [1959].

<sup>b</sup> Rate constants are in units of  $\text{L mol}^{-1} \text{s}^{-1}$ .

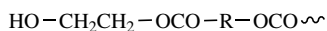
*n*-butanol at 39.7°C in toluene solution with triethylamine as the catalyst [Brock, 1959, 1961]. It is clear that a methyl substituent deactivates the isocyanate group by decreasing its electronegativity; the effect is greater when the substituent is at the nearby ortho position. For the diisocyanates in Table 2-3  $k_1$  is the rate constant for the more reactive isocyanate group, while  $k_2$  is the rate constant for the reaction of the less reactive isocyanate group after the more reactive one has been converted to a urethane group. One isocyanate group activates the other by electron withdrawal, as shown by the increased reactivity in the diisocyanates relative to the monoisocyanates. However, once the first isocyanate group has reacted the reactivity of the second group decreases, since the urethane group is a much weaker electron-pulling substituent than the isocyanate group. For 2,4-tolylene diisocyanate analysis of the experimental data at low conversion shows the para isocyanate group at be 2.7 times as reactive as the ortho groups. However, the effective difference in reactivity of the two functional groups is much greater ( $k_1/k_2 = 11.9$ ), since the reactivity of the ortho group drops an additional factor of approximately 4 after reaction of the para isocyanate group.

The reactivity differences of the two functional groups in 2,4-tolylene diisocyanate result from its unsymmetric and aromatic structure. The environments (steric and electrostatic) of the two isocyanate groups are different to begin with, and the effect of reaction of one group is efficiently transmitted through the conjugated  $\pi$ -electron system of the aromatic ring. These differences disappear for a reactant such as 1,4-cyclohexylene diisocyanate, which is symmetric to begin with and possesses no aromatic system to transmit the effect of the reacted isocyanate group to the unreacted group.

The change in reactivity of one functional group upon reaction of the other has been noted in several systems as a difference in the reactivity of monomer compared to the other-sized species, although all other species from dimer on up had the same reactivity [Hodkin, 1976; Yu et al., 1986]. This behavior usually occurs with monomers having two functional groups in close proximity and where polymerization involves a significant change in the electron-donating or electron-withdrawing ability of the functional group. Thus the reactivity of the hydroxyl group in ethylene glycol (V) toward esterification is considerably higher than the hydroxyl of a half-esterified glycol (VI) [Yamanis and Adelman, 1976]. The nucleophilicity



V



VI

of a hydroxyl group is enhanced more by an adjacent hydroxyl relative to an adjacent ester group. Similarly, in the polymerization of sodium *p*-fluorothiophenoxide (an A—B reactant), nucleophilic substitution at the aromatic C—F bond occurs faster at fluorophenyl end groups of a growing polymer compared to monomer [Lenz et al., 1962]. The electron-donating effect of the para  $\text{S}^-$  group in the monomer decreases the electron deficiency of the para carbon more than does a  $\phi\text{S}$  group in species larger than monomer.

Polymerization of terephthalic acid with 4,6-diamino-1,3-benzenediol via oxazole formation (Eq. 2-219) proceeds with a sharp and continuous decrease in reaction rate with increasing polymer molecular weight [Cotts and Berry, 1981]. Reaction becomes progressively more diffusion-controlled with increasing molecular size due to the increasing rigid-rod structure of the growing polymer.

Trifunctional monomers constitute an important class of monomers. One often encounters such reactants in which the various functional groups have different reactivities. Thus, the polyesterification of glycerol (VII) with phthalic anhydride proceeds with incomplete

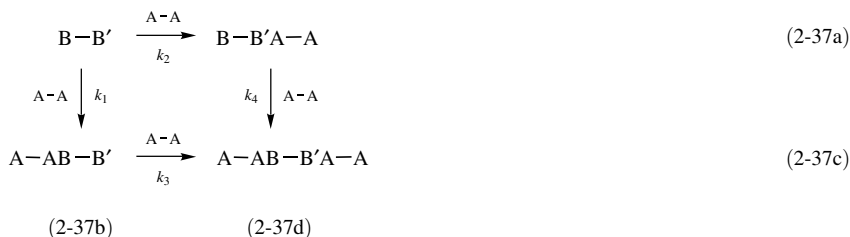


## VII

utilization of the hydroxyl groups [Kienle et al., 1939]. This has been attributed to the lowered reactivity of the secondary hydroxyl group compared to the two primary hydroxyls.

### 2-2d-2 Kinetics

Kinetic analysis of a step polymerization becomes complicated when all functional groups in a reactant do not have the same reactivity. Consider the polymerization of A—A with B—B' where the reactivities of the two functional groups in the B—B' reactant are initially of different reactivities and, further, the reactivities of B and B' each change on reaction of the other group. Even if the reactivities of the two functional groups in the A—A reactant are the same and independent of whether either group has reacted, the polymerization still involves four different rate constants. Any specific-sized polymer species larger than dimer is formed by two simultaneous routes. For example, the trimer A—AB—B'A—A is formed by



The two routes (one is Eqs. 2-37b and 2-37c; the other is Eqs. 2-37a and 2-37d) together constitute a complex reaction system that consists simultaneously of competitive, consecutive and competitive, parallel reactions.

Obtaining an expression for the concentration of A (or B or B') groups or the extent of conversion or  $\bar{X}_n$  as a function of reaction time becomes more difficult than for the case where the equal reactivity postulate holds, that is, where  $k_1 = k_2 = k_3 = k_4$ . As a general approach, one writes an expression for the total rate of disappearance of A groups in terms of the rates of the four reactions 2-37a, b, c, and d and then integrates that expression to find the time-dependent change in [A]. The difficulty arises because the differential equations that must be integrated are not linear equations and do not have exact solutions except in very particular cases. Numerical methods are then needed to obtain an approximate solution.

**2-2d-2-a Polymerization of A—A with B—B'.** The kinetics of the reaction system described in Eq. 2-37 is relatively difficult to treat because there are four different rate constants. Special (and simpler) cases involving only two rate constants can be more easily treated. One such case is where the two functional groups B and B' have different reactivities but

their individual reactivities are decoupled in that neither the reactivity of B nor of B' changes on reaction of the other group:

$$k_1 \neq k_2 \quad (2-38a)$$

$$k_1 = k_4 \quad (2-38b)$$

$$k_2 = k_3 \quad (2-38c)$$

The reaction system converts from one (Eq. 2-37), that is, from the kinetic viewpoint, simultaneously competitive, consecutive (series) and competitive, simultaneous (parallel) to one (Eq. 2-38) that is only competitive, simultaneous. The polymerization consists of the B and B' functional groups reacting independently with A groups. The rates of disappearance of A, B, and B' functional groups are given by

$$\frac{-d[B]}{dt} = k_1[A][B] \quad (2-39)$$

$$\frac{-d[B']}{dt} = k_2[A][B'] \quad (2-40)$$

$$\frac{-d[A]}{dt} = k_1[A][B] + k_2[A][B'] \quad (2-41)$$

The polymerization rate is synonymous with the rate of disappearance of A groups (or the sum of the rates of disappearance of B and B' groups).

In the typical polymerization one has equimolar concentrations of the A—A and B—B' reactants at the start of polymerization. The initial concentrations of A, B, and B' groups are

$$[A]_0 = 2[B]_0 = 2[B']_0 \quad (2-42)$$

and the relationship between the concentrations of A, B, and B' at any time during polymerization is

$$[A] = [B] + [B'] \quad (2-43)$$

Combination of Eqs. 2-41 and 2-43 yields the polymerization rate as

$$\frac{-d[A]}{dt} = (k_1 - k_2)[A][B] + k_2[A]^2 \quad (2-44)$$

Introduction of the dimensionless variables  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\tau$  and the parameter  $s$  defined by

$$\alpha = \frac{[A]}{[A]_0} \quad (2-45a)$$

$$\beta = \frac{[B]}{[B]_0} \quad (2-45b)$$

$$\gamma = \frac{[B']}{[B']_0} \quad (2-45c)$$

$$\tau = [B]_0 k_2 t \quad (2-45d)$$

$$s = \frac{k_2}{k_1} \quad (2-45e)$$

simplifies the mathematical solution of Eq. 2-44.  $\alpha$ ,  $\beta$ , and  $\gamma$  are the fractions of A, B, and B' groups, respectively, which remain unreacted at any time.  $\tau$  is dimensionless time and  $s$  is the ratio of two rate constants. It is then possible to solve the coupled system of Eqs. 2-39 through 2-44 to give

$$\tau = \int_{\beta}^1 \frac{s d\beta}{\beta^2 [1 + \beta^{(s-1)}]} \quad (2-46)$$

$$\gamma = \beta^s \quad (2-47)$$

where

$$\alpha = \frac{\beta + \gamma}{2} = \frac{\beta + \beta^s}{2} \quad (2-48)$$

The integral in Eq. 2-46 yields simple integrals for  $s$  values of 0, 1, and  $\infty$ . The dependencies of  $\alpha$ ,  $\beta$ , and  $\gamma$  on  $\tau$  in these instances are

1. For  $s = 1$ , that is,  $k_2 = k_1$ ,

$$\beta = \frac{1}{1 + 2\tau} = \gamma = \alpha \quad (2-49)$$

2. For  $s = 0$ , that is,  $k_1 \gg k_2$ , where  $k_1$  has some value and  $k_2 \rightarrow 0$ : B' groups do not react ( $\gamma = 1$ ) and

$$\ln \left[ \frac{(1 + \beta)}{2\beta} \right] = \tau \quad (2-50a)$$

$$\alpha = \frac{(1 + \beta)}{2} \quad (2-50b)$$

3. For  $s = \infty$ , that is,  $k_2 \gg k_1$ , where  $k_2$  has some value and  $k_1 \rightarrow 0$ : B groups do not react ( $\beta = 1$ ) and

$$\ln \left[ \frac{(1 + \gamma)}{2\gamma} \right] = \tau \quad (2-51a)$$

$$\alpha = \frac{(1 + \gamma)}{2} \quad (2-51b)$$

For almost all other values of  $s$  the integral in Eq. 2-46 must be numerically evaluated. The results of such calculations are presented in graphical form in Figs. 2-3 and 2-4 as plots of  $\alpha$ ,  $\beta$ , and  $\gamma$  versus  $\log \tau$  for  $s$  values of 1 and larger [Ozizmir and Odian, 1980]. There is no need for plots for  $s < 1$ , since the B and B' groups have interchangeable roles due to the symmetry of the reaction system.  $\alpha$  at any time is exactly the same for  $s = z$  or  $s = 1/z$ , where  $z$  is any number. The only difference for an  $s$  value of  $z$  or  $1/z$  is whether it is the B or B' type of group, which reacts rapidly while the other reacts slowly. Figure 2-3 gives  $\beta$  and  $\gamma$  as a function of  $\tau$ . When  $s = 1$  both  $\beta$  and  $\gamma$  decay at the same rate according to Eq. 2-49. As  $s$  increases the  $\beta$  plots move sharply above the plot for  $s = 1$  since B groups react more slowly with A. Although  $k_2$  is fixed, increasing values of  $s$  help move the  $\gamma$  plots gradually below the plot for  $s = 1$ , since B groups reacting more slowly with A leaves comparably more [A] for

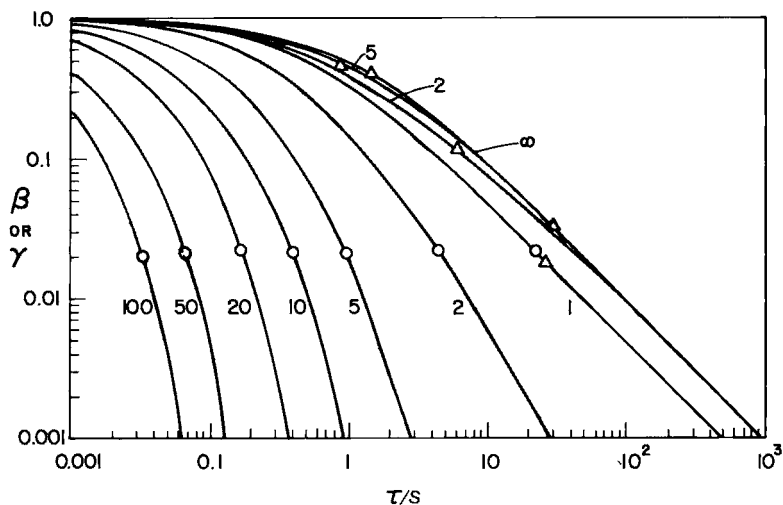


Fig. 2-3 Decay in  $\beta$  and  $\gamma$  with time in the polymerization of A—A with B—B'.  $\beta$  plots are indicated by  $\triangle$ ;  $\gamma$  plots, by  $\circ$ . Values of  $s$  are noted for each curve. After Ozizmir and Odian [1980] (by permission of Wiley-Interscience, New York).

B' groups to react with. As  $s \rightarrow \infty$  the condition is reached in which  $[B]$  remains constant at  $[B]_0$  during the complete decay of B' according to Eq. 2-51b.

Figure 2-4 shows the decay in  $\alpha$  and the corresponding increase in  $\bar{X}_n$  with  $\tau$  (since  $\bar{X}_n = 1/\alpha$ ). It becomes progressively more difficult to achieve high degrees of polymerization in reasonable times for reaction systems of  $s > 1$ . At sufficiently large  $s$  (small  $k_1$ ) the

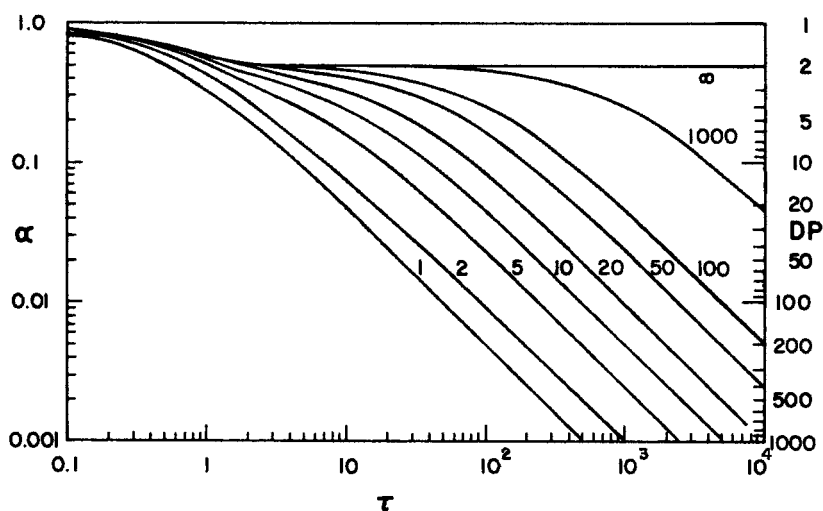


Fig. 2-4 Decay in  $\alpha$  and increase in degree of polymerization with time in polymerization of A—A with B—B'. Values of  $s$  are noted for each plot. After Ozizmir and Odian [1980] (by permission of Wiley-Interscience, New York).

reaction time to obtain high polymer ( $\bar{X}_n > 50\text{--}100$ ) becomes impractical. The extreme situation occurs at  $s \rightarrow \infty$  ( $k_1 \rightarrow 0$ ), where the maximum degree of polymerization is 2. Reaction systems with very small  $k_1$  values must be avoided in order to achieve high degrees of polymerization. The desirable system from the viewpoint of polymerization rate and  $\bar{X}_n$  is that with  $s = 1$ . (The exception to this generalization is for systems of  $s > 1$  where both  $k_1$  and  $k_2$  are large but  $k_2$  is larger.)

The A—A plus B—B' system with  $k_1 \neq k_4$  and  $k_2 \neq k_3$  has been treated in a similar manner [Ozizmir and Odian, 1981]. The parameters  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $s$  as defined by Eqs. 2-45a, 2-45b, 2-45c, and 2-45e are retained in the treatment.  $\tau$  is redefined as

$$\tau = (k_1 + k_2)[B]_0 t \quad (2-52)$$

and the parameters  $u_1$  and  $u_2$

$$u_1 = \frac{k_4}{k_1} \quad (2-53)$$

$$u_2 = \frac{k_3}{k_2} \quad (2-54)$$

are introduced to describe the changes in the rate constants for the B and B' functional groups. The results are shown in Fig. 2-5 as a plot of  $\alpha$  and the degree of polymerization versus  $\tau$  for a range of values of  $s$ ,  $u_1$ , and  $u_2$ . For the case where the two functional groups B and B' have the same initial reactivity ( $s = 1$ ) (plots 1–3), the polymerization rate decreases if the reactivity of either B or B' decreases on reaction of the other group (i.e., if  $u_1 < 1$  or  $u_2 < 1$ ). The polymerization rate increases if the reactivity of either B or B' increases on reaction of the other group ( $u_1 > 1$  or  $u_2 > 1$ ). The effects reinforce each other

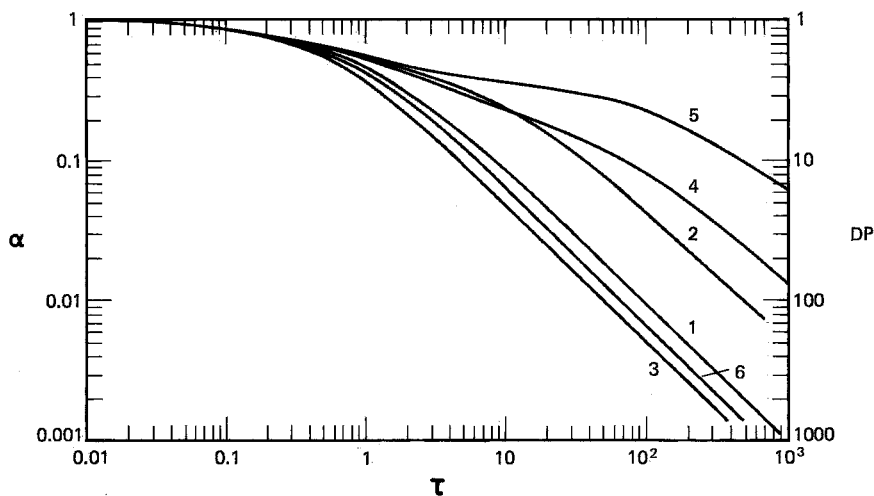


**Fig. 2-5** Decay in  $\alpha$  and increase in degree of polymerization of A—A with B—B' for  $k_1 \neq k_4$  and  $k_2 \neq k_3$ . Values of  $s$ ,  $u_1$ ,  $u_2$  are 1, 1, 1 (plot 1); 1, 0.2, 0.2 (plot 2); 1, 5, 5 (plot 3); 5, 1, 1 (plot 4); 5, 0.2, 1 (plot 5); 5, 5, 1 (plot 6). After Ozizmir and Odian [1980] (by permission of Wiley-Interscience, New York).

when both  $u_1$  and  $u_2$  change in the same direction, but tend to cancel each other when  $u_1$  and  $u_2$  change in opposite directions. When the B and B' groups have different initial reactivities, for example,  $s = 5$  (B' five times more reactive than B), the polymerization rate is decreased (compare plots 1 and 4) unless compensated for by an increase in the reactivity of B on reaction of B' ( $u_1 > 1$ ). There is an increase in polymerization rate when the increased reactivity of B is large (compare plots 4 and 6). The polymerization rate becomes more depressed when B groups decrease in reactivity on reaction of B' ( $u_1 < 1$ ) (compare plots 4 and 5).

**2-2d-2-b Variation of Rate Constant with Size.** The usual kinetic analysis of step polymerization, including that described for the A—A plus B—B' system, assumes the rate constants are independent of molecular size. The effect of a rate constant dependence on molecular size has been analyzed for A—B or A—A plus B—B polymerizations where a functional group on a monomer molecule has a different reactivity from the same group in species

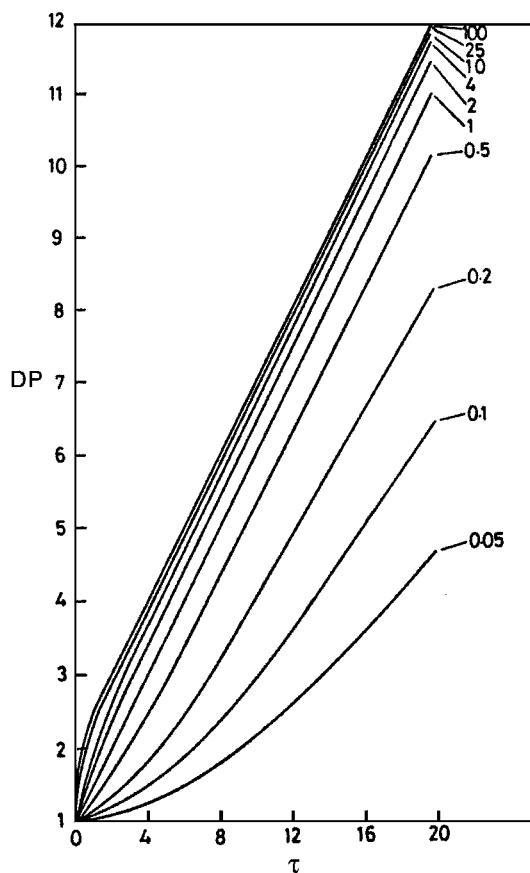


**Fig. 2-6** Variation of degree of polymerization with time when monomer has a different reactivity from large-sized species. Values of  $u$  are noted for each plot; the plots for  $u = 25$  and  $100$  are indistinguishable from each other. After Gupta et al. [1979a,b] (by permission of Pergamon Press, London and Elsevier, Oxford).

larger than monomer (i.e., for dimer and larger) [Goel et al., 1977; Gupta et al., 1979a,b]. The following terms are defined:

$$u = \frac{k_m}{k_p} \quad (2-55)$$

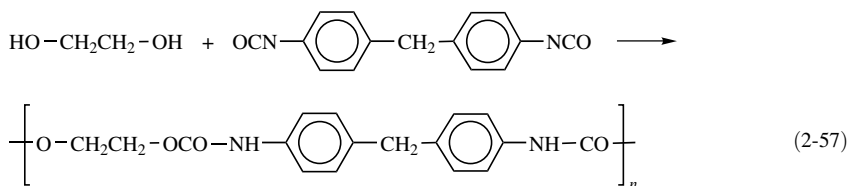
$$\tau = [A]_0 k_p t \quad (2-56)$$

where  $k_m$  is the rate constant for A and B groups that are part of monomer molecules and  $k_p$  is the corresponding rate constant for A and B groups that are part of all species larger than monomer.

Figure 2-6 shows the results plotted as the polymer degree of polymerization versus  $\tau$  for various values of  $u$ . The mathematical solution of this case shows that the initial limiting slope (at  $\tau \rightarrow 0$ ) is  $u/2$  while the final limiting slope (at large values of  $\tau$ ) is  $\frac{1}{2}$  independent of the value of  $u$ . Most of these features are evident in Fig. 2-6. Dimer is produced more rapidly when monomer is more reactive than the larger-sized species (that is, the larger the value of  $u$ ). There is a subsequent slower rate of increase in  $\bar{X}_n$  with the limiting slope of  $\frac{1}{2}$  being reached more rapidly for larger  $u$  values. The initial rate of increase of  $\bar{X}_n$  is slower for  $u < 1$  (monomer less reactive than larger sized species), and it takes longer to reach the limiting slope of  $\frac{1}{2}$ . More significantly, it takes much longer reaction times to reach a particular degree of polymerization when  $u < 1$ . This is a kinetic characteristic of consecutive (series) reaction systems—the overall rate of production of the final product (high polymer) is faster when the initial reaction (reaction of monomer) is faster and the later reaction (reaction of dimer and larger sized species) is slow than vice versa. The trends described in this section would also apply (qualitatively at least) for the case where  $k$  is a continuously varying function of molecular size. If  $k$  increases with molecular size, the situation is qualitatively analogous to the above system for  $u < 1$ . The situation is analogous to  $u > 1$  when  $k$  decreases with molecular size.

## 2-3 ACCESSIBILITY OF FUNCTIONAL GROUPS

In order for a polymerization to yield high polymers the polymer must not precipitate from the reaction mixture before the desired molecular weight is reached. Premature precipitation effectively removes the growing polymer molecules from the reaction; further growth is prevented because the polymer's functional end groups are no longer accessible to each other. The effect can be seen in Table 2-4 for the polymerization of bis(4-isocyanatophenyl)-methane with ethylene glycol [Lyman, 1960]:



The inherent viscosity  $\eta_{inh}$  is a measure of the polymer molecular weight. Larger values of  $\eta_{inh}$  indicate higher molecular weights. Early precipitation of the polyurethane occurs in

**TABLE 2-4** Effect of Solvent on Molecular Weight in Polymerization of Bis(4-isocyanatophenyl)methane with Ethylene Glycol<sup>a, b</sup>

| Solvent            | $\eta_{inh}^c$ | Solubility of Polymer              |
|--------------------|----------------|------------------------------------|
| Xylene             | 0.06           | Precipitates at once               |
| Chlorobenzene      | 0.17           | Precipitates at once               |
| Nitrobenzene       | 0.36           | Precipitates after $\frac{1}{2}$ h |
| Dimethyl sulfoxide | 0.69           | Polymer is soluble                 |

<sup>a</sup> Data from Lyman [1960].<sup>b</sup> Polymerization temperature: 115°C.<sup>c</sup> Measured in dimethylformamide at room temperature.

xylene and chlorobenzene and limits the polymerization to a low molecular weight. Higher molecular weights are obtained when the solvent for the reaction becomes a better solvent for the polymer. The highest polymer molecular weight is obtained in DMSO (dimethylsulfoxide), a highly polar aprotic solvent, in which the polyurethane is completely soluble during the entire course of the polymerization.

Figure 2-7 shows similar behavior for the polymerization between terephthaloyl chloride and *trans*-2,5-dimethylpiperazine in mixtures of chloroform with carbon tetrachloride or

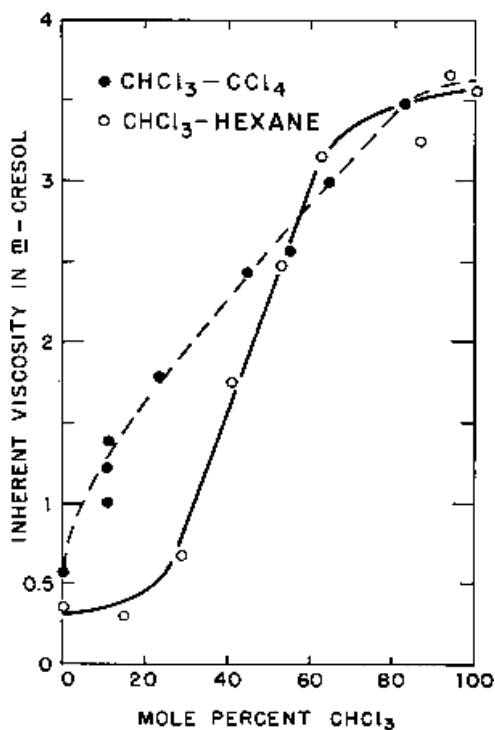


**Fig. 2-7** Polymerization of terephthaloyl chloride and *trans*-2,5-dimethylpiperazine in mixed solvents. After Morgan [1963, 1965] (by permission of Wiley-Interscience, New York).

*n*-hexane [Morgan, 1963, 1965]. Chloroform is a good solvent for the polymer, while carbon tetrachloride and *n*-hexane are poor solvents. The inherent viscosity of the polymer (measured at 30°C in *m*-cresol) increases as the reaction mixture contains a larger proportion of chloroform. The better the reaction medium as a solvent for the polymer the longer the polymer stays in solution and the larger the polymer molecular weight. With a solvent medium that is a poor solvent for polymer, the molecular weight is limited by precipitation. Other examples of this behavior are described in Secs. 2-8c and 2-14.

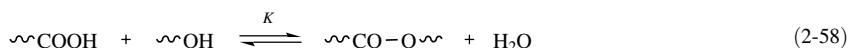
In addition to the effect of a solvent on the course of a polymerization because the solvent is a poor or good solvent for the polymer, solvents affect polymerization rates and molecular weights due to preferential solvation or other specific interactions with either the reactants or transition state of the reaction or both. The direction of the solvation effect is generally the same in polymerization as in the corresponding small molecule reaction and will not be considered in detail. Thus polar solvents enhance the rate of a polymerization with a transition state more polar than the reactants. Polar solvents are not desirable for reactions involving transition states that are less polar than the reactants. The course of a polymerization can be dramatically affected by specific interactions of a solvent with the functional groups of a reactant. The reactivity of a functional group can be altered by specific interaction with solvent. Thus solvents markedly affect the polymer molecular weight in the polymerization of adipic acid and hexamethylene diamine with certain ketone solvents yielding the highest molecular weights [Ogata, 1973]. The molecular weight enhancement by ketones has been ascribed to an enhancement of the diamine nucleophilicity due possibly to a polar interaction between ketone and amine. Alternately, the intermediate formation of an imine may be responsible, since imines can be formed from the diamine and ketone. The imine would be expected to be more reactive than the amine toward the carboxylic acid.

## 2-4 EQUILIBRIUM CONSIDERATIONS

### 2-4a Closed System

Many, if not most, step polymerizations involve equilibrium reactions, and it becomes important to analyze how the equilibrium affects the extent of conversion and, more importantly, the polymer molecular weight. A polymerization in which the monomer(s) and polymer are in equilibrium is referred to as an *equilibrium polymerization* or *reversible polymerization*. A first consideration is whether an equilibrium polymerization will yield high-molecular-weight polymer if carried out in a closed system. By a *closed system* is meant one where none of the products of the forward reaction are removed. Nothing is done to push or drive the equilibrium point for the reaction system toward the polymer side. Under these conditions the concentrations of products (polymer and usually a small molecule such as water) build up until the rate of the reverse reaction becomes equal to the polymerization rate. The reverse reaction is referred to generally as a *depolymerization* reaction; other terms such as *hydrolysis* or *glycolysis* may be used as applicable in specific systems. The polymer molecular weight is determined by the extent to which the forward reaction has proceeded when equilibrium is established.

Consider an external acid-catalyzed polyesterification



in which the initial hydroxyl group and carboxyl group concentrations are both  $[M]_0$ . The concentration of ester groups  $[\text{COO}]$  at equilibrium is  $p_e[M]_0$ , where  $p_e$  is the extent of reaction at equilibrium.  $p_e[M]$  also represents  $[\text{H}_2\text{O}]$  at equilibrium. The concentrations of hydroxyl and carboxyl groups at equilibrium are each  $([M]_0 - p_e[M]_0)$ . The equilibrium constant for the polymerization is given by

$$K = \frac{[\text{COO}][\text{H}_2\text{O}]}{[\text{COOH}][\text{OH}]} = \frac{(p_e[M]_0)^2}{([M]_0 - p_e[M]_0)^2} \quad (2-59)$$

which simplifies to

$$K = \frac{p_e^2}{(1 - p_e)^2} \quad (2-60)$$

Solving for  $p_e$  yields

$$p_e = \frac{K^{1/2}}{1 + K^{1/2}} \quad (2-61)$$

Equation 2-61 yields the extent of conversion as a function of the equilibrium constant. To obtain an expression for the degree of polymerization as a function of  $K$ , Eq. 2-61 is combined with Eq. 2-27 to yield

$$\bar{X}_n = 1 + K^{1/2} \quad (2-62)$$

Table 2-5 shows  $p_e$  and  $\bar{X}_n$  values calculated for various  $K$  values. These calculations clearly indicate the limitation imposed by equilibrium on the synthesis of even a modest molecular weight polymer. A degree of polymerization of 100 (corresponding to a molecular weight of approximately  $10^4$  in most systems) can be obtained in a closed system only if the equilibrium constant is almost  $10^4$ . The higher molecular weights that are typically required for practical applications would require even larger equilibrium constants. A consideration of the equilibrium constants for various step polymerizations or the corresponding small

**TABLE 2-5 Effect of Equilibrium Constant on Extent of Reaction and Degree of Polymerization in Closed System**

| Equilibrium Constant ( $K$ ) | $p$    | $\bar{X}_n$ |
|------------------------------|--------|-------------|
| 0.001                        | 0.0099 | 1.01        |
| 0.01                         | 0.0909 | 1.10        |
| 1                            | 0.500  | 2           |
| 16                           | 0.800  | 5           |
| 81                           | 0.900  | 10          |
| 361                          | 0.950  | 20          |
| 2,401                        | 0.980  | 50          |
| 9,801                        | 0.990  | 100         |
| 39,601                       | 0.995  | 200         |
| 249,001                      | 0.998  | 500         |

molecule reactions quickly shows that polymerizations cannot be carried out as closed systems [Allen and Patrick, 1974; Saunders and Dobinson, 1976; Zimmerman, 1988]. For example, the equilibrium constants for a polyesterification is typically no larger than 1–10,  $K$  for a transesterification is in the range 0.1–1 and  $K$  for polyamidation is in the range  $10^2$ – $10^3$ . Although the equilibrium constant for a polyamidation is very high as  $K$  values go, it is still too low to allow the synthesis of high-molecular-weight polymer. Further, even for what appear to be essentially irreversible polymerizations, reversal of polymerization is a potential problem if the by-product small molecule is not removed (or, alternately, the polymer is not removed).

It is worth mentioning that  $K$  values reported in the literature for any specific step polymerization often differ considerably. Thus,  $K$  values for the polymerization of adipic acid and hexamethylene diamine range from a low of 250 to a high of 900. There are several reasons for these differences, not the least of which is the experimental difficulty in carrying out measurements on polymerizations involving highly concentrated systems (often containing only the monomers, without any solvent) at moderately high temperatures (200–300°C). Other reasons for the variation in  $K$  values are the effects of temperature and the concentration of the small molecule by-product on  $K$ . Most step polymerizations are exothermic and  $K$  decreases with increasing temperature (see Sec. 2-8a). The common practice of extrapolating values of  $K$  determined at certain temperatures to other temperatures can involve considerable error if  $\Delta H$  is not accurately known. The variation of  $K$  with the concentration of the small molecule by-product has been established in the polyamidation reaction but the quantitative effect has not been generally studied. The effect may be due to a change of  $K$  with polarity of the reaction medium.

## 2-4b Open, Driven System

The inescapable conclusion is that except in a minority of systems a step polymerization must be carried out as an *open, driven* system. That is, we must remove at least one of the products of the forward (polymerization) reaction so as to drive the equilibrium toward high molecular weights. It is usually more convenient to remove the small molecule by-product rather than the polymer. When water is the by-product, it can be removed by a combination of temperature, reduced pressure, and purging with inert gas. Conveniently one often carries out step polymerizations at temperatures near or above the boiling point of water. This is usually done for purposes of obtaining desired reaction rates, but it has the added advantage of facilitating water removal. A small molecule by-product such as HCl can be removed in the same manner or by having a base present in the reaction system to neutralize the hydrogen chloride. Driving an equilibrium toward polymer requires considerable effort, since the water or hydrogen chloride or other small molecule must diffuse through and out of the reaction mixture. Diffusion is not so easy since the typical step polymerization system is fairly viscous at very high conversions. The polymerization can become diffusion-controlled under these conditions with the polymerization being controlled by the rate of diffusion of the small molecule by-product [Campbell et al., 1970].

The extent to which one must drive the system in the forward direction can be seen by calculating the lowering of the small molecule concentration, which is necessary to achieve a particular molecular weight. For the polyesterification (Eq. 2-58) one can rewrite Eq. 2-59 as

$$K = \frac{p[\text{H}_2\text{O}]}{[\text{M}]_0(1-p)^2} \quad (2-63)$$

which is combined with Eq. 2-27 to yield

$$K = \frac{p[\text{H}_2\text{O}]\bar{X}_n^2}{[\text{M}]_0} \quad (2-64)$$

and this result combined with Eq. 2-27 to give

$$[\text{H}_2\text{O}] = \frac{K[\text{M}]_0}{\bar{X}_n(\bar{X}_n - 1)} \quad (2-65)$$

Equation 2-65, which applies equally to A–B polymerizations, indicates that  $[\text{H}_2\text{O}]$  must be greatly reduced to obtain high  $\bar{X}_n$  values.  $[\text{H}_2\text{O}]$  is inversely dependent on essentially the square of  $\bar{X}_n$  since  $(\bar{X}_n - 1)$  is close to  $\bar{X}_n$  for large values of  $\bar{X}_n$ . It is also seen that the level to which the water concentration must be lowered to achieve a particular degree of polymerization increases with increasing  $K$  and increasing initial concentration of the reactants. Table 2-6 shows the calculated  $[\text{H}_2\text{O}]$  values for selected values of  $K$  and  $\bar{X}_n$  at

**TABLE 2-6 Effect of Water Concentration on Degree of Polymerization in Open, Driven System**

| $K$ | $\bar{X}_n$       | $[\text{H}_2\text{O}]^a$ (mol L <sup>-1</sup> ) |
|-----|-------------------|-------------------------------------------------|
| 0.1 | 1.32 <sup>b</sup> | 1.18 <sup>b</sup>                               |
|     | 20                | $1.32 \times 10^{-3}$                           |
|     | 50                | $2.04 \times 10^{-4}$                           |
|     | 100               | $5.05 \times 10^{-5}$                           |
|     | 200               | $1.26 \times 10^{-5}$                           |
|     | 500               | $2.00 \times 10^{-6}$                           |
| 1   | 2 <sup>b</sup>    | 2.50 <sup>b</sup>                               |
|     | 20                | $1.32 \times 10^{-2}$                           |
|     | 50                | $2.04 \times 10^{-3}$                           |
|     | 100               | $5.05 \times 10^{-4}$                           |
|     | 200               | $1.26 \times 10^{-4}$                           |
|     | 500               | $2.01 \times 10^{-5}$                           |
| 16  | 5 <sup>b</sup>    | 4.00 <sup>b</sup>                               |
|     | 20                | 0.211                                           |
|     | 50                | $3.27 \times 10^{-2}$                           |
|     | 100               | $8.10 \times 10^{-3}$                           |
|     | 200               | $2.01 \times 10^{-3}$                           |
|     | 500               | $3.21 \times 10^{-4}$                           |
| 81  | 10 <sup>b</sup>   | 4.50 <sup>b</sup>                               |
|     | 20                | 1.07                                            |
|     | 50                | 0.166                                           |
|     | 100               | $4.09 \times 10^{-2}$                           |
|     | 200               | $1.02 \times 10^{-2}$                           |
|     | 500               | $1.63 \times 10^{-3}$                           |
| 361 | 20 <sup>b</sup>   | 4.75 <sup>b</sup>                               |
|     | 50                | 0.735                                           |
|     | 100               | 0.183                                           |
|     | 200               | $4.54 \times 10^{-2}$                           |
|     | 500               | $7.25 \times 10^{-3}$                           |

<sup>a</sup>  $[\text{H}_2\text{O}]$  values are for  $[\text{M}]_0 = 5$ .

<sup>b</sup> These values are for a closed reaction system at equilibrium.

$[M]_0 = 5 M$ . A concentration of 5 M is fairly typical of a step polymerization that is often carried out with only the reactant(s) present (without solvent). The lowering of  $[H_2O]$  to achieve a particular  $\bar{X}_n$  is less the more favorable the equilibrium (that is, the larger the  $K$  value). Thus the synthesis of polyamides (with typical  $K$  values  $> 10^2$ ) is clearly easier from the equilibrium viewpoint than polyester synthesis ( $K \sim 0.1$ -1). Polyesterification requires a greater lowering of  $[H_2O]$  than does polyamidation. It should be understood that simply to lower  $[H_2O]$  as much as possible is not the desired approach. One needs to control the  $[H_2O]$  so as to obtain the desired degree of polymerization.

## 2-4c Kinetics of Reversible Polymerization

Although reversible or equilibrium polymerizations would almost always be carried out in an irreversible manner, it is interesting to consider the kinetics of polymerization for the case in which the reaction was allowed to proceed in a reversible manner. (The kinetics of reversible ring-opening polymerizations are discussed in Sec. 7-2b-5).

Consider the polyesterification of Eq. 2-58 under stoichiometric conditions, where  $k_1$  and  $k_2$  are the rate constants for the forward and back reactions. The initial carboxyl and hydroxyl group concentrations are  $[M]_0$ . The values at any time are  $[M]$ , which is given by  $(1 - p)[M]_0$ . The concentrations of the products,  $[COO]$  and  $[H_2O]$ , at any time are equal because of the stoichiometry and are given by  $p[M]_0$ . The polymerization rate is the difference between the rates of the forward and back reactions

$$\frac{-d[M]}{dt} = \frac{-[M]_0 d(1-p)}{dt} = k_1(1-p)^2[M]_0^2 - k_2 p^2[M]_0^2 \quad (2-66)$$

which can be simplified to

$$\frac{-dp}{dt} = [M]_0[k_1(1-p)^2 - k_2 p^2] \quad (2-67)$$

Integration of Eq. 2-67 [Levenspiel, 1972; Moore and Pearson, 1981] yields

$$\ln \left[ \frac{p_e - p(2p_e - 1)}{p_e - p} \right] = 2k_1 \left( \frac{1}{p_e} - 1 \right) [M]_0 t \quad (2-68)$$

Equation 2-68 can be used to calculate the extent of conversion at any time if  $k_1$  and  $p_e$  are known.  $p_e$  is experimentally determined, or calculated from Eq. 2-61 if  $K$  is known. From experimental values of  $p$  as a function of time, Eq. 2-68 yields a straight line when the left side of the equation is plotted against time. The slope of the line then allows one to calculate  $k_1$ .

## 2-5 CYCLIZATION VERSUS LINEAR POLYMERIZATION

### 2-5a Possible Cyclization Reactions

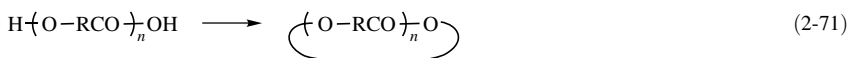
The production of linear polymers by the step polymerization of polyfunctional monomers is sometimes complicated by the competitive occurrence of *cyclization reactions*. Ring formation is a possibility in the polymerizations of both the A-B and A-A plus B-B types.

Reactants of the A–B type such as amino or hydroxy acids may undergo intramolecular cyclization instead of linear polymerization

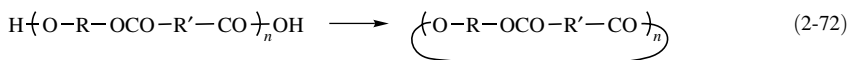


Reactants of the A–A (or B–B) type are not likely to undergo direct cyclization instead of linear polymerization. A groups do not react with each other and B groups do not react with each other under the conditions of step polymerization. Thus there is usually no possibility of anhydride formation from reaction of the carboxyl groups of a diacid reactant under the reaction conditions of a polyesterification. Similarly, cyclization does not occur between hydroxyl groups of a diol, amine groups of a diamine, isocyanate groups of a diisocyanate, and so on.

Once linear polymerization has reached the dimer size, intramolecular cyclization is a possibility throughout any A–B



or A–A + B–B polymerization



The extent to which cyclization occurs during polymerization depends on whether the polymerization proceeds under equilibrium control or kinetic control, the ring sizes of the possible cyclic products, and the specific reaction conditions.

## 2-5b Cyclization Tendency versus Ring Size

Whether cyclization is competitive with linear polymerization for a particular reactant or pair of reactants depends on thermodynamic and kinetic considerations of the size of the ring structure that may be formed. An understanding of the relative ease of cyclization or linear polymerization comes from a variety of sources. These include direct studies with various bifunctional monomers in cyclization reactions (such as those in Eqs. 2-69 through 2-72) as well as ring-opening polymerizations (Chap. 7) and data such as the heats of combustion of cyclic compounds [Carothers and Hill, 1933; Eliel, 1962; Sawada, 1976]. Consider first the thermodynamic stability of different sized ring structures. Some of the most useful data on the effect of ring size on thermodynamic stability is that on the heats of combustion of cycloalkanes (Table 2-7) ( $1 \text{ kJ} = 0.2388 \text{ kcal}$ ). A comparison of the heats of combustion per methylene group in these ring compounds with that in an open-chain alkane yields a general measure of the thermodynamic stabilities of different-sized rings. More precisely, thermodynamic stability decreases with increasing strain in the ring structure as measured by the differences in the heats of combustion per methylene group of the cycloalkane and the  $n$ -alkane. The strain in cyclic structures is very high for the 3- and 4-membered rings, decreases sharply for 5-, 6-, and 7-membered rings, increases for 8–13-membered rings, and then decreases again for larger rings.

The strain in ring structures is of two types—*angle strain* and *conformational strain*. Ring structures of less than five atoms are highly strained due to the high degree of angle strain,

**TABLE 2-7** Heats of Combustion and Strains of Cycloalkanes per Methylene Group<sup>a</sup>

| $(\text{CH}_2)_n$ | Heat of Combustion<br>per Methylene Group<br>(kJ mol <sup>-1</sup> ) | Strain per<br>Methylene Group <sup>b</sup><br>(kJ mol <sup>-1</sup> ) |
|-------------------|----------------------------------------------------------------------|-----------------------------------------------------------------------|
| 3                 | 697.6                                                                | 38.6                                                                  |
| 4                 | 686.7                                                                | 27.7                                                                  |
| 5                 | 664.5                                                                | 5.5                                                                   |
| 6                 | 659.0                                                                | 0.0                                                                   |
| 7                 | 662.8                                                                | 3.8                                                                   |
| 8                 | 664.1                                                                | 5.1                                                                   |
| 9                 | 664.9                                                                | 5.9                                                                   |
| 10                | 664.1                                                                | 5.1                                                                   |
| 11                | 663.2                                                                | 4.2                                                                   |
| 12                | 660.3                                                                | 1.3                                                                   |
| 13                | 660.7                                                                | 1.7                                                                   |
| 14                | 659.0                                                                | 0.0                                                                   |
| 15                | 659.5                                                                | 0.5                                                                   |
| 16                | 659.5                                                                | 0.5                                                                   |
| 17                | 658.2                                                                | -0.8                                                                  |
| <i>n</i> -Alkane  | 659.0                                                                | 0.0                                                                   |

<sup>a</sup> Data from Eliel [1962].<sup>b</sup> Calculated as the heat of combustion per methylene group minus the value (659.0) for the *n*-alkane methylene group.

that is, the large distortion of their bond angles from the normal tetrahedral bond angle. Bond angle distortion is virtually absent in rings of five or more members. For rings larger than five atoms the strain due to bond angle distortion would be excessive for planar rings. For this reason rings larger than five atoms exist in more stable, nonplanar (puckered) forms. The differences in strain among rings of five members and larger are due to differences in conformational strain. The 5- and 7-membered rings are somewhat strained in comparison to the 6-membered ring because of the *torsional strain* arising from eclipsed conformations on adjacent atoms of the ring. Rings of 8 or more members have *transannular strain* arising from repulsive interactions between hydrogens or other groups which are forced to crowd positions in the interior of the ring structure. Transannular strain virtually disappears for rings larger than 13 members; the ring becomes sufficiently large to accommodate substituents without transannular repulsions.

The general order of thermodynamic stability of different-sized rings is given by  $3, 4 \ll 5, 7-13 < 6, 14$  and larger. This same order of stability is generally observed for a variety of ring structures, including those containing atoms or groups other than methylene. Although data are not as extensive for ring structures such as ethers, lactones, or lactams, the general expectation is borne out. The substitution of an oxygen, carbonyl, nitrogen, or other group for methylene does not appreciably alter the bond angles in the ring structure. Replacement of a methylene group by a less bulky oxygen atom or carbonyl group may, however, slightly increase the stability of the ring structure by a decrease in the conformational strain. It has also been observed that substituents, other than hydrogen, on a ring structure generally increase its stability relative to the linear structure as repulsive interactions between substituents are less severe in the ring structure.

In addition to thermodynamics stability kinetic feasibility is important in determining the competitive position of cyclization relative to linear polymerization. Kinetic feasibility for the cyclization reaction depends on the probability of having the functional end groups of the reactant molecules approach each other. As the potential ring size increases, the monomers which would give rise to ring structures have many conformations, very few of which involve the two ends being adjacent. The probability of ring formation decreases as the probability of the two functional groups encountering each other decreases. The effect is reflected in an increasingly unfavorable entropy of activation. Specifically, the kinetic factor becomes less favorable with increasing ring size [Jacobson and Stockmayer, 1950; Semlyen, 1996].

The overall ease of cyclization is thus dependent on the interplay of two factors: (1) the continuous decrease in kinetic feasibility with ring size, and (2) the thermodynamic stability, which varies with ring size as indicated above. From the practical viewpoint of obtaining linear polymer, ring formation in A—B polymerizations is a major problem when the monomer can form a 6-membered ring, that is, when R in Eqs. 2-69 and 2-70 contributes 4 atoms to the ring. With rare exceptions, such monomers do not undergo linear polymerization. Cyclization also predominates at the dimer stage ( $n = 2$  and 1, respectively, in Eqs. 2-71 and 2-72) for monomers with R and R' groups containing only one carbon. The extent of cyclization for species larger than dimer (larger  $n$ ) depends on the specific reaction conditions. Monomers that can cyclize to 5- and 7-membered rings undergo polymerization, but there is a significant tendency to cyclize—although much less than for monomers that cyclize to 6-membered rings.

## 2-5c Reaction Conditions

High concentrations of monomers favor linear polymerization since cyclization is a unimolecular (intramolecular) reaction, while linear polymerization is a bimolecular (intermolecular) reaction. The ratio of cyclization to linear polymerization varies inversely with the first power of monomer concentration according to

$$\frac{\text{Cyclization}}{\text{Linear polymerization}} = \frac{k_c [\text{M}]}{k_p [\text{M}]^2} = \frac{k_c}{k_p [\text{M}]} \quad (2-73)$$

where  $k_c$  and  $k_p$  are the rate constants for cyclization and polymerization, respectively,

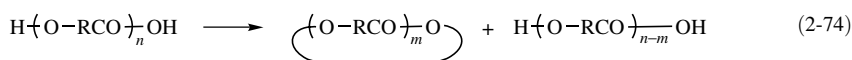
There is a crossover phenomenon at  $[\text{M}] = 1 \text{ M}$ . From the viewpoint of monomer concentration linear polymerization is favored above 1 M with cyclization favored below 1 M. The rate constants  $k_c$  and  $k_p$  are also important in determining the competition between linear polymerization and cyclization.  $k_p$  does not change as linear polymerization proceeds (the equal reactivity of functional groups assumption), but  $k_c$  decreases as the linear polymer increases in molecular weight (kinetic feasibility decreases with increasing ring size). The effects of the rate constants and  $[\text{M}]$  oppose each other and the outcome will be determined by their quantitative interplay in Eq. 2-73. In general, the decrease in  $k_c$  is greater than the decrease in  $[\text{M}]$  and linear polymerization is still favored over cyclization even at high conversions.

Monomer structure can affect the competition between cyclization and linear polymerization. For example, phthalic acid (ortho isomer) is more prone to cyclization than terephthalic acid (para isomer) at the very-low-molecular-weight end, for example, the dimer stage. The ortho structure makes more likely the conformations that are more favorable for cyclization. Stiff linear chains such as those formed in the reaction between an aromatic diamine and aromatic diacid chloride are much less prone to cyclization than the flexible chains formed from the corresponding aliphatic monomers.

## 2-5d Thermodynamic versus Kinetic Control

Kricheldorf and coworkers [2001a,b,c] have stressed that step polymerizations can proceed either with kinetic control or thermodynamic control. Polymerizations under thermodynamic control proceed with an equilibrium between cyclic and linear products. Polymerizations under kinetic control proceed without an equilibrium between cyclic and linear products.

The reactions used in most industrial step polymerizations proceed under thermodynamic control, and most frequently the equilibrium favors linear polymerization over cyclization. However, the extent of cyclization, or at least the presence of cyclic products, is not necessarily zero. Although data are not available for a wide range of systems, the total cyclic content in some polymerizations (e.g., polyesterification and polyamidation) has been found to be as high as 1–3% [Goodman, 1988; Semlyen, 1986; Zimmerman, 1988]. (The cyclic content in polysiloxanes is higher; see Sec. 2-12f.) The cyclics present in these polymerizations are generally oligomers with little high-molecular-weight cyclics. Most of the cyclic oligomers are not formed by cyclization reactions between end groups of growing linear polymers (Eqs. 2-71, 2-72) [Kricheldorf and Schwarz, 2003; Kricheldorf et al., 2001a,b,c]. The cyclic oligomers are formed mostly by *backbiting*, which involves an intramolecular (interchange) nucleophilic substitution reaction, for example, the attack of the hydroxyl end group of a polyester chain on one of its ester carbonyl groups



The presence of even small amounts of cyclic oligomers can be detrimental for the utilization of a polymer if the cyclics migrate out of the product during its use. Many commercial processes remove cyclic by extraction (e.g., with steam in polyamide production) or thermal devolatilization (polysiloxane).

Kinetic control instead of thermodynamic control occurs in reaction systems in which the small-molecule by-product does not react with linkages in the cyclic or linear products. Thus, whereas polyesterification between diacids and diols proceeds with thermodynamic control, polyesterification between diacyl chlorides and diols proceeds with kinetic control. The by-product water in the former reaction is reactive with ester linkages to reverse the reaction. There is no reversal in the latter reaction because the by-product HCl is not reactive with ester linkages. The end result is that there is a continuous increase in cyclic products with increasing conversion even though the rate of cyclization decreases with polymer chain length (which increases with conversion). The cyclic products formed by reaction between end groups of linear chains are inert under the polymerization conditions. Their concentration increases whereas the concentration of linear chains decreases. A number of polymerizations systems with kinetic control have been observed [Kricheldorf et al., 2001a,b,c], almost all of which are not industrial polymerizations. However, Kricheldorf and colleagues reported the presence of considerable cyclic oligomer and polymer in commercial samples of polyethersulfones (Sec. 2-14c), and it may turn out cyclization is important in other industrial polymerizations.

The Carothers equation (Eq. 2-27) has been reformulated as

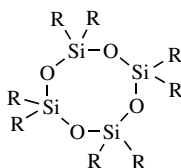
$$\bar{X}_n = \frac{1}{1 - p[1 - (1/X^a)]} \quad (2-75)$$

to include linear polymerization with varying extents of cyclization.  $X$  is a constant greater than 1 and dependent on the reactant concentration.  $a$  is the ratio of the rate of linear

polymerization to the rate of cyclization. Equation 2-75 shows that cyclization decreases  $\bar{X}_n$  from the value predicted by the Carothers equation. However, the utility of Eq. 2-75 is limited because values of  $X$  and  $a$  are unavailable. When cyclization is negligible,  $a$  is large, and Eq. 2-75 becomes the Carothers equation.

## 2-5e Other Considerations

The previous discussions have concerned rings containing C, C and O, or C and N atoms. The situation regarding the competition between cyclization and linear polymerization as a function of ring size may be altered when other atoms make up the ring structure. Thus in the case of polysiloxanes where the ring structure **VIII** contains alternating O and Si atoms, rings of less than eight atoms are quite strained because of the large size of the Si atom, the longer



**VIII**

length of the Si—O bond, and the larger Si—O—Si bond angle. The optimum ring size is the 8-membered ring, although the preference is not overwhelming because of the kinetic factor. Larger-sized rings are not as favored for the reasons previously discussed.

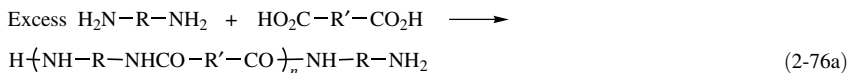
## 2-6 MOLECULAR WEIGHT CONTROL IN LINEAR POLYMERIZATION

### 2-6a Need for Stoichiometric Control

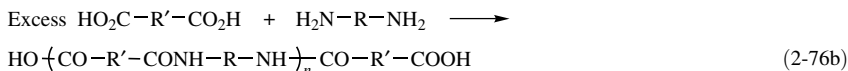
There are two important aspects with regard to the control of molecular weight in polymerizations. In the synthesis of polymers, one is usually interested in obtaining a product of very specific molecular weight, since the properties of the polymer will usually be highly dependent on molecular weight. Molecular weights higher or lower than the desired weight are equally undesirable. Since the degree of polymerization is a function of reaction time, the desired molecular weight can be obtained by quenching the reaction (e.g., by cooling) at the appropriate time. However, the polymer obtained in this manner is unstable in that subsequent heating leads to changes in molecular weight because the ends of the polymer molecules contain functional groups (referred to as *end groups*) that can react further with each other.

This situation is avoided by adjusting the concentrations of the two monomers (e.g., diol and diacid) so that they are slightly nonstoichiometric. One of the reactants is present in slight excess. The polymerization then proceeds to a point at which one reactant is completely used up and all the chain ends possess the same functional group—the group that is in excess. Further polymerization is not possible, and the polymer is stable to subsequent molecular-weight changes. Thus the use of excess diamine in the polymerization of a diamine with a diacid (Eq. 1-1) yields a polyamide (**IX**) with amine end groups in the absence of any diacid for further polymerization. The use of excess diacid accomplishes the same result; the polyamide (**X**) in this case has carboxyl end groups which are incapable of further

reaction, since the diamine has completely reacted.

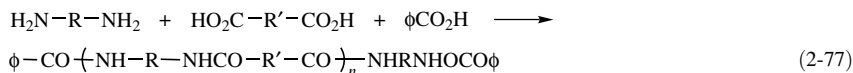


### IX



### X

Another method of achieving the desired molecular weight is by addition of a small amount of a *monofunctional monomer*, a monomer with only one functional group. Acetic acid or lauric acid, for example, are often used to achieve molecular weight stabilization of polyamides. The monofunctional monomer, often referred to as a *chain stopper*, controls and limits the polymerization of bifunctional monomers because the growing polymer yields chain ends devoid of functional groups and therefore incapable of further reaction. Thus, the use of benzoic acid in the polyamide synthesis yields a polyamide (XI) with phenyl end groups that are unreactive toward polymerization.



### XI

## 2-6b Quantitative Aspects

In order to properly control the polymer molecular weight, one must precisely adjust the stoichiometric imbalance of the bifunctional monomers or of the monofunctional monomer. If the nonstoichiometry is too large, the polymer molecular weight will be too low. It is therefore important to understand the quantitative effect of the stoichiometric imbalance of reactants on the molecular weight. This is also necessary in order to know the quantitative effect of any reactive impurities that may be present in the reaction mixture either initially or that are formed by undesirable side reactions. Impurities with A or B functional groups may drastically lower the polymer molecular weight unless one can quantitatively take their presence into account. Consider now the various different reactant systems which are employed in step polymerizations:

TYPE I. For the polymerization of the bifunctional monomers A—A and B—B (e.g., diol and diacid or diamine and diacid) where B—B is present in excess, the numbers of A and B functional groups are given by  $N_A$  and  $N_B$ , respectively.  $N_A$  and  $N_B$  are equal to twice the number of A—A and B—B molecules, respectively, that are present.  $r$ , called the *stoichiometric ratio* or *imbalance*, is always defined to have a value equal to or less than unity but never greater than unity, that is, the B groups are those in excess. The total number of monomer molecules is given by  $(N_A + N_B)/2$  or  $N_A(1 + 1/r)/2$ .

The extent of reaction  $p$  is defined as the fraction of the limiting groups (A groups) that have reacted at a particular time. The fraction of B groups that have reacted is given by  $rp$ . The fractions of unreacted A and B groups are  $(1 - p)$  and  $(1 - rp)$ , respectively. The total numbers of unreacted A and B groups are  $N_A(1 - p)$  and  $N_B(1 - rp)$ , respectively. The total number of polymer chain ends is given by the sum of the total number of unreacted

A and B groups. Since each polymer chain has two chain ends, the total number of polymer molecules is one half the total number of chain ends or  $[N_A(1-p) + N_B(1-rp)]/2$ .

The number-average degree of polymerization  $\bar{X}_n$  is the total number of A—A and B—B molecules initially present divided by the total number of polymer molecules

$$\bar{X}_n = \frac{N_A(1 + 1/r)/2}{[N_A(1-p) + N_B(1-rp)]/2} = \frac{1+r}{1+r-2rp} \quad (2-78)$$

Equation 2-78 shows the variation of  $\bar{X}_n$  with the stoichiometric imbalance  $r$  and the extent of reaction  $p$ . There are two limiting forms of this relationship. When the two bifunctional monomers are present in stoichiometric amounts ( $r = 1$ ), Eq. 2-78 reduces to the previous discussed Carothers relationship (Eq. 2-27)

$$\bar{X}_n = \frac{1}{(1-p)} \quad (2-27)$$

On the other hand, for 100% conversion ( $p = 1$ ), Eq. 2-78 becomes

$$\bar{X}_n = \frac{(1+r)}{(1-r)} \quad (2-79)$$

In actual practice,  $p$  may approach but never becomes equal to unity.

Figure 2-8 shows plots of  $\bar{X}_n$  versus the stoichiometric ratio for several values of  $p$  in accordance with Eq. 2-78. The stoichiometric imbalance is expressed as both the ratio  $r$  and the mole percent excess of the B—B reactant over the A—A reactant. The various plots show how  $r$  and  $p$  must be controlled so as to obtain a particular degree of polymerization. However, one does not usually have complete freedom of choice of the  $r$  and  $p$  values in a polymerization. Complete control of the stoichiometric ratio is not always possible, since reasons of economy and difficulties in the purification of reactants may prevent one from obtaining  $r$  values very close to 1.000. Similarly, many polymerizations are carried out to less than 100% completion (i.e., to  $p < 1.000$ ) for reasons of time and economy. The time required to achieve each of the last few percent of reaction is close to that required for the first ~97–98% of reaction. Thus a detailed consideration of Fig. 2-2 shows that the time required to go from  $p = 0.97$  ( $\bar{X}_n = 33.3$ ) to  $p = 0.98$  ( $\bar{X}_n = 50$ ) is approximately the same as that to reach  $p = 0.97$  from the start of reaction.

Consider a few examples to illustrate the use of Eq. 2-78 and Fig. 2-8. For stoichiometric imbalances of 0.1 and 1 mol% ( $r$  values of 1000/1001 and 100/101, respectively) at 100% reaction, the values of  $\bar{X}_n$  are 2001 and 201, respectively. The degree of polymerization decreases to 96 and 66, respectively, at 99% reaction and to 49 and 40 at 98% reaction. It is clear that step polymerizations will almost always be carried out to at least 98% reaction, since a degree of polymerization of at least approximately 50–100 is usually required for a useful polymer. Higher conversions and the appropriate stoichiometric ratio are required to obtain higher degrees of polymerization. The exact combination of  $p$  and  $r$  values necessary to obtain any particular degree of polymerization is obtained from Fig. 2-8 and Eq. 2-78. One can also calculate the effect of losses of one reactant or both during the polymerization through volatilization, or side reactions. The precision required in the control of the stoichiometric ratio in a polymerization is easily found from Eq. 2-78. An error in the experimentally employed  $r$  value yields a corresponding error in  $\bar{X}_n$ . The shape of the plots in Fig. 2-8 shows that the effect of an error in  $r$ , however, is progressively greater at higher degrees of polymerization. Progressively greater control is required to synthesize the higher-molecular-weight polymer.

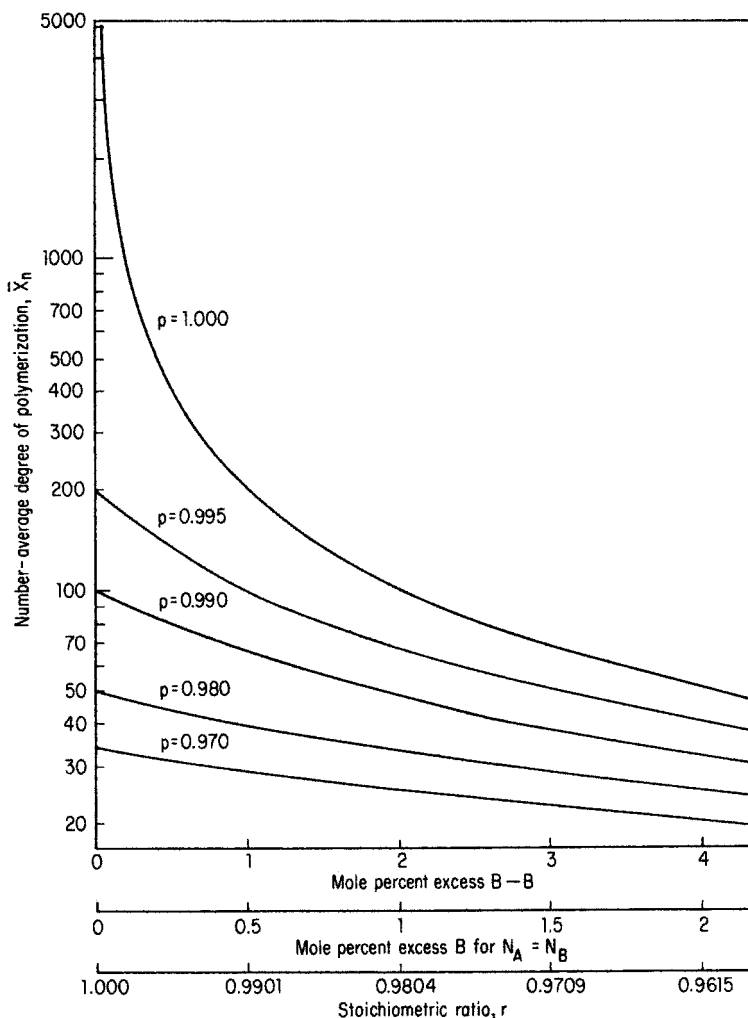


**Fig. 2-8** Dependence of the number-average degree of polymerization  $\bar{X}_n$  on the stoichiometric ratio  $r$  for different extents of reaction  $p$  in the polymerization of A—A with B—B.

TYPE 2. The control of the degree of polymerization in the polymerization of an equimolar mixture A—A and B—B by the addition of small amounts of a monofunctional reactant, for example, B, has been described above. The same equations that apply to a type 1 polymerization are also applicable here, except that  $r$  must be redefined as

$$r = \frac{N_A}{N_B + 2N_{B'}} \quad (2-80)$$

where  $N_{B'}$  is the number of B molecules present and  $N_A = N_B$ . The coefficient 2 in front of  $N_{B'}$  is required since one B molecule has the same quantitative effect as one excess B—B

molecule in limiting the growth of a polymer chain. Equations 2-78 to 2-80 do not apply to type 2 systems unless equimolar amounts of A—A and B—B are present. Other situations are correctly analyzed only by Eqs. 2-137 and 2-139 in Sec. 2-10a.

TYPE 3. Polymerizations of A—B type monomers such as hydroxy and amino acids automatically take place with internally supplied stoichiometry. For such a polymerization Eqs. 2-78 and 2-79 apply with  $r$  equal to 1. This leads to a polymer product that is subsequently unstable toward molecular weight changes because the end groups of the polymer molecules can react with each other. Molecular weight stabilization is usually accomplished by using a monofunctional B reactant. In this latter case the same equations apply with  $r$  redefined as

$$r = \frac{N_A}{N_B + 2N_{B'}} \quad (2-81)$$

where  $2N_{B'}$  has the same meaning as in a type 2 polymerization, and  $N_A = N_B$  = the number of A—B molecules. (Bifunctional A—A or B—B monomers can also be employed to control molecular weight in this polymerization.)

The plots in Fig. 2-8 apply equally well to polymerizations of types 1, 2, and 3, although the scale of the  $x$  axis may be different. When the  $x$  axis is expressed as the stoichiometric ratio  $r$  the scale is exactly the same for all three types of polymerization. Different scales will be applicable when the  $x$  axis is expressed in terms of the mole percent excess of the molecular weight controlling reactant. Thus, the  $x$  axis is shown as the mole percent excess of the B—B reactant for type 1 polymerizations. For polymerizations of type 2 when  $N_A = N_B$  and those of type 3, the  $x$  axis is shown as the mole percent excess of B groups. The two  $x$  axes differ by a factor of 2 because one B—B molecule is needed to give the same effect as one B molecule. The relationship between the degree of polymerization and the stoichiometric ratio (Eqs. 2-78 through 2-81 and Fig. 2-8) has been verified in a large number of step polymerizations. Its verification and use for molecular weight control has been reviewed in several systems, including polyamides, polyesters, and polybenzimidazoles [Korshak, 1966]. The effect of excess bifunctional reactants as well as monofunctional reactants follows the expected behavior.

The discussion in this section, including the derivations of Eqs. 2-78 through 2-80 assumes that the initial stoichiometric ratio of reactants is the effective stoichiometric ratio throughout the polymerization from start to finish. However, this is seldom the case, as there may be losses of one or all reactants as polymerization proceeds. Losses are of two types. Monomer loss due to volatilization is not uncommon, since moderately high reaction temperatures are often used. For example, volatilization losses of the diamine reactant are a problem in polyamidation because of the much higher vapor pressure of diamine compared to the diacid. The extent of this loss depends on the particular diamine used, the specific reaction conditions (temperature, pressure) and whether the polymerization reactor has provision for preventing or minimizing the losses. Aside from volatilization losses, the other pathway by which reactant losses occur is by side reactions. Many polymerization systems involve reactants that can undergo some reaction(s) other than polymerization. Specific examples of such side reactions are described in Secs. 2-8, 2-12, and 2-14. Polymerization conditions usually involve a compromise between conditions that yield the highest reaction rates and those that minimize side reactions and volatilization losses. Because of the very large effect of  $r$  on polymer molecular weight, this compromise may be much closer to reaction conditions that minimize any change in  $r$ . An alternate and/or simultaneous approach involves adjusting the stoichiometric imbalance by a continuous or batchwise replenishment of the

“lost” reactant. The amount of added reactant must be precisely calculated based on a chemical analysis of the  $r$  value for the reaction system as a function of conversion. Also the additional amount of the “lost” reactant must be added at the appropriate time. Premature addition or the addition of an incorrect amount results in performing the polymerization at other than the required stoichiometric ratio.

There is a reaction condition in which high polymer molecular weights have been obtained independent of the stoichiometric ratio—when one of the two monomers is only slightly soluble in the reaction mixture and is present in excess. An example is the reaction of bis(*o*-aminophenol) with terephthalic acid in polyphosphoric acid (Sec. 2-14h) [So, 2001]. Bis(*o*-aminophenol) is soluble but terephthalic acid is only slightly soluble in the reaction mixture. At any instant the polymer chain ends are those from the soluble monomer bis(*o*-aminophenol), but these chain ends react quickly with the small amount of dissolved terephthalic acid, and then there is reaction again with bis(*o*-aminophenol). Polymerization proceeds to high molecular weight because there is a continuous dissolution of terephthalic acid to maintain its saturation concentration. On the other hand, high molecular weights are not achieved when the soluble monomer is present in excess. Similar results have been reported for the polymerization of terephthalic acid with ethylene glycol, *p*-dichlorobenzene with sodium sulfide, and some aromatic diacid chlorides with aromatic diamines [Goodman, 1988; Liou and Hsiao, 2001a].

### 2-6c Kinetics of Nonstoichiometric Polymerization

The kinetics of polymerizations involving nonstoichiometric amounts of A and B functional groups can be handled in a straightforward manner. Consider the external acid-catalyzed A—A plus B—B polymerization with  $r < 1$ . The polymerization rate, defined as the rate of disappearance of the functional groups present in deficient amount, is given by

$$\frac{-d[A]}{dt} = k[A][B] \quad (2-82)$$

The following stoichiometry holds:

$$[A]_0 - [A] = [B]_0 - [B] \quad (2-83)$$

where  $[A]_0$  and  $[B]_0$  are the initial concentrations of A and B groups. Combination of Eqs. 2-82 and 2-83 followed by integration [Moore and Pearson, 1981] yields

$$\frac{1}{[B]_0 - [A]_0} \ln \left[ \frac{[A]_0[B]}{[B]_0[A]} \right] = kt \quad (2-84)$$

which is combined with  $r = [A]_0/[B]_0$  to give

$$\ln \frac{[B]}{[A]} = -\ln r + [B]_0(1-r)kt \quad (2-85)$$

A plot of  $\ln ([B]/[A])$  versus  $t$  is linear with a positive slope of  $[B]_0(1-r)k$  and an intercept of  $-\ln r$ .

When  $r$  is close to unity the polymerization rate is adequately described by the expressions in Secs. 2-2a and 2-2b for the case of  $r = 1$ . Only when  $r$  is considerably different from unity does it become necessary to use Eq. 2-85 or its equivalent. Most step polymerizations

are carried out with close to stoichiometric amounts of the two reacting functional groups. The main exceptions to this generalization are some of the reaction systems containing poly-functional reactants (Secs. 2-10 and 2-12).

## 2-7 MOLECULAR WEIGHT DISTRIBUTION IN LINEAR POLYMERIZATION

The product of a polymerization is a mixture of polymer molecules of different molecular weights. For theoretical and practical reasons it is of interest to discuss the distribution of molecular weights in a polymerization. The *molecular weight distribution* (MWD) has been derived by Flory by a statistical approach based on the concept of equal reactivity of functional groups [Flory, 1953; Howard, 1961; Peebles, 1971]. The derivation that follows is essentially that of Flory and applies equally to A—B and stoichiometric A—A plus B—B types of step polymerizations.

### 2-7a Derivation of Size Distributions

Consider the probability of finding a polymer molecule containing  $x$  structural units. This is synonymous with the probability of finding a molecule with  $(x - 1)$  A groups reacted and one A group unreacted. The probability that an A group has reacted at time  $t$  is defined as the extent of reaction  $p$ . The probability that  $(x - 1)$  A groups have reacted is the product of  $(x - 1)$  separate probabilities or  $p^{x-1}$ . Since the probability of an A group being unreacted is  $(1 - p)$ , the probability  $N_x$  of finding the molecule in question, with  $x$  structural units, is given by

$$\underline{N}_x = p^{x-1}(1 - p) \quad (2-86)$$

Since  $\underline{N}_x$  is synonymous with the *mole* or *number fraction* of molecules in the polymer mixture that are  $x$ -mers (i.e., that contain  $x$  structural units), then

$$N_x = Np^{x-1}(1 - p) \quad (2-87)$$

where  $N$  is the total number of polymer molecules and  $N_x$  is the number that are  $x$ -mers. If the total number of structural units present initially is  $N_0$ , then  $N = N_0(1 - p)$  and Eq. 2-87 becomes

$$N_x = N_0(1 - p)^2 p^{x-1} \quad (2-88)$$

Neglecting the weights of the end groups, the *weight fraction*  $w_x$  of  $x$ -mers (i.e., the weight fraction of the molecules that contains  $x$  structural units) is given by  $w_x = xN_x/N_0$  and Eq. 2-88 becomes

$$w_x = x(1 - p)^2 p^{x-1} \quad (2-89)$$

Equations 2-86 and 2-89 give the *number-* and *weight-distribution functions*, respectively, for step polymerizations at the extent of polymerization  $p$ . These distributions are usually referred to as the *most probable* or *Flory* or *Flory-Schulz distributions*. Plots of the two distribution functions for several values of  $p$  are shown in Figs. 2-9 and 2-10. It is seen that on a

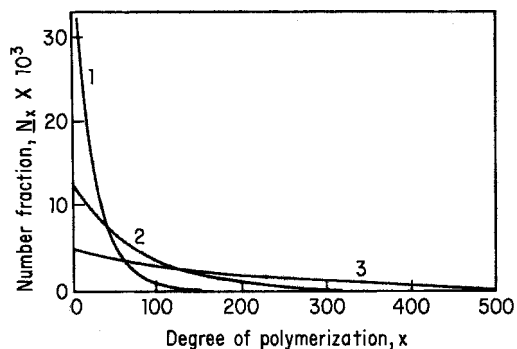


**Fig. 2-9** Number-fraction distribution curve for linear polymerization. Plot 1,  $p = 0.9600$ ; plot 2,  $p = 0.9875$ ; plot 3,  $p = 0.9950$ . After Howard [1961] (by permission of Iliffe Books, London and Elsevier, Oxford).

number basis there are more monomer molecules than any polymer species regardless of the extent of reaction. Although the number of monomer molecules decreases as  $p$  increases, they are still the most plentiful species. The situation is quite different for the weight distribution of molecular weights. On a weight basis, the proportion of low-molecular-weight species is very small and decreases as  $p$  increases. The maxima in Fig. 2-10 occur at  $x = -(1/\ln p)$ , which is very near the number-average degree of polymerization given by Eq. 2-27.

The experimental determination of a molecular weight distribution is frequently obtained in an integral form in which the *combined* or *cumulative weight fraction*  $I_x$  of all polymer molecules having degrees of polymerization up to and including  $x$  are plotted against  $x$ . For this purpose it is useful to express the Flory distribution function in terms of  $I_x$ . This is done by summing  $w_x$  values from Eq. 2-89

$$I_x = \sum w_x = (1-p)^2 \sum xp^{(x-1)} \quad (2-90)$$

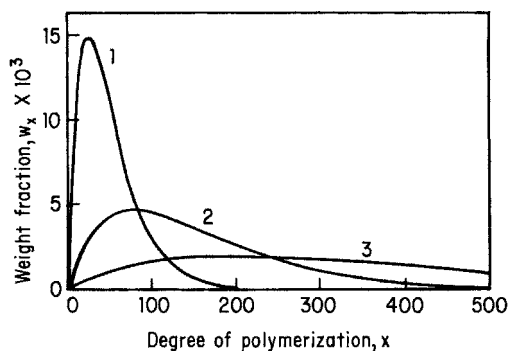


**Fig. 2-10** Weight fraction distribution plot for linear polymerization. Plot 1,  $p = 0.9600$ ; plot 2,  $p = 0.9875$ ; plot 3,  $p = 0.9950$ . After Howard [1961] (by permission of Iliffe Books, London and Elsevier, Oxford).

for all values of  $x$  from 1 to  $x$  to yield

$$I_x = 1 - p^x - xp^x(1 - p) \quad (2-91)$$

The limit of  $I_x$  at high values of  $x$  is 1 and is reached at progressively higher values of  $x$  for higher conversions.

### 2-7b Breadth of Molecular Weight Distribution

The number- and weight-average degree of polymerization  $\bar{X}_n$  and  $\bar{X}_w$  can be derived from the number and weight distribution functions, respectively. The number- and weight-average molecular weights have been defined by Eqs. 1-15 and 1-17. Dividing Eq. 1-15 by the weight  $M_o$  of a structural unit yields the number-average degree of polymerization as

$$\bar{X}_n = \frac{\sum x N_x}{\sum N_x} = \sum x \underline{N}_x \quad (2-92)$$

where the summations are over all values of  $x$ . Combination of Eqs. 2-86 and 2-92 gives

$$\bar{X}_n = \sum xp^{x-1}(1 - p) \quad (2-93)$$

Evaluation of this summation yields

$$\bar{X}_n = \frac{1}{(1 - p)} \quad (2-27)$$

which is the same result obtained earlier. Dividing Eq. 1-17 by  $M_o$  yields

$$\bar{X}_w = \sum xw_x \quad (2-94)$$

Combination of Eqs. 2-89 and 2-94 gives

$$\bar{X}_w = \sum x^2 p^{x-1}(1 - p)^2 \quad (2-95)$$

which is evaluated as

$$\bar{X}_w = \frac{(1 + p)}{(1 - p)} \quad (2-96)$$

The *breadth of the molecular weight distribution* is then given by

$$\frac{\bar{X}_w}{\bar{X}_n} = (1 + p) \quad (2-97)$$

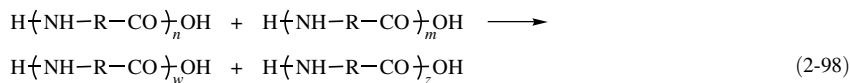
The ratio  $\bar{X}_w/\bar{X}_n$  is synonymous with the ratio  $\bar{M}_w/\bar{M}_n$  discussed in Sec. 1-4. It is a measure of the polydispersity of a polymer sample. The value of  $\bar{X}_w/\bar{X}_n$  increases with the extent of reaction and approaches 2 in the limit of large extents of reaction. The ratio  $\bar{X}_w/\bar{X}_n$  is also referred to as the *polydispersity index* (PDI).

The most probable distribution of Flory is generally well established, although its experimental verification has been somewhat limited. Direct evidence for the most probable

distribution requires the fractionation of polymer samples followed by molecular-weight measurements on the fractions to allow the construction of experimental plots of  $\bar{N}_x$ ,  $w_x$ ,  $I_x$  versus  $x$  for comparison with the theoretical plots. The experimental difficulties involved in polymer fractionation previously limited the number of polymerizations that had been extensively studied. The availability of automated *size exclusion chromatography* (SEC), also referred to as *gel permeation chromatography* (GPC), has significantly increased the available data on molecular-weight distributions of polymers. (The availability of calibration standards for only certain polymers is a limiting factor for size exclusion chromatography. However, the combination of SEC with osmometry and light-scattering measurements of molecular weight offers a powerful combination for examining polymer size distributions.) The Flory distribution has been experimentally verified for a number of step polymerizations, including polyamides and polyesters. Less direct verification of the most probable distribution has been made in many instances by determining the ratio  $\bar{X}_w/\bar{X}_n$ . For many different step polymerizations, this ratio has been found to be close to 2 as required by Eq. 2-97.

## 2-7c Interchange Reactions

Some polymers (polyesters, polyamides, polysulfides, and others) undergo *interchange reactions* under appropriate conditions. Interchange involves reaction between the terminal functional group of one polymer molecule with the interunit repeating linkage of another polymer molecule, for example, between the terminal  $-\text{NH}_2$  and interunit  $-\text{CONH}-$  groups of polyamide molecules. Two polymer chains may react to yield one shorter and one longer chain,

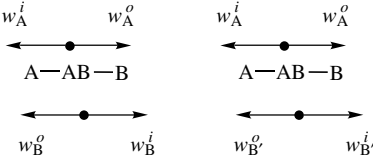


If free interchange occurs, the molecular weight distribution will be the Flory distribution described by Eqs. 2-86 and 2-89. Free interchange corresponds to all interunit linkages in all polymer molecules having equal probabilities of interchange. This is analogous to the concept of functional group reactivity independent of molecular size as applied to the interchange reaction. It is apparent that the presence of interchange during a polymerization will not affect the size distribution from that expected for the random polymerization. The Flory or most probable distribution is also that expected for the random scission of the interunit linkages of polymer chains, for example, in the hydrolysis of cellulose.

## 2-7d Alternate Approaches for Molecular-Weight Distribution

A number of treatments other than that by Flory have been given for the molecular weight distributions in linear step polymerizations [Burchard, 1979; Durand and Bruneau, 1979a,b]. However, a knowledge of the average properties ( $\bar{M}_n$ ,  $\bar{M}_w$ , and PDI) is often sufficient for many practical purposes. Macosko and Miller [1976] developed a useful statistical approach for obtaining the average properties without the need to calculate the molecular weight distributions. This approach will be described for a polymerization system composed of A—A, B—B, and B'—B' where A groups can react with B groups and with B' groups [Ozizmir and Odian, 1980]. To keep the system as simple as possible, the molecular weights of the three structural units are taken as equal (and denoted by  $M_o$ ) and the initial system contains equimolar amounts of B—B and B'—B' monomers where the total moles of A—A is equal to the sum of B—B and B'—B'.

The expected masses of polymers which contain a randomly selected A, B, or B' group in the system are denoted by  $w_A$ ,  $w_B$ , and  $w_{B'}$ . In order to obtain these quantities it is convenient to introduce the quantities  $w_A^i$ ,  $w_B^i$ ,  $w_{B'}^i$ , and  $w_A^o$ ,  $w_B^o$ ,  $w_{B'}^o$ . Here  $w_A^i$  represents the expected mass attached to a randomly selected A group in the system looking inward toward the other A group of the A—AB structural unit of which it is a part and  $w_A^o$  represents the expected mass attached looking outward from the randomly selected A group as shown in **XII**. Similarly,  $w_B^i$ ,  $w_B^o$ ,  $w_{B'}^i$ , and  $w_{B'}^o$  represent the expected inward and outward masses attached to B and B' groups.

**XII**

The following relationships hold for this system:

$$w_A = w_A^i + w_A^o \quad (2-99)$$

$$w_B = w_B^i + w_B^o \quad (2-100)$$

$$w_{B'} = w_{B'}^i + w_{B'}^o \quad (2-101)$$

$$w_A^i = M_o + w_A^o \quad (2-102)$$

$$w_A^o = p_A \left\{ \frac{p_B w_B^i}{(p_B + p_{B'})} + \frac{p_{B'} w_{B'}^i}{(p_B + p_{B'})} \right\} = \frac{(p_B w_B^i + p_{B'} w_{B'}^i)}{2} \quad (2-103)$$

$$w_B^i = M_o + w_B^o \quad (2-104)$$

$$w_B^o = p_B w_A^i \quad (2-105)$$

$$w_{B'}^i = M_o + w_{B'}^o \quad (2-106)$$

$$w_{B'}^o = p_{B'} w_A^i \quad (2-107)$$

$$p_A = \frac{(p_B + p_{B'})}{2} \quad (2-108)$$

Most of these relationships are simple material balance statements. Equations 2-99 through 2-101 state that the total mass of polymer attached to an A, B, or B' group is the sum of the inward and outward masses attached to that group. Equations 2-102, 2-104, and 2-106 state that the difference between the inward and outward masses attached to a group is  $M_o$ . Equation 2-107 indicates that the polymer mass attached to a B' group looking outward from the B' group equals the probability of that group having reacted with an A group multiplied by the mass of polymer attached to the A group looking inward from that A group. The corresponding descriptions for  $w_A^o$  and  $w_B^o$  are Eqs. 2-103 and 2-105.

Equations 2-102 through 2-108 can be solved and their results combined with Eqs. 2-99 through 2-101 to yield

$$w_A = U - M_o \quad (2-109a)$$

$$w_B = M_o + p_B U \quad (2-109b)$$

$$w_{B'} = M_o + p_{B'} U \quad (2-109c)$$

where

$$U = 2w_A^j = \frac{2M_o + (p_B M_o + p_{B'} M_o)}{1 - (p_B^2 + p_{B'}^2)/2} \quad (2-110)$$

The weight-average molecular weight, obtained by a weight averaging of  $w_A$ ,  $w_B$ , and  $w_{B'}$ , is given by

$$\overline{M}_w = \frac{w_A}{2} + \frac{w_B}{4} + \frac{w_{B'}}{4} \quad (2-111)$$

which yields

$$\overline{M}_w = \frac{M_o}{4} \left\{ \frac{(2 + p_B + p_{B'})^2}{1 - (p_B^2 + p_{B'}^2)/2} \right\} \quad (2-112)$$

on substitution for  $w_A$ ,  $w_B$ , and  $w_{B'}$ . The number-average molecular weight, obtained by dividing the total number of moles of reactants initially present divided by the total present at any time, yields

$$\overline{M}_n = \frac{M_o}{(1 - p_A)} \quad (2-29)$$

It is useful to introduce the fractions of unreacted A, B, and B' functional groups

$$\alpha = 1 - p_A \quad (2-113a)$$

$$\beta = 1 - p_B \quad (2-113b)$$

$$\gamma = 1 - p_{B'} \quad (2-113c)$$

For the case where B and B' groups have the same reactivity:

$$\gamma = \beta \quad (2-114)$$

Combination of Eqs. 2-108, 2-112 through 2-114, and 2-29 yields the polydispersity index as

$$PDI = \frac{(2 - \alpha)^2}{2 - (\beta^2 + \gamma^2)/2\alpha} \quad (2-115)$$

Equation 2-115 yields PDI as a function of conversion in a straightforward manner without having to solve differential equations to obtain the number- and weight-average molecular weight distributions. One need only take a set of  $\beta$  values and then calculate the corresponding  $\gamma$ ,  $\alpha$ , and PDI values from Eqs. 2-114 and 2-115. The limit of PDI at complete conversion ( $p_A = 1, \alpha = 0$ ) is 2 as for the Flory distribution. The Macosko-Miller method has also been applied to other polymerizations, including the A-B plus A'-B' system. In addition to being a simpler method for obtaining the average properties compared to the Flory and similar methods, it more readily allows an evaluation of the effect of various reaction parameters such as unequal group reactivity or nonstoichiometric amounts of reactants on  $\overline{M}_n$ ,  $\overline{M}_w$ , and PDI (see Sec. 2-7e).

## 2-7e Effect of Reaction Variables on MWD

### 2-7e-1 Unequal Reactivity of Functional Groups

The molecular weight distribution and/or PDI has been described for several cases where the assumption of equal reactivity of functional groups is not valid. Unequal reactivity is easily handled by the Macosko–Miller method. For the  $A-A + B-B + B'-B'$  system described in the previous section, we simply redefine the relationship between  $\beta$  and  $\gamma$  by

$$\gamma = \beta^s \quad (2-47)$$

(which was derived previously in Sec. 2-2d-2) where  $s$  is the ratio of rate constants for reaction of  $B'$  and  $B$  groups [Ozizmir and Odian, 1980].

The polydispersity index increases (for conversions  $< 100\%$ ) when the reactivities of  $B$  and  $B'$  groups are different compared to the case where the reactivities are the same. The opposite trend is found for the  $A-A + B-B'$  system [Gandhi and Babu, 1979, 1980]. There is a basic difference between the two- and the three-species reaction systems. In the three-species system, when  $B'$  groups have higher reactivity than  $B$  groups, the  $B'-B'$  monomer continues polymerization with  $A-A$  monomer, independently of the  $B-B$  monomer, to form large-sized polymer chains. In the two-species system, long chains cannot be formed without participation of  $B$  groups in the polymerization process. The extents of the broadening and narrowing effects in the two systems increase as the difference in reactivities of  $B$  and  $B'$  become larger. The effects are significant at low conversions; for instance, PDI is 2.10 at 50% conversion for the three-species system when  $B'$  is 20-fold more reactive than  $B$  compared to a PDI of 1.50 for the equal reactivity case. However, the PDI at complete conversion equals 2 in both the two- and three-species systems, which is the same limit as for the equal-reactivity case.

### 2-7e-2 Change in Reactivity on Reaction

An increase in the reactivity of one functional group in a bifunctional reactant on reaction of the other functional group results in an increase in PDI [Gandhi and Babu, 1979, 1980]. The PDI at complete conversion exceeds 2 when there is a greater than twofold increase in reactivity. PDI decreases when there is a decrease in reactivity of one functional group on reaction of the other group but the PDI at complete conversion is 2. The same trends are found but are more exaggerated when functional group reactivity varies continuously with molecular size [Gupta et al., 1979a,b; Nanda and Jain, 1968].

### 2-7e-3 Nonstoichiometry of Functional Groups

Using the Macosko–Miller approach for the  $A-A + B-B + B'-B'$  system, we introduce  $r_1$  and  $r_2$

$$r_1 = \frac{[B]_0}{[A]_0} \quad (2-116a)$$

$$r_2 = \frac{[B']_0}{[A]_0} \quad (2-116b)$$

$$p_A = r_1 p_B + r_2 p_{B'} \quad (2-116c)$$

to describe the relative amounts and extents of reaction of the three reactant groups and reformulate Eqs. 2-103 and 2-110 as

$$w_A^o = (p_B r_1 w_B^i + p_{B'} r_2 w_{B'}^i) \quad (2-117)$$

$$U = 2w_A^i = \frac{2M_o + (p_B r_1 M_o + p_{B'} r_2 M_o)}{1 - (p_B^2 r_1 + p_{B'}^2 r_2)/2} \quad (2-118)$$

The expressions for  $\overline{M}_w$ ,  $\overline{M}_n$ , and PDI are complicated but can be solved numerically [Ozizmir and Odian, 1990]. When B and B' groups together are in excess over A groups ( $r_1 + r_2 > 1$ ) and the reactivities of B and B' are the same ( $s = 1$ ), PDI is very slightly decreased at all conversions in comparison to the stoichiometric case ( $r_1 + r_2 = 1$ ). The final PDI is 1.98. For  $s > 1$  (B' more reactive than B), PDI is initially decreased but increases with conversion and the final PDI is above 2. The trends are more exaggerated when B' is in excess over B and less exaggerated when B is in excess over B'. For example, for the case  $r_1 + r_2 = 1.25$ ,  $s = 20$ , the final PDI is 2.63, 6.50, and 2.16, respectively, when  $r_1/r_2$  is 1, 3, and  $\frac{1}{3}$ . When A groups are in excess over B and B', PDI is very slightly decreased at all conversions in comparison to the stoichiometric case. The final PDI is 1.98 independent of  $s$ ,  $r_1/r_2$ , and  $(r_1 + r_2)$ .

Nonstoichiometric amounts of reactants decrease PDI at all conversions for A—A + B—B' polymerizations [Gandi and Babu, 1979, 1980]. The decrease in PDI is greater the larger the difference in the reactivities of B and B' groups when B—B' is in excess over A—A. The decrease in PDI is independent of the difference in reactivities of B and B' when A—A is in excess. The trend is the same with A—A in excess when B and B' have the same initial reactivity but the reactivity of each group changes on reaction of the other. However, a different trend is seen when B—B' is in excess. PDI increases with a limiting value at complete conversion of 2 or greater than 2 depending on whether the difference in reactivity of B and B' is less than or greater than 2.

## 2-8 PROCESS CONDITIONS

### 2-8a Physical Nature of Polymerization Systems

Several considerations are common to all processes for step polymerizations in order to achieve high molecular weights. One needs to employ a reaction with an absence or at least a minimum of side reactions, which would limit high conversions. Polymerizations are carried out at high concentrations to minimize cyclization and maximize the reaction rate. High-purity reactants in stoichiometric or near-stoichiometric amounts are required. The molecular weight is controlled by the presence of controlled amounts of monofunctional reagents or an excess of one of the bifunctional reagents. Equilibrium considerations are also of prime importance. Since many step polymerizations are equilibrium reactions, appropriate means must be employed to displace the equilibrium in the direction of the polymer product. Distillation of water or other small molecule products from the reaction mixture by suitable reaction temperatures and reduced pressures are often employed for this purpose.

Table 2-8 shows values of some kinetic and thermodynamic characteristics of typical step polymerizations [Bekhli et al., 1967; Chelnokova et al., 1949; Fukumoto, 1956; Hamann et al., 1968; Malhotra and Avinash, 1975, 1976; Ravens and Ward, 1961; Saunders and Dobinson, 1976; Stevenson, 1969; Ueberreiter and Engel, 1977]. These data have implications on the temperature at which polymerization is carried out. Most step polymerizations

TABLE 2-8 Values of Reaction Parameters in Typical Polymerizations

| Reactants <sup>a</sup>                                                                                                           | <i>T</i><br>(°C) | <i>k</i> × 10 <sup>3</sup><br>(L mol <sup>-1</sup> s <sup>-1</sup> ) | <i>E<sub>a</sub></i><br>(kJ mol <sup>-1</sup> ) | Δ <i>H</i><br>(kJ mol <sup>-1</sup> ) |
|----------------------------------------------------------------------------------------------------------------------------------|------------------|----------------------------------------------------------------------|-------------------------------------------------|---------------------------------------|
| <b>Polyester</b>                                                                                                                 |                  |                                                                      |                                                 |                                       |
| HO(CH <sub>2</sub> ) <sub>10</sub> OH + HOOC(CH <sub>2</sub> ) <sub>4</sub> COOH                                                 | 161              | 7.5 × 10 <sup>-2</sup>                                               | 59.4                                            |                                       |
| HO(CH <sub>2</sub> ) <sub>10</sub> OH + HOOC(CH <sub>2</sub> ) <sub>4</sub> COOH <sup>c</sup>                                    | 161              | 1.6                                                                  |                                                 |                                       |
| HOCH <sub>2</sub> CH <sub>2</sub> OH + <i>p</i> -HOOC-φ-COOH                                                                     | 150              | —                                                                    |                                                 | -10.9                                 |
| HO(CH <sub>2</sub> ) <sub>6</sub> OH + ClOC(CH <sub>2</sub> ) <sub>8</sub> COCl                                                  | 58.8             | 2.9                                                                  | 41                                              |                                       |
| <i>p</i> -HOCH <sub>2</sub> CH <sub>2</sub> OOCC-φ-COOCH <sub>2</sub> CH <sub>2</sub> OH                                         | 275              | 0.5                                                                  | 188                                             |                                       |
| <i>p</i> -HOCH <sub>2</sub> CH <sub>2</sub> OOCC-φ-COOCH <sub>2</sub> CH <sub>2</sub> OH <sup>d</sup>                            | 275              | 10                                                                   | 58.6                                            |                                       |
| <b>Polyamide</b>                                                                                                                 |                  |                                                                      |                                                 |                                       |
| H <sub>2</sub> N(CH <sub>2</sub> ) <sub>6</sub> NH <sub>2</sub> + HOOC(CH <sub>2</sub> ) <sub>8</sub> COOH                       | 185              | 1.0                                                                  | 100.4                                           |                                       |
| Piperazine + <i>p</i> -Cl—CO—φ—CO—Cl                                                                                             |                  | 10 <sup>7</sup> —10 <sup>8</sup>                                     |                                                 |                                       |
| H <sub>2</sub> N(CH <sub>2</sub> ) <sub>5</sub> COOH                                                                             | 235              |                                                                      |                                                 | -24                                   |
| <b>Polyurethane</b>                                                                                                              |                  |                                                                      |                                                 |                                       |
| <i>m</i> -OCN—φ—NCO + HOCH <sub>2</sub> CH <sub>2</sub> OCO(CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>2</sub> CH <sub>2</sub> OH | 60               | 0.40 <sup>e</sup>                                                    | 31.4                                            |                                       |
| <i>m</i> -OCN—φ—NCO + HOCH <sub>2</sub> CH <sub>2</sub> OCO(CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>2</sub> CH <sub>2</sub> OH | 60               | 0.23 <sup>f</sup>                                                    | 35.0                                            |                                       |
| <b>Phenol-formaldehyde polymer</b>                                                                                               |                  |                                                                      |                                                 |                                       |
| φ—OH + H <sub>2</sub> CO <sup>c</sup>                                                                                            | 75               | 1.1 <sup>g</sup>                                                     | 77.4                                            |                                       |
| φ—OH + H <sub>2</sub> CO <sup>h</sup>                                                                                            | 75               | 0.048 <sup>g</sup>                                                   | 76.6                                            |                                       |

<sup>a</sup>Uncatalyzed unless otherwise noted.<sup>b</sup>1 cal = 4.184 J.<sup>c</sup>Acid-catalyzed.<sup>d</sup>Catalyzed by Sb<sub>2</sub>O<sub>3</sub>.<sup>e</sup>*k*<sub>1</sub> value.<sup>f</sup>*k*<sub>2</sub> value.<sup>g</sup>Average *k* for all functional groups.<sup>h</sup>Base-catalyzed.

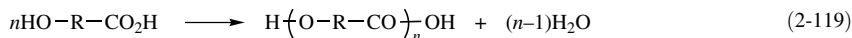
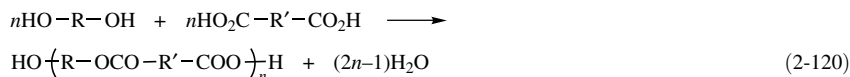
proceed at relatively slow rates at ordinary temperatures. High temperatures in the range of 150–200°C and higher are frequently used to obtain reasonable polymerization rates. Table 2-8 shows that the rate constants are not large even at these temperatures. Typical rate constants are of the order of  $10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ . There are a few exceptions of step polymerizations with significantly larger  $k$  values, for example, the polymerization reaction between acid halides and alcohols. The need to use higher temperatures can present several problems, including loss of one or the other reactant by degradation or volatilization. Oxidative degradation of polymer is also a potential problem in some cases. The use of an inert atmosphere ( $\text{N}_2$ ,  $\text{CO}_2$ ) can minimize oxidative degradation.

*Bulk or mass polymerizations* is the simplest process for step polymerizations, since it involves only the reactants and whatever catalyst, if any, which is required [Menikheim, 1988]. There is a minimum of potentialities for contamination, and product separation is simple. Bulk polymerization is particularly well suited for step polymerization because high-molecular-weight polymer is not produced until the very last stages of reaction. This means that the viscosity is relatively low throughout most of the course of the polymerization and mixing of the reaction mixture is not overly difficult. Thermal control is also relatively easy, since the typically reaction has both a modest activation energy  $E_a$  and enthalpy of polymerization  $\Delta H$ . Although some step polymerizations have moderately high activation energies, for example,  $100.4 \text{ kJ mol}^{-1}$  for the polymerization of sebacic acid and hexamethylene diamine (Table 2-8), the  $\Delta H$  is still only modestly exothermic. The exact opposite is the case for chain polymerizations, which are generally highly exothermic with high activation energies and where the viscosity increases much more rapidly. Thermal control and mixing present much greater problems in chain polymerizations.

Bulk polymerization is widely used for step polymerizations. Many polymerizations, however, are carried out in *solution* with a solvent present to solubilize the reactants, or to allow higher reaction temperatures to be employed, or as a convenience in moderating the reaction and acting as a carrier.

## 2-8b Different Reactant Systems

For many step polymerizations there are different combinations of reactants that can be employed to produce the same type of polymer (Table 1-1). Thus the polymerization of a hydroxy acid yields a polymer very similar to (but not the same as) that obtained by reacting a diol and diacid:

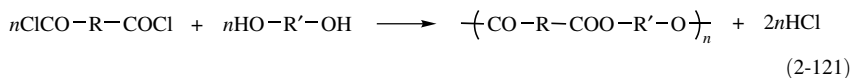
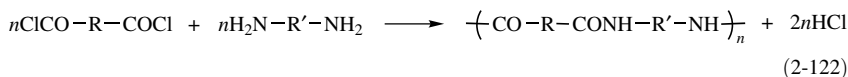


On the other hand, it is apparent that there are different reactant systems that can yield the exact same polymer. Thus the use of the diacid chloride or anhydride instead of the diacid in Eq. 2-120 would give exactly the same polymer product. The organic chemical aspects of the synthesis of various different polymers by different step polymerization processes have been discussed [Elias, 1984; Lenz, 1967; Morgan, 1965]. Whether one particular reaction or another is employed to produce a specific polymer depends on several factors. These include the availability, ease of purification, and properties (both chemical and physical) of the different reactants and whether one or another reaction is more devoid of destructive side reactions.

The ability to obtain high-molecular-weight polymer from a reaction depends on whether the equilibrium is favorable. If the equilibrium is unfavorable as it is in many instances, success depends on the ease with which the polymerization can be driven close to completion. The need for and the ease of obtaining and maintaining stoichiometry in a polymerization is an important consideration. The various requirements for producing a high polymer may be resolved in quite different ways for different polymers. One must completely understand each type of polymerization reaction so as to appropriately meet the stringent requirements for the synthesis of high-molecular-weight polymer. Various step polymerizations are described below and serve to illustrate how the characteristics of a polymerization reaction are controlled so as to obtain high polymer.

## 2-8c Interfacial Polymerization

Many of the polymers that are produced by the usual high-temperature reactions could be produced at lower temperatures by using the faster Schotten–Baumann reactions of acid chlorides. Thus polyesters and polyamides could be produced by replacing the diacid or diester reactant by the corresponding diacyl chloride



### 2-8c-1 Description of Process

The rate constants for these reactions are orders of magnitude greater than those for the corresponding reactions of the diacid or diester reactants (Table 2-8). The use of such reactants in a novel low-temperature polymerization technique called *interfacial polymerization* has been extensively studied [Morgan and Kwolek, 1959a,b; Nikonov and Savinov, 1977]. Temperatures in the range 0–50°C are usually employed. Polymerization of two reactants is carried out at the interface between two liquid phases, each containing one of the reactants (Fig. 2-11). Polyamidation is performed at room temperature by placing an aqueous solution of the diamine on top of an organic phase containing the acid chloride. The reactants diffuse to and undergo polymerization at the interface. The polymer product precipitates and is continuously withdrawn in the form of a continuous film or filament if it has sufficient mechanical strength. Mechanically weak polymers that cannot be removed impede the transport of reactants to the reaction site and the polymerization rate decreases with time. The polymerization rate is usually diffusion-controlled, since the rates of diffusion of reactants to the interface are slower than the rate of reaction of the two functional groups. (This may not be the situation when reactions with small rate constants are employed.)

Interfacial polymerization is mechanistically different from the usual step polymerization in that the monomers diffusing to the interface will react only with polymer chain ends. The reaction rates are so high that diacid chloride and diamine monomer molecules will react with the growing polymer chain ends before they can penetrate through the polymer film to start the growth of new chains. There is thus a strong tendency to produce higher-molecular-weight polymer in the interfacial process compared to the usual processes. Also, interfacial polymerization does not require overall bulk stoichiometry of the reactants in the two phases. Stoichiometry automatically exists at the interface where polymerization proceeds. There is always a supply of both reactants at the interface due to diffusion from the

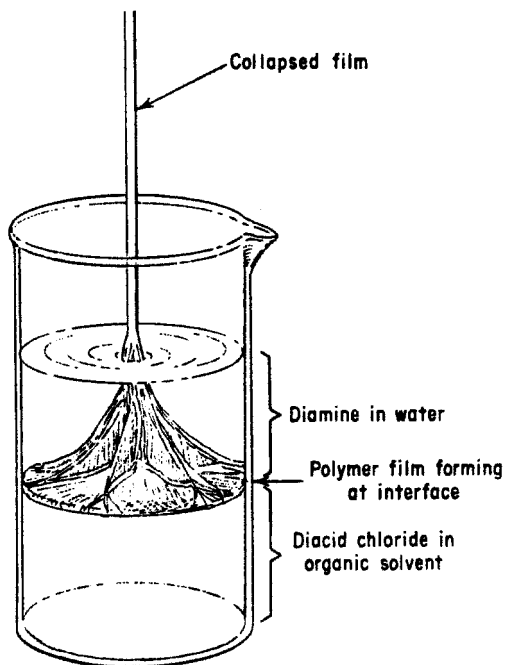


**Fig. 2-11** Interfacial polymerization; removal of polymer film from the interface. From Morgan and Kwolek [1959 a,b] (by permission of Division of Chemical Education, American Chemical Society, Washington, DC and Wiley-Interscience, New York); an original photograph, from which this figure was drawn, was kindly supplied by Dr. P. W. Morgan.

organic and aqueous phases. Furthermore, high-molecular-weight polymer is formed at the interface regardless of the overall percent conversion based on the bulk amounts of the two reactants. The overall percent conversion can be increased by employing a stirred system as a means of increasing the total area of reacting interface.

Several reaction parameters must be controlled in order for interfacial polymerization to proceed successfully. An inorganic base must be present in the aqueous phase to neutralize the by-product hydrogen chloride. If it were not neutralized the hydrogen chloride would tie up the diamine as its unreactive amine hydrochloride salt leading to greatly lowered reaction rates. The acid chloride may undergo hydrolysis to the unreactive acid at high concentrations of the inorganic base or at low polymerization rates. Hydrolysis not only decreases the polymerization rate but also greatly limits the polymer molecular weight, since it converts the diacid chloride into the diacid, which is unreactive at the temperatures employed in interfacial polymerization. The slower the polymerization rate, the greater the problem of hydrolysis as the acid chloride will have more time to diffuse through the interface and into the water layer. Thus acid hydrolysis prevents the use of the interfacial technique for the synthesis of polyesters from diols, since the reaction is relatively slow ( $k \sim 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ ). The reaction of diacid chlorides and diamines is so fast ( $k \sim 10^4\text{--}10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ ) that hydrolysis is usually completely absent.

The choice of the organic solvent is very important in controlling the polymer molecular weight, since it appears that the polymerization actually occurs on the organic solvent side of the interface in most systems. The reason for this is the greater tendency of the diamine to

diffuse into the organic solvent compared to the diffusion of diacid chloride into the aqueous side of the interface. (For some systems, e.g., the reaction of the disodium salt of a dihydric phenol with a diacid chloride, the exact opposite is the case and polymerization occurs on the aqueous side of the interface.) An organic solvent that precipitates the high-molecular-weight polymer but not the low-molecular-weight fractions is desirable. Premature precipitation of the polymer will prevent the production of the desired high-molecular-weight product. Thus, for example, xylene and carbon tetrachloride are precipitants for all molecular weights of poly (hexamethylene sebacate), while chloroform is a precipitant only for the high-molecular-weight polymer. Interfacial polymerization with the former organic solvents would yield only low-molecular-weight polymer. The molecular weight distributions observed in interfacial polymerizations are usually quite different from the most probable distribution [Arai et al., 1985; Korshak, 1966; Morgan, 1965]. Most interfacial polymerizations yield distributions broader than the most probable distribution, but narrower distributions have also been observed. The differences are probably due to fractionation when the polymer undergoes precipitation. The effect is dependent on the organic solvent used and the solubility characteristics of the polymer.

The organic solvent can also affect the polymerization by affecting the diffusion characteristics of the reaction system. A solvent that swells the precipitated polymer is desirable to maximize the diffusion of reactants through it to the reaction site. However, the swelling should not decrease the mechanical strength of the polymer below the level that allows it to be continuously removed from the interface. It has been found that the optimum molar ratio of the two reactants in terms of producing the highest yield and/or highest molecular weight is not always 1 : 1 and often varies with the organic solvent. The lower the tendency of the water-soluble reactant to diffuse into the organic phase, the greater must be its concentration relative to the other reactant's concentration. The optimum ratio of concentrations of the two reactants is that which results in approximately equalizing the rates of diffusion of the two reactants to the interface.

### 2-8c-2 Utility

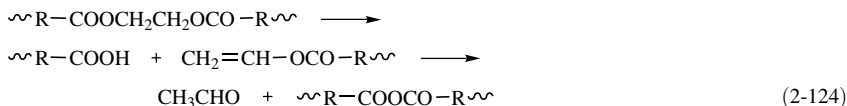
The interfacial technique has several advantages. Bulk stoichiometry is not needed to produce high-molecular-weight polymers and fast reactions are used. The low temperatures allow the synthesis of polymers that may be unstable at the high temperatures required in the typical step polymerization. The interfacial technique has been extended to many different polymerizations, including the formation of polyamides, polyesters, polyurethanes, polysulfonamides, polycarbonates, and polyureas. However, there are disadvantages to the process, which have limited its commercial utility. These include the high cost of acid chloride reactants and the large amounts of solvents that must be used and recovered. Commercial utilization has been limited to some polycarbonates, aliphatic polysulfides, and aromatic polyamides.

### 2-8d Polyesters

Various combinations of reactant(s) and process conditions are potentially available to synthesize polyesters [Fakirov, 2002; Goodman, 1988]. Polyesters can be produced by direct esterification of a diacid with a diol (Eq. 2-120) or self-condensation of a hydroxy carboxylic acid (Eq. 2-119). Since polyesterification, like many step polymerizations, is an equilibrium reaction, water must be continuously removed to achieve high conversions and high molecular weights. Control of the reaction temperature is important to minimize side reactions such as dehydration of the diol to form diethylene glycol



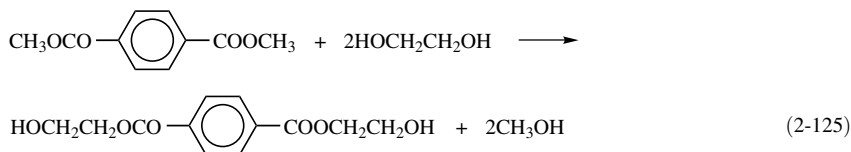
and  $\beta$ -scission of the polyester to form acid and alkene end groups that subsequently react to form an anhydride plus acetaldehyde



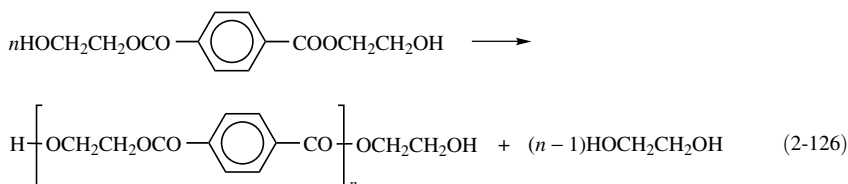
Other reported side reactions include dehydration between alcohol end groups, decarboxylation of diacid monomer, dehydration between carboxyl end groups, and scission and polymerization of the alkene end groups formed in Eq. 2-124. Side reactions directly interfere with the polymerization by altering the stoichiometric ratio of the reacting functional groups, and this affects the polymer molecular weight. Additionally, side reactions can have deleterious effects on polymer properties. For example, diethylene glycol formed by dehydration of ethylene glycol (Eq. 2-123) takes part in the polymerization. For poly(ethylene terephthalate), the  $T_m$  is decreased by the introduction of diethylene glycol units in place of ethylene glycol units in the polymer chain. The presence of acetaldehyde as an impurity causes problems when poly(ethylene terephthalate) is used to produce food and beverage containers. Acetaldehyde also results in discoloration in the final polymer product, due to the formation of aldol-type by-products. The production of food-grade polymers requires the use of purer reactants than those to be used for applications in which the polymers do not contact foodstuffs.

The carboxyl functional groups for synthesizing polyesters can be supplied by using diacids, acid anhydrides, diacid chlorides, or dimethyl esters. The cost and purity of the different reactants is important as are the reaction conditions required. Direct reactions of diacids or anhydrides with diols are often avoided because of the high temperatures required to completely eliminate water. However, these reactions are used to produce low-molecular-weight and crosslinked polyesters based on phthalic and maleic anhydrides (Sec. 2-12a). Diacid chlorides have been used with dihydric phenols to produce polycarbonates (Sec. 2-8e). Ester interchange, typically using a dimethyl ester, has often been used to advantage instead of direct esterification with the diacid or anhydride because the reaction is fast and the dimethyl ester is often more easily purified and has better solubility characteristics. Various weak bases such as the oxides and acetates of manganese, antimony, and zinc are used to catalyze the polymerization [Jabarin, 1996].

The most important commercial polyester is poly(ethylene terephthalate), often referred to as PET. The IUPAC name is poly(oxyethyleneoxyterephthaloyl). Two processes are used for the synthesis of PET, one based on dimethyl terephthalate (DMT) and the other on terephthalic acid (TA). The DMT process was the first to be commercialized because DMT was available in the required purity, but TA was not. That is no longer the case, pure TA is available, and both processes are used. The DMT process is a two-stage ester interchange process between DMT and ethylene glycol. The first stage is an ester interchange to produce bis(2-hydroxyethyl)terephthalate along with small amounts of larger-sized oligomers. The reactants are heated at temperatures increasing from 150 to 210°C and the methanol is continuously distilled off.



In the second-stage the temperature is raised to 270–280°C and polymerization proceeds with the removal of ethylene glycol being facilitated by using a partial vacuum of 0.5–1 torr (66–133 Pa). The first stage of the polymerization is a solution polymerization. The second stage is a melt polymerization since the reaction temperature is above the crystalline melting temperature of the polymer. Figure 2-12 illustrates a commercial process for this polymerization [Ellwood, 1967].



The properties and usefulness of the final polymer depends on controlling its structure by appropriate control of process variables during polymerization and subsequent processing into product. Temperature control and the choice of catalysts are critical in minimizing deleterious side reactions. A dual catalyst system is used in PET synthesis. The first-stage catalyst is an acetate of manganese, zinc, calcium, cobalt, or magnesium. Antimony(III) oxide is usually added as the second-stage catalyst; it is ineffective alone for the first-stage reaction. The first-stage catalyst is often inactivated by the addition of an alkyl or aryl phosphite or phosphate.

The production of high-molecular-weight polymer requires the complete removal of ethylene glycol because of the unfavorable equilibrium that would otherwise exist. If ethylene glycol were not removed, equilibrium would be established at too low an extent of reaction (approximately  $p < 0.7$ ) and the product would be of very low molecular weight (Fig. 2-8). A unique feature of the ester interchange process is the absence of the need for stoichiometric balance of the two functional groups at the start of the polymerization. Stoichiometric balance is inherently achieved at the end of the second stage of the process. In fact, an excess of ethylene glycol is initially used to increase the rate of formation of bis(2-hydroxyethyl)terephthalate.

The TA process is a modification of the DMT process. Terephthalic acid and an excess of ethylene glycol (in the form of a paste) are used to produce the bis(2-hydroxyethyl)terephthalate, which is then polymerized as described above. The TA process has grown to exceed the DMT process.

Poly(ethylene terephthalate), known by the trade names *Mylar*, *Dacron*, and *Terylene*, is a very high volume polymer—the United States production of PET fiber and plastic was over 9.5 billion pounds in 2001. The global production is about 6 times that of the United States. These figures are especially impressive when we note that PET was not introduced as a commercial product until 1953. Because of its high crystalline melting temperature (270°C) and stiff polymer chains, PET has good mechanical strength, toughness, and fatigue resistance up to 150–175°C as well as good chemical, hydrolytic, and solvent resistance. Fiber applications account for about 45% of the total PET production. Poly(ethylene terephthalate) fiber has outstanding crease resistance, has good abrasion resistance, can be treated with crosslinking resins to impart permanent-press (wash-and-wear) properties, and can be blended with cotton and other cellulosic fibers to give better feel and moisture permeation. Fiber applications include wearing apparel, curtain, upholstery, thread, tire cord, and fabrics for industrial filtration. More than 5 billion pounds of PET per year find applications as plastics, mostly for

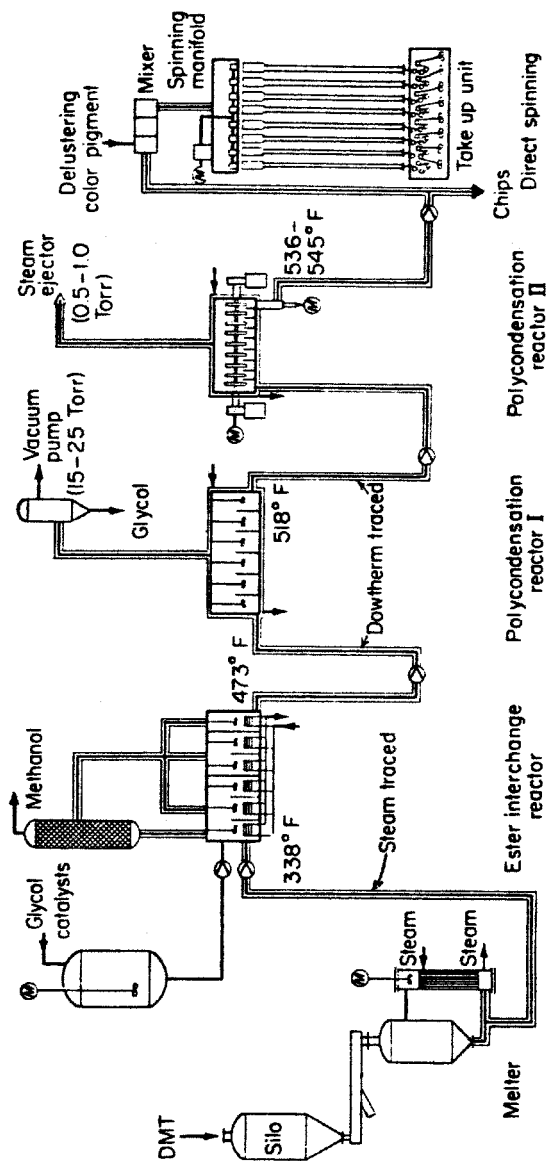


Fig. 2-12 Schematic representation of industrial process for synthesis of poly(ethylene terephthalate). After Ellwood [1967] (by permission of American Chemical Society, Washington, DC).

blow-molded bottles for soft drinks, beers, spirits, and other food products—a result of the outstanding barrier properties of PET. Film applications include photographic, magnetic, and X-ray films or tapes, metallized films, and electrical insulation. PET also finds use as an *engineering plastic* where it replaces steel, aluminum, and other metals in the manufacture of precision moldings for electrical and electronic devices, domestic and office appliances, and automobile parts. In these engineering applications PET is often reinforced with glass fiber or compounded with silicones, graphite, or Teflon to improve strength and rigidity. The glass reinforced grades of PET are rated for continuous use at temperatures up to 140–155°C.

The use of PET as an engineering plastic has been somewhat limited by its relatively low rate of crystallization. Thus results in increased processing costs due to long mold recycle times. (The addition of nucleating agents such as talc, MgO, calcium silicate, zinc stearate, or plasticizers such as long-chain fatty esters helps overcome this problem.) Poly(butylene terephthalate) [IUPAC: poly(oxybutane-1,4-diylxyterephthaloyl)] (PBT), produced by substituting 1,4-butanediol for ethylene glycol, crystallizes much faster than PET, and competes with PET in engineering plastics applications. Its maximum use temperature is 120–140°C, slightly lower than that of PET.

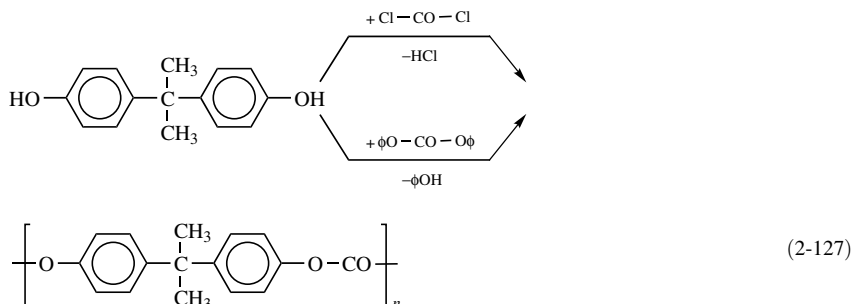
Poly(ethylene 2,6-naphthalate) [IUPAC: poly(oxyethyleneoxycarbonylnaphthalene-2,6-diylcarbonyl)] (PEN) is produced from ethylene glycol and 2,6-naphthalenedicarboxylic acid (2,6-naphthalic acid). The rigidity of the naphthalene ring results in increased strength, heat stability, and barrier properties compared to PET. Among the anticipated applications are specialty photographic and electronic films, and food and beverage bottles that require filling at higher temperatures.

Other polyesters of commercial importance are polycarbonates, liquid crystal polyesters, unsaturated polyesters, and copolymers (Secs. 2-8e, 2-14g, 2-12, 2-13).

Completely aliphatic polyesters, made from aliphatic diacid and aliphatic diol components, are not of major industrial importance because of their low melting temperatures and poor hydrolytic stability. (Low-molecular-weight aliphatic polyesters are used as plasticizers and prepolymer reactants in the synthesis of polyurethanes; see Secs. 2-12e, 2-13c-2).

## 2-8e Polycarbonates

Polycarbonates are polyesters of carbonic acid. The most important commercial polycarbonate is that based on 2,2'-bis(4-hydroxyphenyl)propane (*bisphenol A*) [Freitag et al., 1988; Sehanobish et al., 1996]. It has been synthesized by the reaction of the dihydric phenol with phosgene or by ester interchange with diphenyl carbonate:



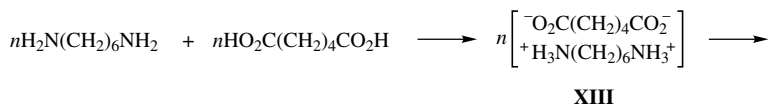
Polymerization by the ester interchange route is carried out as a two-stage melt polymerization very similar to that described for poly(ethylene terephthalate). However, most industrial processes involve the phosgene reaction in a stirred interfacial polymerization. Overall economics and easier control of polymer molecular weight favor the phosgene process over ester interchange. Organic solvents such as chlorobenzene, 1,2-dichloroethane, tetrahydrofuran (THF), anisole, and dioxane are used. The bisphenol A is usually dissolved in aqueous alkali to form the phenolate salt and then the organic solvent added followed by phosgene. The organic solvent prevents the loss of phosgene by hydrolysis and precipitation of the polymer before it has reached the desired molecular weight. Reaction temperatures in the range 0–50°C are used. Phase-transfer catalysts, such as quaternary ammonium and sulfonium salts and crown ethers, may be added to enhance the transfer of the phenolate salt across the interfacial boundary into the organic phase. The polymerization is usually a two-stage reaction. Oligomers are formed in the first stage. Tertiary amines are added in the second stage to catalyze the further reaction to high-molecular-weight polymer. (An alternate route to polycarbonates, the ring-opening polymerization of cyclic polycarbonate oligomers, has some potential advantages over the step polymerization route; see Sec. 7-5c.)

The IUPAC name of the polycarbonate based on bisphenol A is poly(oxycarbonyloxy-1,4-phenylenedimethylmethylen-1,4-phenylene) (trade names: *Lexan*, *Merlon*, *Calibre*); it is usually referred to as *polycarbonate* or PC. Although it can be crystallized ( $T_m = 270^\circ\text{C}$ ), most polycarbonates are amorphous ( $T_g = 150^\circ\text{C}$ ). Chain stiffening due to a combination of the benzene rings and bulky tetrasubstituted carbons in the polymer chain and the high  $T_g$  result in a good combination of mechanical properties over a considerable temperature range (15–130°C). PC has excellent resistance to acids and oxidants, better than PET, but is somewhat less resistant to bases compared to PET. Polycarbonate is comparable to PET in resistance to organic solvents at ambient temperature. At higher temperatures, PC is more resistant to aliphatic and aromatic solvents but less resistant to polar organic solvents.

Although its upper temperature limit (120°C for reinforced grades) and resistance to some solvents are low compared to other engineering plastics, polycarbonate finds many uses because of its exceptional transparency and impact resistance (toughness) as well as good dimensional and creep resistances. Applications include compact disks, glazing (windows, doors, face shields, sunglasses, aircraft interiors), automotive (instrument panels and components, exterior panels, wheel covers), medical (components for dialysis, blood collection, and surgical devices), and other uses (power tool and appliance housings, refrigerator interiors, safety helmets, electrical connectors). The United States production of polycarbonates was more than 800 million pounds in 2001; the global production was about 3 billion pounds.

## 2-8f Polyamides

The synthesis of polyamides follows a different route from that of polyesters. Although several different polymerization reactions are possible, polyamides are usually produced either by direct amidation of a diacid with a diamine or the self-amidation of an amino acid. The polymerization of amino acids is not as useful because of a greater tendency toward cyclization (Sec. 2-5b). Ring-opening polymerization of lactams is also employed to synthesize polyamides (Chap. 7). Poly(hexamethylene adipamide) [IUPAC: poly(iminohexanedioyliminohexane-1,6-diyl) or poly(iminoadipoyliminohexane-1,6-diyl)], also referred to as *nylon 6/6*, is synthesized from hexamethylene diamine and adipic acid [Zimmerman, 1988; Zimmerman and Kohan, 2001]. A stoichiometric balance of amine and carboxyl groups is readily obtained by the preliminary formation of a 1 : 1 ammonium salt (**XIII**) in aqueous solution at a concentration of 50%. The salt is often referred to as a *nylon salt*. Stoichiometric



balance can be controlled by adjusting the pH of the solution by appropriate addition of either diamine or diacid. The aqueous salt solution is concentrated to a slurry of approximately 60% or higher salt content by heating above 100°C. Polymerization is carried out by raising the temperature to about 210°C. Reaction proceeds under a steam pressure of ~250 psi (1.7 MPa), which effectively excludes oxygen. The pressure also prevents salt precipitation and subsequent polymerization on heat-transfer surfaces.

Unlike polyester synthesis, polyamidation is carried out without an external strong acid, since the reaction rate is sufficiently high without it. Further, amidation may not be an acid-catalyzed reaction. The equilibrium for polyamidation is much more favorable than that for the synthesis of polyesters. For this reason the amidation is carried out without concern for shifting the equilibrium until the last stages of reaction. Steam is released to maintain the pressure at about 1.7 MPa, while the temperature is continuously increased to 275°C. When 275°C is reached the pressure is slowly reduced to atmospheric pressure and heating continued to drive the equilibrium to the right. The later stage of the reaction is a melt polymerization since the reaction temperature is above the  $T_m$ . Figure 2-13 represents a commercial process for nylon 6/6 synthesis [Taylor, 1944].

Molecular weight control and stabilization are accomplished by addition of a calculated amount of a monofunctional acid such as acetic acid. Diamine loss during polymerization is unavoidable because of its volatility. The loss must be quantitatively taken into account by careful control of process conditions and initial charges of reactants.

The United States production of polyamides was more than 4 billion pounds in 2001. About two-thirds of that is nylon 6/6; the second most important polyamide is nylon 6, which is produced by the ring-opening polymerization of  $\epsilon$ -caprolactam (Sec. 7-3). Poly(hexamethylene adipamide) is an excellent fiber and engineering plastic with a high-crystalline melting temperature (265°C). Nylon 6/6 is moderately crystalline (~50%) as normally produced, but this is further increased for fiber applications by orientation via mechanical stretching. It has a very good combination of high strength, flexibility, toughness, abrasion resistance, dyeability, low coefficient of friction (self-lubricating), low creep, and resistance to solvents, oils, bases, fungi, and body fluids. The main limitation is its moisture pickup with resulting changes in dimensional and mechanical properties. Polyamides (PAs) are more resistant to alkaline hydrolysis than polyesters but not as resistant to acid hydrolysis. Polyamides have better resistance to a range of organic solvents compared to PET and PC.

More than 60% of nylon production is used in fiber applications—wearing apparel, carpets, upholstery, tire reinforcements, ropes, seatbelts, parachutes, fishing nets, and substrates for industrial coated fabrics. Nylon fiber has been losing market share to PET fiber for apparel applications since the latter is better for producing wrinkle-resistant apparel. However, nylon is still the fiber of choice for hosiery, stretch fabrics, and women's undergarments. Nylons are the largest volume engineering plastic—more than 500 million pounds per year in the United States. Fiber and mineral reinforcements are widely used for engineering plastic uses. The upper temperature for continuous use is 65–75°C for unreinforced grades and 100–115°C for glass and mineral reinforced grades. Applications include almost every industry and market—transportation (auto fender extensions, engine fans, brake and power

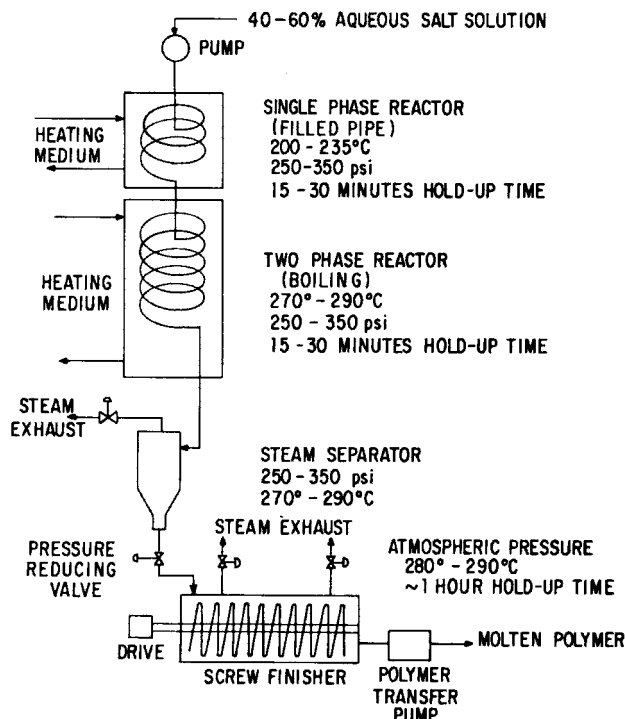


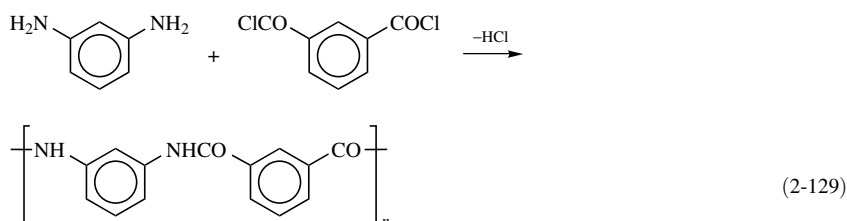
Fig. 2-13 Schematic representation of industrial process for synthesis of poly(hexamethylene adipamide). After Taylor [1944] and Jacobs and Zimmerman [1977] (by permission of Wiley-Interscience, New York).

steering reservoirs, valve covers, lamp housings, roof-rack components, light-duty gears for windshield wipers and speedometers), electrical/electronics (toggle switches, plugs, sockets, antenna-mounting devices, terminal blocks), industrial (self-lubricated gears and bearings, antifriction and snap-fit parts, parts for food and textile-processing equipment, valves, vending machines, pumps), film (meat and cheese packaging, cook-in-pouches, multilayer nylon-polyolefin protective barrier materials for oil and moisture resistance), and consumer (ski boots, racquet frames, kitchen utensils, toys, power tool housings).

Nylons 6/6 and 6 comprise more than 90% of the polyamide market. The two have similar properties but nylon 6 has a lower  $T_m$  (223°C). Small amounts of nylons 6/9, 6/10, 6/12, 11, 12, 12/12, and 4/6 are produced as specialty materials. Those with more methylene groups than nylons 6/6 and 6 have better moisture resistance, dimensional stability, and electrical properties, but the degree of crystallinity,  $T_m$ , and mechanical properties are lower. Specialty nylons made from dimerized fatty acids find applications as hot-melt adhesives, crosslinking agents for epoxy resins, and thermographic inks.

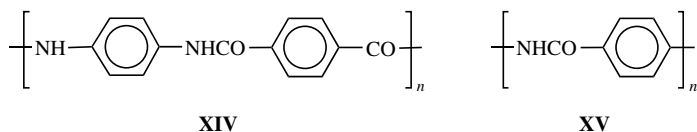
The synthesis of aromatic polyamides (referred to as *aramid* polymers) is difficult to carry out using diacid and diamine reactants because of the lower reactivity of aromatic amines compared to aliphatic amines [Lenk, 1978]. The aromatic ring decreases the electron density of nitrogen through resonance interaction. The elevated temperatures required to achieve polymerization are generally too high, resulting in extensive side reactions that limit polymer molecular weight.

Aromatic polyamides are produced by using the faster reaction of a diamine with a diacid chloride, for example, for poly(*m*-phenylene isophthalamide) or poly(imino-1,3-phenylene-iminoisophthaloyl) (trade name: *Nomex*). The polymerization is carried out in solution at temperatures under 100°C with a tertiary base present to react with the liberated hydrogen chloride. Highly polar aprotic solvents such as dimethylacetamide, 1-methyl-2-pyrrolidinone (NMP), tetramethylurea, and hexamethylphosphoramide have been used to prevent premature precipitation of the growing polyamide chains. This is a significant problem in the synthesis of aromatic polyamides, since the reaction temperature is much lower than for aliphatic polyamides. The presence of LiCl or CaCl<sub>2</sub> promotes solubilization of the polymer, probably by coordination of the metal ion with the amide carbonyl, which decreases the hydrogen-bonding between amide groups [Kwolek and Morgan, 1977]. The resulting polymer solutions from these polymerizations are often used directly to spin fibers.



There have been efforts to form aromatic polyamides directly from diacids at moderate temperatures by using various phosphorus compounds for in situ activation of the carboxyl groups [Arai et al., 1985; Higashi and Kobayashi, 1989; Krigbaum et al., 1985]. A useful agent is diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate, which probably activates the carboxyl group by forming a mixed carboxylic-phosphoric anhydride [Ueda, 1999; Ueda et al., 1991].

Poly(imino-1,4-phenyleneiminoterephthaloyl) (**XIV**) (trade names: *Kevlar*, *Twaron*) is synthesized from the corresponding *para*-substituted diamine and diacid chloride. Poly(iminocarbonyl-1,4-phenylene) (**XV**) (also known as *Kevlar*) is based on *p*-aminobenzoic acid.



The totally aromatic structures of the aramid polymers give them exceptional heat and flame resistance, very high melting points (generally above their decomposition temperature, which are  $\geq 500^\circ\text{C}$ ), ultrahigh strength, and better resistance to solvents, chemicals, and oxidizing agents compared to aliphatic polyamides. *Kevlar* has higher strength and modulus properties compared to *Nomex*. The *para* structure of the former gives a rodlike extended-chain structure that forms liquid crystal solutions. (*Liquid crystal solutions* are solutions in which there is a high degree of ordering of solute molecules; see Sec. 2-14g.) Polymer crystallization from liquid crystal solutions results in a highly oriented, extended-chain morphology in the bulk polymer, resulting in high strength and high modulus.

Aramid polymers are much more expensive than the aliphatic polyamides. The use of aramid polymers is limited to those applications that justify the high cost. The present U.S. market is about 20 million pounds per year. The applications are those where one needs very high flame resistance (clothing for firefighters and welders, welder's protective shield, upholstery and drapes), heat resistance (ironing board covers, insulation film for electrical motors and transformers, aerospace and military), dimensional stability (fire hose, V- and conveyor belts), or strength and modulus (circuit boards, bulletproof vests, fiber optic and power lines, ship mooring ropes, automobile tire cord, puncture-resistant bicycle tires).

## 2-8g Historical Aspects

Wallace Carothers and coworkers at DuPont synthesized aliphatic polyesters in the 1930s [Furukawa, 1998; Hounshell and Smith, 1988]. These had melting points below 100°C, which made them unsuitable for fiber use. Carothers then turned successfully to polyamides, based on the theoretical consideration that amides melt higher than esters. Polyamides were the first synthetic fibers to be produced commercially. The polyester and polyamide research at DuPont had a major impact on all of polymer science. Carothers laid the foundation for much of our understanding of how to synthesize polymeric materials. Out of that work came other discoveries in the late 1930s, including neoprene, an elastomer produced from chloroprene, and Teflon, produced from tetrafluoroethylene. The initial commercial application for nylon 6/6 was women's hosiery, but this was short-lived with the intrusion of World War II. The entire nylon 6/6 production was allocated to the war effort in applications for parachutes, tire cord, sewing thread, and rope. The civilian applications for nylon products burst forth and expanded rapidly after the war.

Carother's work not only secured the future of the DuPont chemical empire but launched the synthetic fiber industry and changed the agricultural patterns of the Southern cotton states. Subsequent to the success of nylon, workers in the United Kingdom in the early 1950s achieved success in producing a polyester fiber by using terephthalate as the acid component. Cotton, no longer King of Fibers, accounts for less than 25% of the U.S. fiber market. Nylon, PET, and rayon (regenerated cellulose) account for the remainder.

## 2-9 MULTICHAIN POLYMERIZATION

### 2-9a Branching

The discussions until this point have been concerned with the polymerization of bifunctional monomers to form *linear polymers*. When one or more monomers with more than two functional groups per molecule are present the resulting polymer will be *branched* instead of linear. With certain monomers *crosslinking* will also take place with the formation of *network structures* in which a branch or branches from one polymer molecule become attached to other molecules. The structures of linear, branched, and crosslinked polymers are compared in Fig. 1-2.

Consider the polymerization of an A—B reactant in the presence of a small amount of a monomer  $A_f$  containing  $f$  functional groups per molecule. The value of  $f$  is termed the *functionality of the monomer*. The product of this polymerization will be a branched polymer in which  $f$  chains are attached to a central branch point (i.e., an  $A_f$  species). For the specific case

of  $f = 3$ , polymerization of A—B in the presence of  $\begin{array}{c} A \\ | \\ A-T-A \\ | \\ A \end{array}$  leads to the structure **XVI**. A



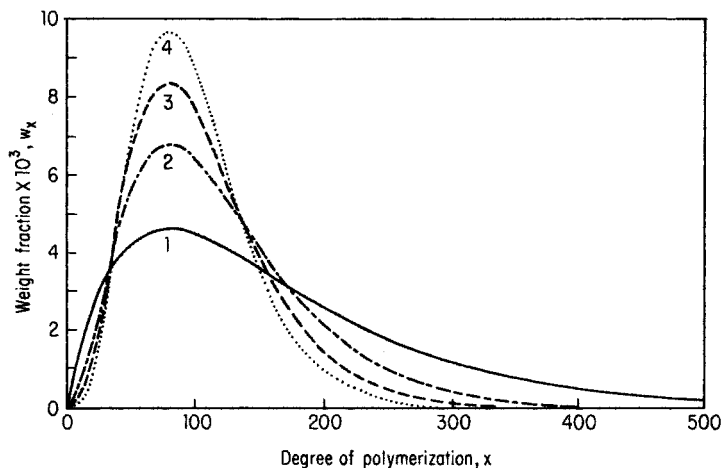


**Fig. 2-14** Weight fraction distribution plot for multichain polymerization. Plot 1,  $f = 1$ ; plot 2,  $f = 2$ ; plot 3  $f = 3$ ; plot 4,  $f = 4$ . After Howard [1961] (by permission of Iliffe Books and Elsevier, London).

which becomes

$$\frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{1}{f} \quad (2-133)$$

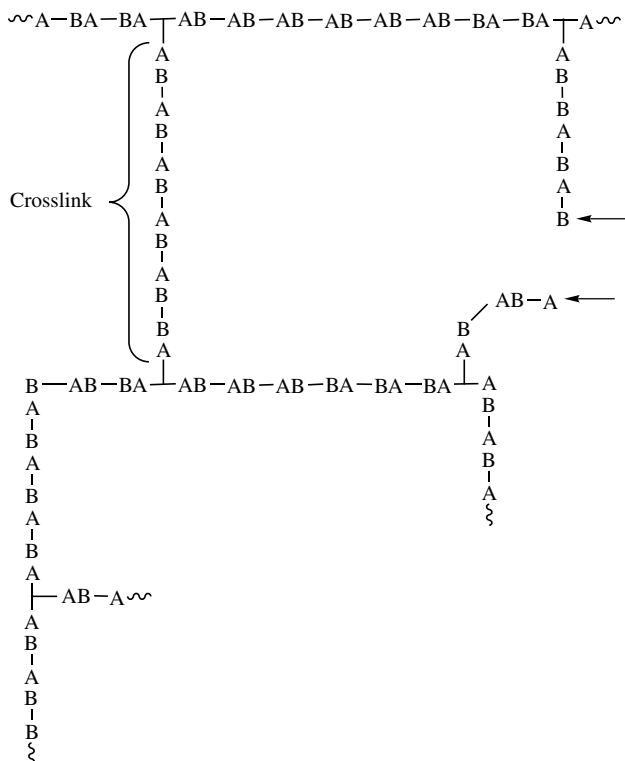
in the limit of  $p = r = 1$ .

The weight distribution (Eq. 2-131) is shown in Fig. 2-14 for several values of  $f$ . The extents of reaction have been adjusted to maintain a constant number-average degree of polymerization of 80 in all four cases. The size distribution becomes progressively narrower with increasing functionality of  $A_f$ . This is also evident from Eq. 2-133, where  $\bar{X}_w/\bar{X}_n$  decreases from 2 for  $f = 1$  to 1.25 for  $f = 4$  (at  $p = 1$ ). Linear polymers are formed for  $f$  values of 1 or 2, while branched polymers are formed when  $f$  is greater than 2. The case of  $f = 1$  corresponds to the type 3 polymerization discussed in Sec. 2-6. The distribution is the exact same as the most probable distribution for linear polymerization (Sec. 2-7). Linear polymerization with  $f = 2$  is of interest in that the distribution is narrower than that for the usual linear polymerization. The linking of two statistically independent A—B type polymer chains into one polymer molecule via an A—A molecule leads to a significantly narrower distribution than in the usual polymerizations of the A—B or A—A plus B—B types.

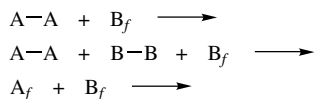
## 2-10 CROSSLINKING

Polymerization of the A—B plus  $A_f$  system (with  $f > 2$ ) in the presence of B—B will lead not only to branching but also to a *crosslinked* polymer structure. Branches from one polymer molecule will be capable of reacting with those of another polymer molecule because of the presence of the B—B reactant. Crosslinking can be pictured as leading to structure **XVII**, in

which two polymer chains have been joined together (crosslinked) by a branch. The branch joining the two chains is referred to as a *crosslink*. A crosslink can be formed whenever there



are two branches (e.g., those indicated in **XVII** by the arrows) that have different functional groups at their ends, that is, one has an A group and the other a B group. Crosslinking will also occur in other polymerizations involving reactants with functionalities greater than two. These include the polymerizations



Crosslinking is distinguished by the occurrence of *gelation* at some point in the polymerization. At this point, termed the *gel point*, one first observes the visible formation of a *gel* or *insoluble polymer fraction*. (The gel point is alternately taken as the point at which the system loses fluidity as measured by the failure of an air bubble to rise in it.) The gel is insoluble in all solvents at elevated temperatures under conditions where polymer degradation does not occur. The gel corresponds to the formation of an infinite network in which polymer molecules have been crosslinked to each other to form a macroscopic molecules. The gel is, in

fact, considered as one molecule. The nongel portion of the polymer remains soluble in solvents and is referred to as *sol*. As the polymerization and gelation proceed beyond the gel point, the amount of gel increases at the expense of the sol as more and more polymer chains in the sol are crosslinked to the gel. There is a dramatic physical change that occurs during the process of gelation. The reaction mixture is transformed into a polymer of infinite viscosity.

The crosslinking reaction is an extremely important one from the commercial standpoint. Crosslinked plastics are increasingly used as engineering materials because of their excellent stability toward elevated temperatures and physical stress. They are dimensionally stable under a wide variety of conditions due to their rigid network structure. Such polymers will not flow when heated and are termed *thermosetting* polymers or simply *thermosets*. More than 10 billion pounds of thermosets are produced annually in the United States. Plastics that soften and flow when heated, that is, uncrosslinked plastics, are called *thermoplastics*. Most of the polymers produced by chain polymerization are thermoplastics. Elastomers are a category of polymers produced by chain polymerization that are crosslinked (Sec. 1-3), but the crosslinking reactions are different from those described here (Sec. 9-2).

In order to control the crosslinking reaction so that it can be used properly, it is important to understand the relationship between gelation and the extent of reaction. Two general approaches have been used to relate the extent of reaction at the gel point to the composition of the polymerization system—based on calculating when  $\bar{X}_n$  and  $\bar{X}_w$ , respectively, reach the limit of infinite size.

## 2-10a Carothers Equation: $\bar{X}_n \rightarrow \infty$

### 2-10a-1 Stoichiometric Amounts of Reactants

Carothers derived a relationship between the extent of reaction at the gel point and the *average functionality*  $f_{\text{avg}}$  of the polymerization system for the case where the two functional groups A and B are present in equivalent amounts [Carothers, 1936]. The derivation follows in a manner similar to that for Eq. 2-78. The average functionality of a mixture of monomers is the average number of functional groups per monomer molecule for all types of monomer molecules. It is defined by

$$f_{\text{avg}} = \frac{\sum N_i f_i}{\sum N_i} \quad (2-134)$$

where  $N_i$  is the number of molecules of monomer  $i$  with functionality  $f_i$ , and the summations are over all the monomers present in the system. Thus for a system consisting of 2 mol of glycerol (a triol) and 3 mol of phthalic acid (a diacid) there is a total of 12 functional groups per five monomer molecules, and  $f_{\text{avg}}$  is  $\frac{12}{5}$  or 2.4. For a system consisting of an equimolar amounts of glycerol, phthalic anhydride, and a monobasic acid, there is a total of six functional groups per three molecules and  $f_{\text{avg}}$  is  $\frac{6}{3}$  or 2.

In a system containing equivalent numbers of A and B groups, the number of monomer molecules present initially is  $N_0$  and the corresponding total number of functional groups is  $N_0 f_{\text{avg}}$ . If  $N$  is the number of molecules after reaction has occurred, then  $2(N_0 - N)$  is the number of functional groups that have reacted. The extent of reaction  $p$  is the fraction of functional groups lost:

$$p = \frac{2(N_0 - N)}{N_0 f_{\text{avg}}} \quad (2-135)$$

while the degree of polymerization is

$$\bar{X}_n = \frac{N_0}{N} \quad (2-136)$$

Combination of Eqs. 2-135 and 2-136 yields

$$\bar{X}_n = \frac{2}{2 - pf_{\text{avg}}} \quad (2-137)$$

which can be rearranged to

$$p = \frac{2}{f_{\text{avg}}} - \frac{2}{\bar{X}_n f_{\text{avg}}} \quad (2-138)$$

Equation 2-138, often referred to as the *Carothers equation*, relates the extent of reaction and degree of polymerization to the average functionality of the system.

An important consequence of Eq. 2-138 is its limiting form at the gel point where the number-average degree of polymerization becomes infinite. The *critical extent of reaction*  $p_c$  at the gel point is given by

$$p_c = \frac{2}{f_{\text{avg}}} \quad (2-139)$$

since the second term of the right side of Eq. 2-138 vanishes. Equation 2-139 can be used to calculate the extent of reaction required to reach the onset of gelation in a mixture of reacting monomers from its average functionality. Thus the glycerol–phthalic acid (2 : 3 molar ratio) system mentioned above has a calculated critical extent of reaction of 0.833.

### 2-10a-2 Extension to Nonstoichiometric Reactant Mixtures

Equations 2-138 and 2-139 apply only to systems containing stoichiometric numbers of the two different functional groups. For nonequivalent numbers of the functional groups, the average functionality calculated from Eq. 2-134 is too high. Thus, consider the extreme example of a mixture of 1 mol of glycerol and 5 mol of phthalic acid. Using Eq. 2-134, one calculates a value of  $\frac{13}{6}$  or 2.17 for  $f_{\text{avg}}$ . This indicates that a high polymer will be obtained. Further, one would predict from Eq. 2-139 that crosslinking will occur at  $p_c = 0.922$ . Both of these conclusions are grossly in error. It is apparent from previous discussions (Sec. 2-6) that the gross stoichiometric imbalance between the A and B functional groups in this system ( $r = 0.3$ ) precludes the formation of any but extremely low-molecular-weight species. The polymerization will stop with the large portion of the acid functional groups being unreacted.

The average functionality of nonstoichiometric mixtures has been deduced [Pinner, 1956] as being equal to twice the total number of functional groups that are not in excess divided by the total number of all molecules present. This simply takes into account the fact that the extent of polymerization (and crosslinking, if it can occur) depends on the deficient reactant. The excess of the other reactant is not useful; in fact, it results in a lowering of the functionality of the system. For the above nonstoichiometric mixture of 1 mol of glycerol and 5 mol of phthalic acid, the  $f_{\text{avg}}$  value is correctly calculated as 6/6 or 1.00. This low value of  $f_{\text{avg}}$  is indicative of the low degree of polymerization that will occur in the system.

In a similar manner the average functionality of nonstoichiometric mixtures containing more than two monomers has been obtained. Consider a ternary mixture of  $N_A$  moles of  $A_{f_A}$ ,  $N_C$  moles of  $A_{f_C}$ , and  $N_B$  moles of  $B_{f_B}$  with functionalities  $f_A$ ,  $f_C$ , and  $f_B$ , respectively. In this system  $A_{f_A}$  and  $A_{f_C}$  contain the same functional groups (i.e., A groups) and the total number of A functional groups is less than the number of B groups (i.e., B groups are in excess). The average functionality in such a system is given by

$$f_{\text{avg}} = \frac{2(N_A f_A + N_C f_C)}{N_A + N_C + N_B} \quad (2-140)$$

or

$$f_{\text{avg}} = \frac{2r f_A f_B f_C}{f_A f_C + r \rho f_A f_B + r(1 - \rho) f_B f_C} \quad (2-141)$$

where

$$r = \frac{N_A f_A + N_C f_C}{N_B f_B} \quad (2-142)$$

$$\rho = \frac{N_C f_C}{N_A f_A + N_C f_C} \quad (2-143)$$

The term  $r$  is the ratio of A groups to B groups and has a value equal to or less than unity.  $r$  is comparable to the previously discussed stoichiometric imbalance. The term  $\rho$  is the fraction of all A functional groups that belong to the reactant with  $f > 2$ .

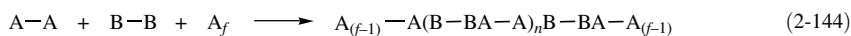
One can easily show by substitution of different values of  $r$ ,  $\rho$ ,  $f_A$ ,  $f_B$ , and  $f_C$  into Eqs. 2-139 through 2-143 that crosslinking is accelerated (i.e.,  $p_c$  decreases) for systems that contain closer to stoichiometric amounts of A and B functional groups ( $r$  closer to 1), systems with larger amounts of polyfunctional reactants ( $\rho$  closer to 1) and systems containing reactants of higher functionality (higher values of  $f_A$ ,  $f_B$ , and  $f_C$ ).

The Carothers equations and Eq. 2-78 overlap but are not equivalent. Recall the brief note in Sec. 2-6b that Eq. 2-78 does not apply to systems containing a monofunctional reactant unless it is present in addition to stoichiometric amounts of bifunctional reactants (either A—A + B—B or A—B). That is, for example, Eq. 2-78 applies to a reaction system of 10 mol each of A—A and B—B plus 1 mol B but does not apply to a system of 10 mol A—A, 9 mol B—B, and 1 mol B. In reality, the two reaction systems yield very nearly the same degree of polymerization at any particular extent of reaction. The Carothers equation yields  $\bar{X}_n$  values of 21.0 and 20.0, respectively, for the two systems at complete conversion. The use of Eq. 2-78 for the second reaction system yields a gross distortion. The value of  $r$  obtained from Eq. 2-80 would be unity (the same as for a perfectly stoichiometric system of 10 mol each of A—A and B—B!) and this leads to a  $\bar{X}_n$  value of infinity at complete conversion. This is correct for the stoichiometric system but clearly is incorrect for the reaction system containing the large amount of monofunctional B reactant. The use of Eq. 2-78 must be limited to situations in which there are stoichiometric amounts of bifunctional reactants (or A—B). Also, Eq. 2-78 is inapplicable to any systems containing a reactant with functionality greater than 2. The Carothers equation, without such limitations, has two general uses. First, it can be used in the form of Eq. 2-137 to calculate the degree of polymerization of a reaction system using the appropriate value of  $f_{\text{avg}}$  (whose calculation depends on whether stoichiometric or nonstoichiometric amounts are present). If one obtains a negative value of  $\bar{X}_n$  in the calculation, it

means that the system is past the gel point at that conversion. Second, the use of Eq. 2-139 allows one to calculate the critical extent of reaction at the gel point. Keep in mind that the extent of reaction calculated from Eq. 2-137 or 2-139 refers to the extent of reaction of the A functional groups (defined as those groups not in excess). The extent of reaction of the B functional groups is  $rp$  or  $rp_c$ .

## 2-10b Statistical Approach to Gelation: $\bar{X}_w \rightarrow \infty$

Flory [1941, 1953] and Stockmayer [1943, 1952, 1953] used a statistical approach to derive an expression for predicting the extent of reaction at the gel point by calculating when  $\bar{X}_w$  approaches infinite size. The statistical approach in its simplest form assumes that the reactivity of all functional groups of the same type is the same and independent of molecular size. It is further assumed that there are no intramolecular reactions between functional groups on the same molecule. (These assumptions are also inherent in the use of Eqs. 2-137 through 2-143). For this derivation the *branching coefficient*  $\alpha$  is defined as the probability that a given functional group of a branch unit at the end of a polymer chain segment leads to another branch unit. For the polymerization of A—A with B—B and  $A_f$  this corresponds to obtaining a chain segment of the type



where  $n$  may have any value from zero to infinity. The multifunctional monomer  $A_f$  is considered a *branch unit*, while the segments between branch units are defined as *chain segments*. The branch units occur on a polymer chain at the branch points (Fig. 1-2). Infinite networks are formed when  $n$  number of chains or chain segments give rise to more than  $n$  chains through branching of some of them. The criterion for gelation in a system containing a reactant of functionality  $f$  is that at least one of the  $(f - 1)$  chain segments radiating from a branch unit will in turn be connected to another branch unit. The probability for this occurring is simply  $1/(f - 1)$  and the *critical branching coefficient*  $\alpha_c$  for gel formation is

$$\alpha_c = \frac{1}{(f - 1)} \quad (2-145)$$

The  $f$  in Eq. 2-145 is the functionality of the branch units, that is, of the monomer with functionality greater than 2. It is not the average functionality  $f_{\text{avg}}$  from the Carothers equation. If more than one type of multifunctional branch unit is present an average  $f$  value of all the monomer molecules with functionality greater than 2 is used in Eq. 2-145.

When  $\alpha(f - 1)$  equals 1 a chain segment will, on the average, be succeeded by  $\alpha(f - 1)$  chains. Of these  $\alpha(f - 1)$  chains a portion  $\alpha$  will each end in a branch point so that  $\alpha^2(f - 1)^2$  more chains are created. The branching process continues with the number of succeeding chains becoming progressively greater through each succeeding branching reaction. The growth of the polymer is limited only by the boundaries of the reaction vessel. If, on the other hand,  $\alpha(f - 1)$  is less than 1, chain segments will not be likely to end in branch units. For a trifunctional reactant ( $f = 3$ ) the critical value of  $\alpha$  is  $\frac{1}{2}$ .

The probability  $\alpha$  is now related to the extent of reaction by determining the probability of obtaining a chain segment of the type shown in Eq. 2-144. The extents of reaction of A and B functional groups are  $p_A$  and  $p_B$ , respectively. The ratio of all A groups, both reacted and unreacted, that are part of branch units, to the total number of all A groups in the mixture is defined by  $\rho$ . This corresponds to the same definition of  $\rho$  as in Eq. 2-143. The probability that a B group has reacted with a branch unit is  $p_B\rho$ . The probability that a B group has

reacted with a nonbranch A—A unit is  $p_B(1 - \rho)$ . Therefore the probability of obtaining a segment of the type in Eq. 2-144 is given by  $p_A[p_B(1 - \rho)p_A]^n p_B \rho$ . Summation of this over all values of  $n$  and then evaluation of the summation yields

$$\alpha = \frac{p_A p_B \rho}{1 - p_A p_B (1 - \rho)} \quad (2-146)$$

Either  $p_A$  or  $p_B$  can be eliminated by using the ratio  $r$  of all A groups to all B groups to substitute  $p_A = r p_B$  into Eq. 2-146 to yield

$$\alpha = \frac{r p_A^2 \rho}{1 - r p_A^2 (1 - \rho)} = \frac{p_B^2 \rho}{r - p_B^2 (1 - \rho)} \quad (2-147)$$

Equation 2-147 is combined with Eq. 2-145 to yield a useful expression for the extent of reaction (of the A groups) at the gel point

$$p_c = \frac{1}{\{r[1 + \rho(f - 2)]\}^{1/2}} \quad (2-148)$$

Several special cases of Eqs. 2-147 and 2-148 are of interest. When the two functional groups are present in equivalent numbers,  $r = 1$  and  $p_A = p_B = p$ , Eqs. 2-147 and 2-148 become

$$\alpha = \frac{p^2 \rho}{1 - p^2 (1 - \rho)} \quad (2-149)$$

and

$$p_c = \frac{1}{[1 + \rho(f - 2)]^{1/2}} \quad (2-150)$$

When the polymerization is carried out without any A—A molecules ( $\rho = 1$ ) with  $r < 1$  the equations reduce to

$$\alpha = r p_A^2 = \frac{p_B^2}{r} \quad (2-151)$$

and

$$p_c = \frac{1}{\{r[1 + (f - 2)]\}^{1/2}} \quad (2-152)$$

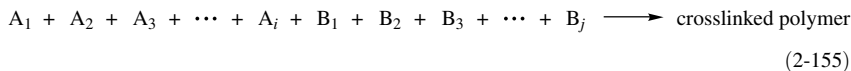
If both of the conditions stated are present, that is,  $r = \rho = 1$ , Eqs. 2-147 and 2-148 become

$$\alpha = p^2 \quad (2-153)$$

and

$$p_c = \frac{1}{[1 + (f - 2)]^{1/2}} \quad (2-154)$$

These equations do not apply for reaction systems containing monofunctional reactants and/or both A and B type of branch units. Consider the more general case of the system



where we have reactants ranging from monofunctional to  $i$ th functional for A functional groups and monofunctional to  $j$ th functional for B functional groups [Durand and Bruneau, 1982a,b; Miller et al., 1979; Miller and Macosko, 1978; Stockmayer, 1952, 1953; Stafford, 1981.] The extent of reaction at the gel point is given by

$$p_c = \frac{1}{\{r(f_{w,A} - 1)(f_{w,B} - 1)\}^{1/2}} \quad (2-156)$$

where  $f_{w,A}$  and  $f_{w,B}$  are weight-average functionalities of A and B functional groups, respectively, and  $r$  is the stoichiometric imbalance (Sec. 2-6b). The functionalities  $f_{w,A}$  and  $f_{w,B}$  are defined by

$$f_{w,A} = \frac{\sum f_{A_i}^2 N_{A_i}}{\sum f_{A_i} N_{A_i}} \quad (2-157)$$

$$f_{w,B} = \frac{\sum f_{B_j}^2 N_{B_j}}{\sum f_{B_j} N_{B_j}} \quad (2-158)$$

The summations in Eq. 2-157 are for all molecules containing A functional groups with  $N_{A_i}$  representing the number of moles of reactant  $A_i$  containing  $f_{A_i}$  number of A functional groups per molecule. The summations in Eq. 2-158 are for all molecules containing B functional groups with  $N_{B_j}$  representing the number of moles of reactant  $B_j$  containing  $f_{B_j}$  number of B functional groups per molecule.

The utility of Eq. 2-156 can be illustrated for the system:

|              |              |
|--------------|--------------|
| 4 mol $A_1$  | 2 mol $B_1$  |
| 40 mol $A_2$ | 50 mol $B_2$ |
| 2 mol $A_3$  | 3 mol $B_3$  |
| 3 mol $A_4$  | 3 mol $B_5$  |

$r$ ,  $f_{w,A}$ ,  $f_{w,B}$ , and  $p_c$  are calculated as

$$r = \frac{1(4) + 2(40) + 3(2) + 4(3)}{1(2) + 2(50) + 3(3) + 5(3)} = 0.80952 \quad (2-159)$$

$$f_{w,A} = \frac{1^2(4) + 2^2(40) + 3^2(2) + 4^2(3)}{1(4) + 2(40) + 3(2) + 4(3)} = 2.25490 \quad (2-160)$$

$$f_{w,B} = \frac{1^2(2) + 2^2(50) + 3^2(3) + 5^2(3)}{1(2) + 2(50) + 3(3) + 5(3)} = 2.41270 \quad (2-161)$$

$$p_c = \frac{1}{\{0.80952(2.25490)(2.41270)\}^{1/2}} = 0.83475 \quad (2-162)$$

Keeping in mind that  $p_c$  is the gel point conversion for A groups since B groups are in excess (A groups are limiting), consider the effects of adding more monofunctional reagent to the system. The effect is different for adding  $A_1$  versus adding  $B_1$ . For example, increasing  $A_1$  from 4 to 18 mol increases  $r$  to 0.92063 and decreases  $f_{w,A}$  to 2.10345, with  $f_{w,B}$  unchanged. The changes in  $r$  and  $f_{w,A}$  cancel each other and Eq. 2-156 calculates that  $p_c$  is unchanged at 0.83475. On the other hand, increasing  $B_1$  from 2 to 16 mol decreases  $r$  to 0.72857 and also decreases  $f_{w,B}$  to 2.27143, with  $f_{w,A}$  unchanged. The changes in  $r$  and  $f_{w,A}$  reinforce each other and  $p_c$  increases to 0.92750.

The effect of increasing  $A_1$  is different from increasing  $B_1$  because B groups are in excess. The additional A groups added by increasing  $A_1$  results only in changing some of the end groups of the polymer chains from B groups to A groups, with no effect on  $p_c$ . When  $B_1$  is increased, it tends to degrade the crosslinking process. The bifunctional and polyfunctional A reactants depend on the polyfunctional B reactants to build up the crosslinked network. Monofunctional B acts as a capping agent for chain ends to limit the extent of crosslinking and increase  $p_c$ .

### 2-10c Experimental Gel Points

The two approaches to the problem of predicting the extent of reaction at the onset of gelation differ appreciably in their predictions of  $p_c$  for the same system of reactants. The Carothers equation predicts the extent of reaction at which the number-average degree of polymerization becomes infinite. This must obviously yield a value of  $p_c$  that is too large because polymer molecules larger than  $\bar{X}_n$  are present and will reach the gel point earlier than those of size  $\bar{X}_n$ . The statistical treatment theoretically overcomes this error, since it predicts the extent of reaction at which the polymer size distribution curve first extends into the region of infinite size.

The gel point is usually determined experimentally as that point in the reaction at which the reacting mixture loses fluidity as indicated by the failure of bubbles to rise in it. Experimental observations of the gel point in a number of systems have confirmed the general utility of the Carothers and statistical approaches. Thus in the reactions of glycerol (a triol) with equivalent amounts of several diacids, the gel point was observed at an extent of reaction of 0.765 [Kienle and Petke, 1940, 1941]. The predicted values of  $p_c$ , are 0.709 and 0.833 from Eqs. 148 (statistical) and 2-139 (Carothers), respectively. Flory [1941] studied several systems composed of diethylene glycol ( $f = 2$ ), 1,2,3-propanetricarboxylic acid ( $f = 3$ ), and either succinic or adipic acid ( $f = 2$ ) with both stoichiometric and nonstoichiometric amounts of hydroxyl and carboxyl groups. Some of the experimentally observed  $p_c$  values are shown in Table 2-9 along with the corresponding theoretical values calculated by both the Carothers and statistical equations.

**TABLE 2-9 Gel Point Determinations for Mixture of 1,2,3-Propanetricarboxylic Acid, Diethylene Glycol, and Either Adipic or Succinic Acid<sup>a</sup>**

| Extent of Reaction at Gel Point ( $p_c$ )       |        |                           |                           |                       |
|-------------------------------------------------|--------|---------------------------|---------------------------|-----------------------|
| $r = \frac{[\text{CO}_2\text{H}]}{[\text{OH}]}$ | $\rho$ | Calculated from Eq. 2-139 | Calculated from Eq. 2-148 | Observed <sup>a</sup> |
| 1.000                                           | 0.293  | 0.951                     | 0.879                     | 0.911                 |
| 1.000                                           | 0.194  | 0.968                     | 0.916                     | 0.939                 |
| 1.002                                           | 0.404  | 0.933                     | 0.843                     | 0.894                 |
| 0.800                                           | 0.375  | 1.063                     | 0.955                     | 0.991                 |

<sup>a</sup> Data from Flory [1941].

The observed  $p_c$  values in Table 2-9 as in many other similar systems fall approximately midway between the two calculated values. The Carothers equation gives a high value of  $p_c$  for reasons mentioned above. The experimental  $p_c$  values are close to but always higher than those calculated from Eq. 2-148. There are two reasons for this difference: the occurrence of intramolecular cyclization and unequal functional group reactivity. Both factors were ignored in the theoretical derivations of  $p_c$ . Intramolecular cyclization reactions between functional groups are wasteful of the reactants and require the polymerization to be carried out to a greater extent of reaction to reach the gel point. Stockmayer [1945] showed this to be the case for the reaction of pentaerythritol,  $C(CH_2OH)_4$  ( $f = 4$ ) with adipic acid. Gelation was studied as a function of concentration and the results extrapolated to infinite concentration where intramolecular reactions would be expected to be nil. The experimental  $p_c$  value of  $0.578 \pm 0.005$  compared exceptionally well with the theoretical value of 0.577. The value of  $p_c$  calculated by the Carothers equation is 0.75 for this system.

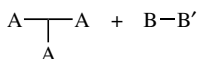
In many reaction systems the difference between the observed  $p_c$  values and those calculated from Eq. 2-148 are at least partially ascribed to the failure of the assumption of equal reactivity of all functional groups of the same type. An example is the glycerol-phthalic acid system previously mentioned. The difference between the calculated and observed values of  $p_c$  (0.709 vs. 0.765) would be decreased, but not eliminated, if the calculation were corrected for the known lower reactivity of the secondary hydroxyl group of glycerol.

It is difficult to find crosslinking systems that are ideal in that all functional groups are of equal reactivity and intramolecular cyclization is negligible. The crosslinking of vinyl terminated poly(dimethylsiloxane) polymers with tri- and tetrafunctional silanes appears to be an exception. Thus the calculated and experimental  $p_c$  values were 0.578 and 0.583, respectively, for the tetrafunctional silane and 0.708 and 0.703, respectively, for the trifunctional silane (with  $r = 0.999$ ) [Valles and Macosko, 1979].

Although both the Carothers and statistical approaches are used for the practical predication of gel points, the statistical approach is the more frequently employed. The statistical method is preferred, since it theoretically gives the gel point for the largest-sized molecules in a size distribution. From the practical viewpoint the use of the Carothers approach alone can be disastrous, since the Carothers approach always predicts a higher  $p_c$  than observed. Crosslinked polymer becomes intractable above  $p_c$ ; the reaction must be stopped at an extent of reaction below  $p_c$  before starting the technological step of fabricating the polymer into the shape of final desired product (see Sec. 2-12). Further, the statistical approach offers a greater possibility of adaption to various systems of reactants as well as the inclusion of corrections for the nonapplicability of the equal reactivity assumption and the occurrence of intramolecular reactions. Equation 2-148 and its modifications have been used extensively in the technology of crosslinked polymers.

## 2-10d Extensions of Statistical Approach

The statistical approach has been applied to systems containing reactants with functional groups of unequal reactivity [Case, 1957; Macosko and Miller, 1976; Miller and Macosko, 1978; Miller et al., 1979]. In this section we will consider some of the results for such systems. Figure 2-15 shows a plot of  $\bar{M}_w$  vs. extent of reaction for the various values of  $s$  at  $r = 1$  for the system



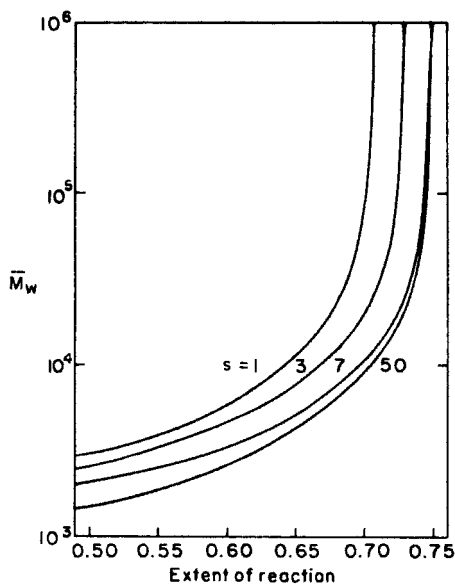
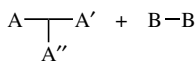


Fig. 2-15  $\bar{M}_w$  versus extent of reaction for polymerization of  $A_3$  with  $B-B'$  for different  $s$  values. After Miller and Macosko [1978] (by permission of American Chemical Society, Washington, DC).

where the two functional groups in the  $B-B'$  reactant have a difference in reactivity by a factor of  $s$ .  $s$  is the ratio of the rate constants for  $B$  and  $B'$  groups reacting with  $A$  groups.  $p_c$  is the value of  $p$  at which the curve becomes essentially vertical (i.e.,  $\bar{M}_w \rightarrow \infty$ ). The curves shift to the right with increasing  $s$ , although the shift becomes progressively smaller with increasing  $s$ . The extent of reaction at the gel point increases as the  $B$  and  $B'$  groups differ in reactivity. The more reactive  $B$  groups react to a greater extent earlier in the overall process, but gelation does not occur without reaction of the less reactive  $B'$  groups. Overall there is a wastage of the more reactive  $B$  groups and  $p_c$  is increased. There is an upper limit to this wastage with increasing  $s$  and  $p_c$  levels off with increasing  $s$ .

Figure 2-16 shows a  $p_c$  contour map for the system



at  $r = 1$  for various values of  $s_1$  and  $s_2$  with

$$s_1 = \frac{k}{k'} \quad (2-163a)$$

$$s_2 = \frac{k}{k''} \quad (2-163b)$$

where  $k$ ,  $k'$ , and  $k''$  are the rate constants for the reactions of  $A$ ,  $A'$ , and  $A''$  groups, respectively, with  $B$  groups.  $p_c$  increases as  $s_1$  or  $s_2$  becomes larger than 1. If both  $s_1$  and  $s_2$  are larger than 1, the increase in  $p_c$  is greater the larger is the difference between  $s_1$  and  $s_2$ . Plots such as Figs. 2-15 and 2-16 can be used to calculate the expected  $p_c$  for a system where the reactivities of the functional groups are known or the relative reactivities ( $s$  in the first

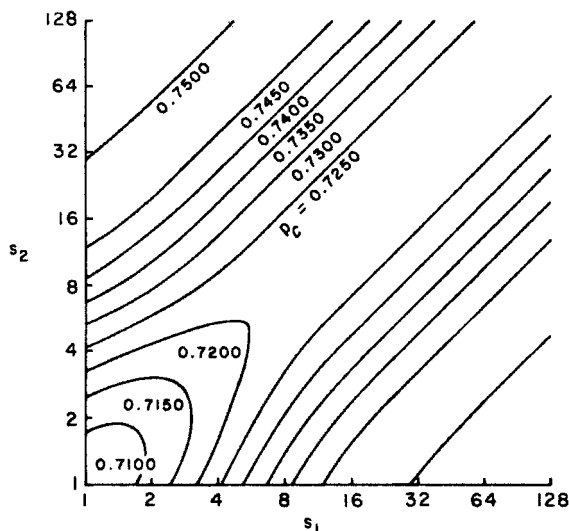
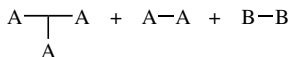


**Fig. 2-16** Effect of  $s_1$  and  $s_2$  on  $p_c$  for polymerization of B-B with A-A'.  $p_c$  values are shown on the plot. After Miller and Macosko [1978] (by permission of American Chemical Society, Washington, DC).

system,  $s_1$  and  $s_2$  in the second system) in a particular reaction system can be determined from the measurement of  $p_c$ .

Some theoretical evaluations of the effect of intramolecular cyclization on gelation have been carried out [Gordon and Ross-Murphy, 1975; Kilb, 1958; Kumar et al., 1986; Stafford, 1981]. The main conclusion is that, although high reactant concentrations decrease the tendency toward cyclization, there is at least some cyclization occurring even in bulk polymerizations. Thus, even after correcting for unequal reactivity of functional groups, one can expect the actual  $p_c$  in a crosslinking system to be higher than the calculated value.

Various relationships have been derived to describe the crosslinking density of a system past  $p_c$  [Argyropoulos et al., 1987; Durand and Bruneau, 1982a,b; Dusek, 1979a,b; Dusek et al., 1987; Flory, 1953; Miller and Macosko, 1976] (see also Sec. 2-11). The density of crosslinks in a reaction system increases with conversion and with increasing functionality of reactants. For a system such as



the crosslink density increases as  $\rho$  increases. Varying the crosslink density by changing  $\rho$  is of practical interest in that it allows one to control the flexibility or rigidity of the final cross-linked polymer.

## 2-11 MOLECULAR WEIGHT DISTRIBUTIONS IN NONLINEAR POLYMERIZATIONS

The molecular size distribution functions for three-dimensional polymers are derived in a manner analogous to those for linear polymers, but with more difficulty. The derivations have been discussed elsewhere [Flory, 1946, 1953; Somvarsky et al., 2000; Stockmayer,

1943, 1952, 1953], and only their results will be considered here. The number  $N_x$ , number or mole fraction  $\underline{N}_x$ , and weight fraction  $w_x$  of  $x$ -mer molecules in a system containing monomer(s) with  $f > 2$  are given, respectively, by

$$N_x = N_0 \left[ \frac{(fx - x)! f}{x! (fx - 2x + 2)!} \right] \alpha^{x-1} (1 - \alpha)^{fx - 2x + 2} \quad (2-164)$$

$$\underline{N}_x = \left[ \frac{(fx - x)! f}{x! (fx - 2x + 2)! (1 - \alpha f/2)} \right] \alpha^{x-1} (1 - \alpha)^{fx - 2x + 2} \quad (2-165)$$

$$w_x = \left[ \frac{(fx - x)! f}{(x - 1)! (fx - 2x + 2)!} \right] \alpha^{x-1} (1 - \alpha)^{fx - 2x + 2} \quad (2-166)$$

The number- and weight-average degrees of polymerization are given by

$$\bar{X}_n = \frac{1}{1 - (\alpha f/2)} \quad (2-167)$$

$$\bar{X}_w = \frac{(1 + \alpha)}{1 - (f - 1)\alpha} \quad (2-168)$$

$$\frac{\bar{X}_w}{\bar{X}_n} = \frac{(1 + \alpha)(1 - \alpha f/2)}{1 - (f - 1)\alpha} \quad (2-169)$$

These equations are general and apply equally for multifunctional reactions such as that of  $A_f$  with  $B_f$  or that of  $A_f$  with  $A-A$  and  $B-B$ . Depending on which of these reactant combinations is involved, the value of  $\alpha$  will be appropriately determined by the parameters  $r, f, p$ , and  $\rho$ . For convenience the size distributions in the reaction of equivalent amounts of trifunctional reactants alone, that is, where  $\alpha = p$ , will be considered. A comparison of Eqs. 2-89 and 2-166 shows that the weight distribution of branched polymers is broader than that of linear polymers at equivalent extents of reaction. Furthermore, the distribution for the branched polymers becomes increasingly broader as the functionality of the multifunctional reactant increases. The distributions also broaden with increasing values of  $\alpha$ . This is seen in Fig. 2-17, which shows the weight fraction of  $x$ -mers as a function of  $\alpha$  for the polymerization involving only trifunctional reactants.

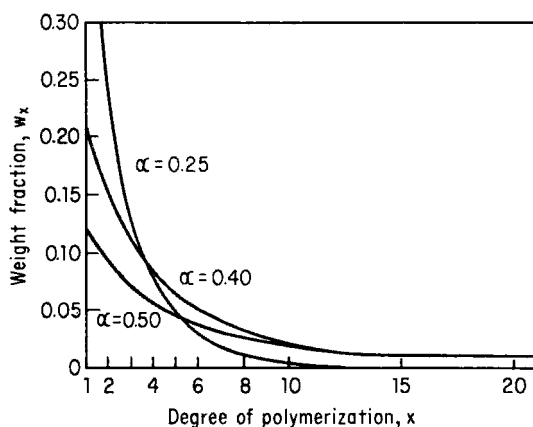


**Fig. 2-17** Molecular weight distribution as a function of the extent of reaction for the polymerization of trifunctional reactants where  $\alpha = p$ . After Flory [1946] (by permission of American Chemical Society, Washington, DC).

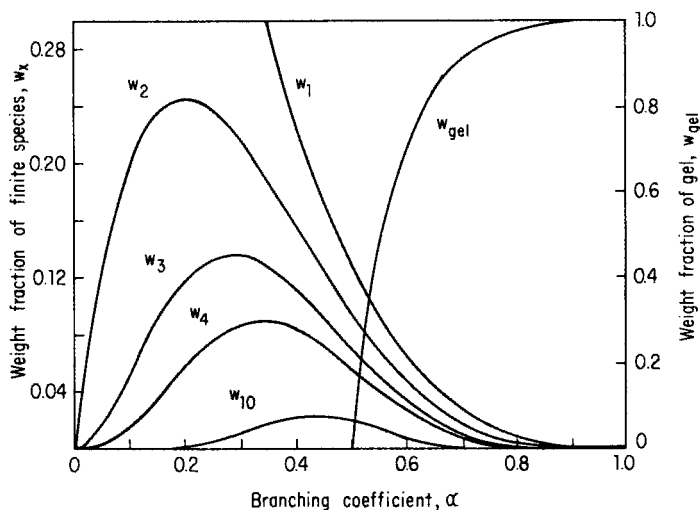


Fig. 2-18 Weight fractions of various finite species and of gel in a trifunctional polymerization where  $\alpha = p$ . After Flory [1946] (by permission of American Chemical Society, Washington, DC).

Figure 2-18 shows a plot of the weight fraction of different  $x$ -mers versus  $\alpha$  or  $p$  for the trifunctional polymerization. The weight fraction  $w_{\text{gel}}$  of the gel or  $\infty$ -mer is also plotted. A comparison of Figs. 2-17 and 2-18 with Fig. 2-9 for linear polymerization shows that the weight fraction of monomer is always greater than that of any one of the other species (up to the point where the curves for  $w_1$  and  $w_{\text{gel}}$  intersect). As the reaction proceeds, larger species are built up at the expense of the smaller ones, and a maximum is reached at a value of  $p$  less than  $\frac{1}{2}$ . The maximum shifts to higher values of  $p$  for the larger species. The distribution broadens and reaches maximum heterogeneity at the gel point ( $\alpha = \frac{1}{2}$ ), where the fraction of species that are highly branched is still small. The infinite network polymer is first formed at the gel point, and its weight fraction rapidly increases. The species in the sol (consisting of all species other than gel) decrease in average size because the larger, branched species are preferentially tied into the gel. Past the point of intersection for the  $w_1$  and  $w_{\text{gel}}$  curves gel is the most abundant species on a weight basis.

The broadening of the distribution with increasing  $\alpha$  can also be noted by the  $\bar{X}_w/\bar{X}_n$  value. Equations 2-167 and 2-169 show that the difference between the number- and weight-average degrees of polymerization increases very rapidly with increasing extent of reaction. At the gel point the breadth of the distribution  $\bar{X}_w/\bar{X}_n$  is enormous, since  $\bar{X}_w$  is infinite, while  $\bar{X}_n$  has a finite value of 4 (Fig. 2-19). Past the gel point the value of  $\bar{X}_w/\bar{X}_n$  for the sol fraction decreases. Finally, at  $\alpha = p = 1$ , the whole system has been converted to gel (i.e., one giant molecule) and  $\bar{X}_w/\bar{X}_n$  equals 1.

As mentioned previously, the behavior of systems containing bifunctional as well as trifunctional reactants is also governed by the equations developed above. The variation of  $w_x$  for the polymerization of bifunctional monomers, where the branching coefficient  $\alpha$  is varied by using appropriate amounts of a trifunctional monomer, is similar to that observed for the polymerization of trifunctional reactants alone. The distribution broadens with increasing extent of reaction. The effect of unequal reactivity of functional groups and intramolecular

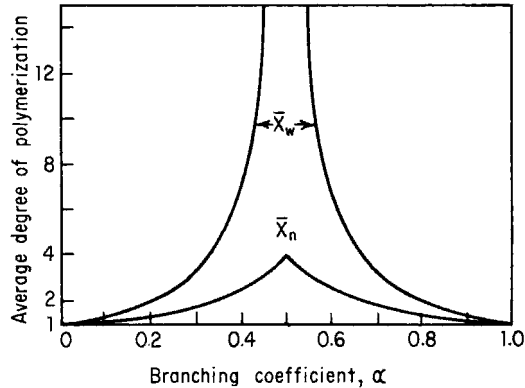


**Fig. 2-19** Number- and weight-average degrees of polymerization as a function of  $\alpha$  for a trifunctional polymerization. The portions of the plots after the gel point ( $\alpha = \frac{1}{2}$ ) are for the sol fraction only. After Flory [1946] (by permission of American Chemical Society, Washington, DC).

cyclization is to broaden the molecular weight distribution [Case, 1957; Macosko and Miller, 1976; Miller and Macosko, 1980; Muller and Burchard, 1978].

## 2-12 CROSSLINKING TECHNOLOGY

Control of crosslinking is critical for processing thermoset plastics, both the reaction prior to the gel point and that subsequent to the gel point. The period after the gel point is usually referred to as the curing period. Too slow or too rapid crosslinking can be detrimental to the properties of a desired product. Thus, in the production of a thermoset foamed product, the foam structure may collapse if gelation occurs too slowly. On the other hand, for reinforced and laminated products the bond strength of the components may be low if crosslinking occurs too quickly.

The fabrication techniques for producing objects from thermosetting and thermoplastic polymers are vastly different. In the case of the thermoplastics the polymerization reaction is completed by the plastics manufacturer. The fabricator takes the polymer and applies heat and pressure to produce a flowable material that can be shaped into the desired finished object. The situation is quite different for thermosetting plastics. A completely polymerized thermoset is no longer capable of flow and cannot be processed into an object. Instead, the fabricator receives an incompletely polymerized polymer—termed a *prepolymer*—from the plastics manufacturer and polymerization (and crosslinking) is completed during the fabrication step. For example, a prepolymer can be poured into an appropriate mold and then solidified to form the desired finished object by completing the polymerization. The prepolymers are usually in the molecular weight range 500–5000 and may be either liquid or solid. The molds used for thermosets must be hinged so that they can be opened after crosslinking to remove the finished product.

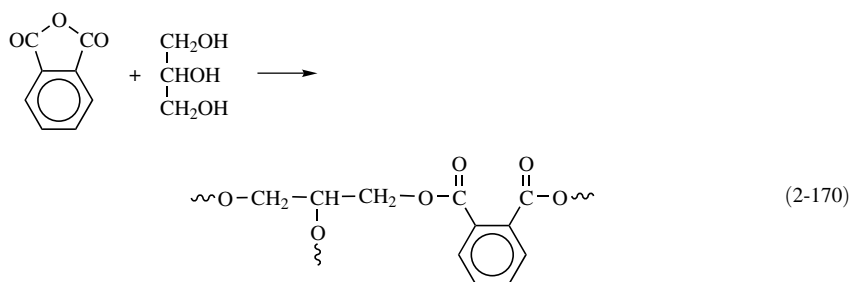
Thermoset polymers are classified as *A-stage*, *B-stage*, and *C-stage* polymers according to their extent of reaction  $p$  compared to the extent of reaction at gelation  $p_c$ . The polymer is an *A-stage* polymer if  $p < p_c$ , *B-stage* if the system is close to the gel point ( $p_c$ ), and *C-stage* when it is well past  $p_c$ . The *A-stage* polymer is soluble and fusible. The *B-stage*

polymer is still fusible but is barely soluble. The *C*-stage polymer is highly crosslinked and both infusible and insoluble. The prepolymer employed by a fabricator is usually a *B*-stage polymer, although it may be an *A*-stage one. The subsequent polymerization of the prepolymer takes it through to the *C* stage.

Thermoset plastics can generally be grouped into two types depending on whether the same chemical reaction is used to both synthesize and crosslink the prepolymer. Generally, the older thermosetting materials involve the random crosslinking of bifunctional monomers with monomers of functionality greater than 2. The prepolymer is obtained in a first step by stopping the reaction, usually by cooling, at the desired extent of conversion (either *A*- or *B*-stage). Polymerization with crosslinking is completed during a second-step fabrication process, usually by heating. The newer thermosets involve prepolymers of a more specially designed structure. These prepolymers undergo crosslinking in the second step by a chemical reaction different from that for the first step. Because there is different chemistry in the two steps, one is not involved in any  $p_c$  considerations in the first step. The reactants are bifunctional with respect to the first-step chemistry. However, one or more of the reactants has some functional group capable of reaction under other conditions. Such prepolymer systems are advantageous because they generally offer greater control of the polymerization and crosslinking reactions, and very importantly, of the structure of the final product. The uses and markets for these newer thermosets are growing more rapidly than those of the older systems.

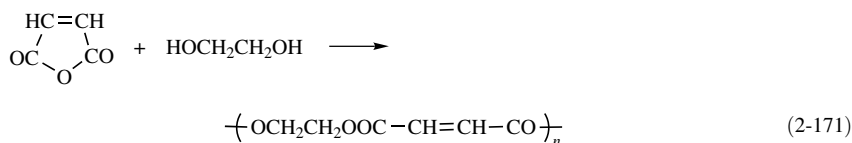
## 2-12a Polyesters, Unsaturated Polyesters, and Alkyds

Polyesters formed from phthalic anhydride and glycerol were among the first commercial crosslinked polyesters. Linear polyesters seldom are synthesized by the direct reactions of acids or acid anhydrides with alcohols because the higher temperatures required for high conversions lead to side reactions, which interfere with obtaining high molecular weights. This consideration is not overwhelmingly important for crosslinking systems, since crosslinking is achieved at far lower extents of reaction than are needed to obtain high polymer in a linear polymerization. Crosslinked polyesters are typically synthesized by direct esterification of acid or acid anhydride with alcohol.



Simple polyesters of the type described by Eq. 2-170 are too limited to be of commercial interest. Almost all crosslinked polyesters are either unsaturated polyesters or alkyd polyesters. These offer a greater ability to vary the final product properties to suit a targeted market. Also, they offer greater process control since different chemical reactions are involved in the polymerization and crosslinking reactions. A typical unsaturated polyester

is that obtained by the polymerization of maleic anhydride and ethylene glycol. Maleic anhydride is only a bifunctional reactant in the polyesterification reaction, but it has the potential



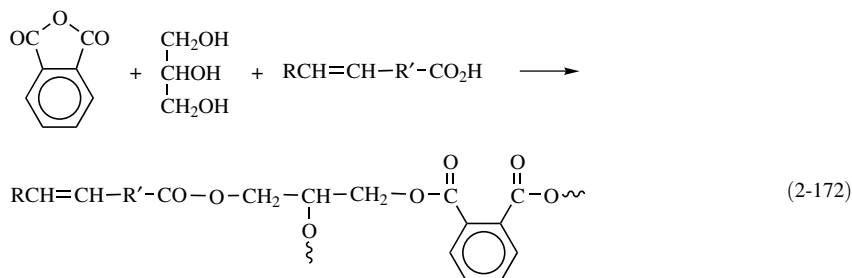
for a higher functionality under the appropriate reaction conditions. The alkene double bond is reactive under radical chain polymerization conditions. Crosslinking is accomplished in a separate step by radical copolymerization with alkene monomers such as styrene, vinyl toluene, methyl methacrylate, triallyl cyanurate, and diallyl phthalate (Sec. 6-6a).

Fumaric and itaconic acids are also used as the diacid component. Most reaction formulations involve a mixture of a saturated diacid (iso- and terephthalic, adipic) with the unsaturated diacid or anhydride in appropriate proportions to control the density of crosslinking (which depends on the carbon-carbon double-bond content of the prepolymer) for specific applications [Parker and Pepper, 1977; Selley, 1988]. Propylene glycol, 1,4-butanediol, neopentyl glycol, diethylene glycol, and bisphenol A are also used in place of ethylene glycol as the diol component. Aromatic reactants are used in the formulation to improve the hardness, rigidity, and heat resistance of the crosslinked product. Halogenated reactants are used to impart flame resistance.

The United States production of unsaturated polyesters was more than 1.7 billion pounds in 2001. Almost all unsaturated polyesters are used with fibrous reinforcements or fillers. More than 80% of the market consists of structural applications that require the strengthening imparted by fibrous (usually fiber glass) reinforcement. The remainder is used without fibrous reinforcement but with inexpensive fillers to lower costs. Unsaturated polyesters have a good combination of resistance to softening and deformation at high temperature, electrical properties, resistance to corrosion, weak alkalis, and strong acids and possess very good weatherability. The liquid polyester prepolymers are especially easy to fabricate into infusible thermoset objects by casting in open molds, spray techniques as well as compression, hand layup, and resin-transfer molding. Unsaturated polyesters are used extensively in the construction (tub and shower units, building facades, specialty flooring, cultured onyx and marble, chemical storage tanks), transportation (truck cabs, auto body repair), and marine (boat hulls) industries as well as for business machine and electric handtool-molded parts.

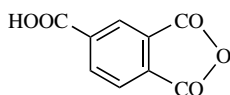
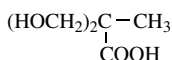
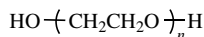
*Alkyds* are unsaturated polyesters in which the unsaturation is located at chain ends instead of within the polymer chain [Lanson, 1986]. This is accomplished by using an unsaturated monocarboxylic acid in the polymerization (Eq. 2-172). Various unsaturated fatty acids are used. Some contain a single double bond (oleic, ricinoleic); others contain two or more double bonds, either isolated (linoleic, linolenic) or conjugated (eleostearic). The unsaturated fatty acid is typically used together with a saturated monoacid (typically a fatty acid such as lauric, stearic, palmitic but also benzoic and *p*-*t*-butylbenzoic). (The unsaturated and saturated fatty acids are often referred to as *drying* and *nondrying oils*, respectively.) The fatty acid content is in the range 30–60% or higher and the alkyd is referred to as a *short*, *medium* or *long oil alkyd* depending on the fatty acid content. Although glycerol is the major polyhydric alcohol in alkyd formulations, a variety of other alcohols with functionality from 2 to 8 (diethylene glycol, sorbitol, pentaerythritol, tripentaerythritol) are used either alone or in combination. Alkyd prepolymers are crosslinked via oxidation with atmospheric oxygen

(Sec. 9-2a). The crosslinking process is referred to as *drying* and is directly dependent on the content of unsaturated fatty acid. The crosslinking reaction involves chemical reactions different from those involved in prepolymer synthesis.



More than 200 million pounds of alkyds are produced annually in the United States. Almost all of this is used in coating applications. Alkyds undergo rapid drying and possess good adhesion, flexibility, strength, and durability. The upper temperature limit for continuous use for both alkyds and unsaturated polyesters is about 130°C. Considerable variations are possible in properties by manipulation of the alkyd formulation. For example, the use of higher-functionality alcohols allows an increase in the fatty acid content, which imparts faster drying as well as increased hardness, better gloss retention, and improved moisture resistance. Alkyds are used as architectural enamels, exterior paints, top-side marine paints, and various metal primers and paints. Alkyds with carboxyl end groups are modified by reaction with hydroxy groups of nitrocellulose to produce lacquers. Modifications with amino resins (Sec. 2-12b-2) yields resins suitable as baked-on enamels for metal cabinets, appliances, venetian blinds, and toys. Blends of chlorinated rubber with alkyds are used as paints for highway marking, concrete, and swimming pools.

Water-based alkyds now represent a significant part of the total market. Alkyd prepolymers are rendered water-soluble or soluble in mixtures of water and alcohol (2-butoxyethanol, 2-butanol) by various changes in prepolymer synthesis. One approach is to introduce unesterified carboxyl groups into the polymer chain, for example, by using trimellitic anhydride (**XVIII**) or dimethylolpropionic acid (**XIX**). The carboxyl groups are neutralized with base to form carboxylate groups along the polymer chain to promote water solubility. Another approach is to use poly(ethylene oxide) (**XX**) with hydroxyl end groups as an alcohol in the prepolymer synthesis.

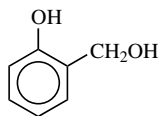
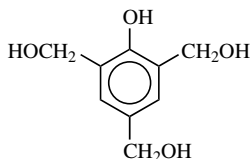
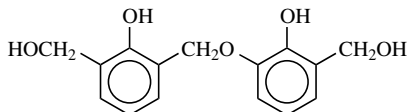
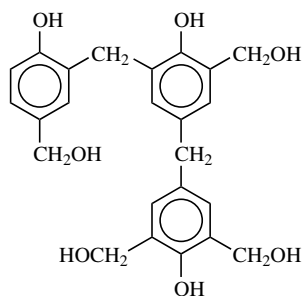
**XVIII****XIX****XX**

## 2-12b Phenolic Polymers

### 2-12b-1 Resole Phenolics

Phenolic polymers are obtained by the polymerization of phenol ( $f = 3$ ) with formaldehyde ( $f = 2$ ) [Bogan, 1991; Brydson, 1999; Kopf, 1988; Lenz, 1967; Manfredi et al., 2001; Peng

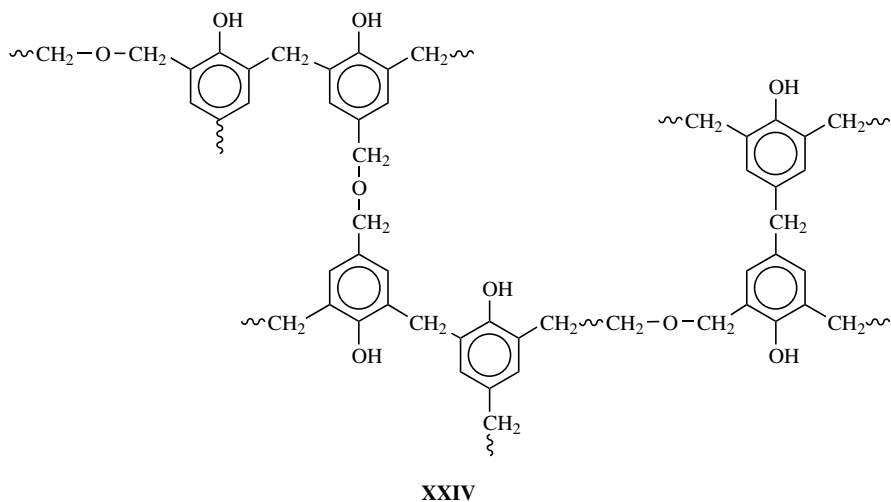
and Riedel, 1995]. The polymerization rate is pH-dependent, with the highest rates occurring at high and low pH. The strong base-catalyzed polymerization yields *resole prepolymers* (*resole phenolics*), mixtures of mononuclear methylolphenols (**XXI**) and various dinuclear and polynuclear compounds such as **XXII** and **XXIII**. The specific compounds shown as **XXI**, **XXII**, and **XXIII** are only some of the possible products. The other products are those differing in the extent and position (*o* versus *p*) of substitution, and the type of bridge between rings (methylene versus ether). The polymerization is carried out using a molar ratio of formaldehyde to phenol of 1.2–3.0 : 1. A 1.2 : 1 ratio is the typical formulation. The formaldehyde is supplied as a 36–50% aqueous solution (referred to as *formalin*). The catalyst is 1–5% sodium, calcium or barium hydroxide. Heating at 80–95°C for 1–3 h is sufficient to form the prepolymer. Vacuum dehydration is carried out quickly to prevent overreaction and gelation.

**XXIa****XXIb****XXII****XXIII**

Although phenol itself is used in the largest volume, various substituted phenols such as cresol (*o*-, *m*-, *p*-), *p*-butylphenol, resorcinol, and bisphenol A are used for specialty applications. Some use is also made of aldehydes other than formaldehyde—acetaldehyde, glyoxal, 2-furaldehyde.

The exact composition and molecular weight of the resole depend on the formaldehyde to phenol ratio, pH, temperature and other reaction conditions [Maciel et al., 1984; Westler, 1986]. For example, higher formaldehyde compositions will yield resoles containing more of the mononuclear compounds. The resole prepolymer may be either a solid or liquid polymer and soluble or insoluble in water depending on composition and molecular weight. Molecular weights are in the range 500–5000; most are below 2000. The resoles are usually neutralized or made slightly acidic. The pH of the prepolymer together with its composition determine whether it will be slow curing or highly reactive. Crosslinking (curing) is carried out by heating at temperatures up to 180°C. The crosslinking process involves the same chemical reactions as for synthesizing the prepolymer—the formation of methylene and ether bridges between benzene rings to yield a network structure of type **XXIV**. The relative

importance of methylene and ether bridges is dependent on temperature [Lenz, 1967]. Higher curing temperatures favor the formation of methylene bridges but not to the exclusion of ether bridges.



The polymerization and crosslinking of phenol-formaldehyde is a highly useful industrial process. However, the reactions that take place are quite difficult to handle in a quantitative manner for a number of reasons. The assumption of equal reactivity of all functional groups in a monomer, independent of the other functional groups in the molecule and of whether the others are reacted, is dubious in this polymerization. Consider, for example, the routes by which trimethylolphenol (**XXIb**) can be produced in this system:

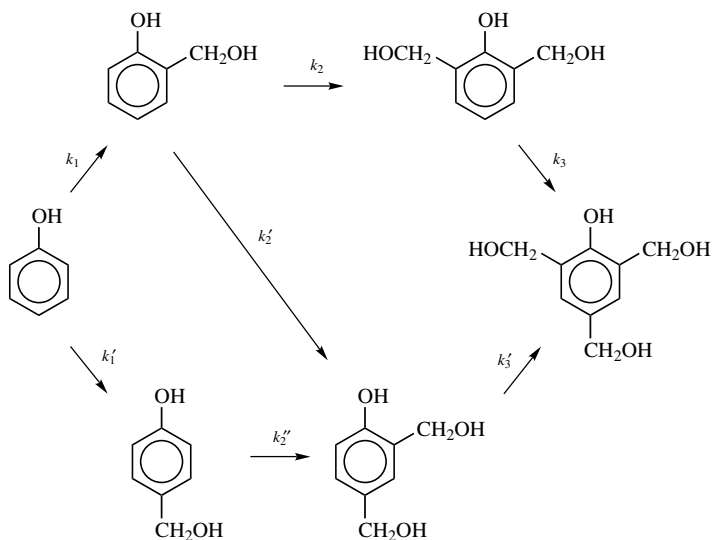
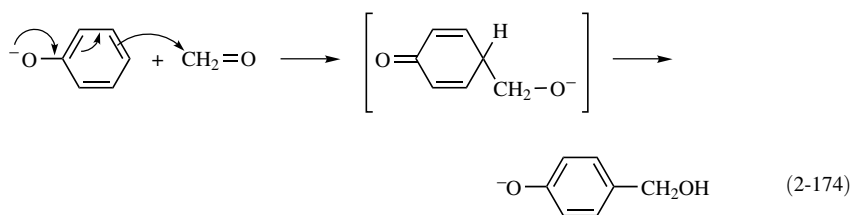


**TABLE 2-10 Reaction of Phenol with Formaldehyde Catalyzed by Base<sup>a, b</sup>**

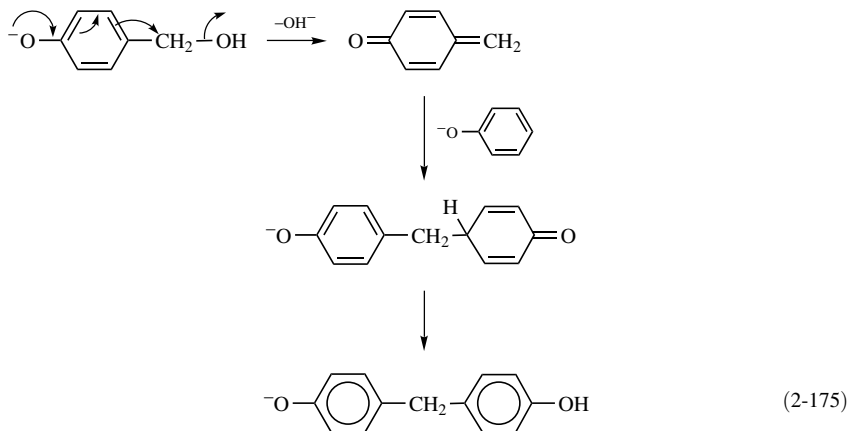
| Reaction | Rate Constant $\times 10^4$ (L mol <sup>-1</sup> s <sup>-1</sup> ) |
|----------|--------------------------------------------------------------------|
| $k_1$    | 14.63                                                              |
| $k'_1$   | 7.81                                                               |
| $k_2$    | 13.50                                                              |
| $k'_2$   | 10.21                                                              |
| $k''_2$  | 13.45                                                              |
| $k_3$    | 21.34                                                              |
| $k'_3$   | 8.43                                                               |

<sup>a</sup> Data from, Zavitsas [1968]; Zavitsas et al., [1968].<sup>b</sup> Reaction conditions: pH = 8.3,  $T = 57^\circ\text{C}$ .

Table 2-10 shows the rate constants for the various reactions. It is apparent that there are significant differences in the reactivities of the different functional groups in phenol (i.e., in the different positions on the ring). The reaction between phenol and formaldehyde involves a nucleophilic attack by the phenolate anion on formaldehyde (Eq. 2-174) (or its hydrated form). The electron-pushing methylol groups generally increase the reactivity of phenol toward further substitution although steric hindrance modifies this effect. It is difficult to quantitatively discuss the reasons for the specific differences in reactivity, since there is no general agreement on even the relative values of the seven different rate constants. The evaluation of the different rate constants is difficult from both the viewpoints of chemical analysis of the mono-, di-, and trimethylolphenols and the mathematical analysis [Katz and Zwei, 1978] of the kinetic data.



Not only are the different ring positions on phenol of different reactivity, but one expects that the two functional groups of formaldehyde would also differ. The second functional group of formaldehyde actually corresponds to the methylol group, since the reaction of a methylolphenol with a phenol molecule (or with a second methylolphenol) probably proceeds by a sequence such as

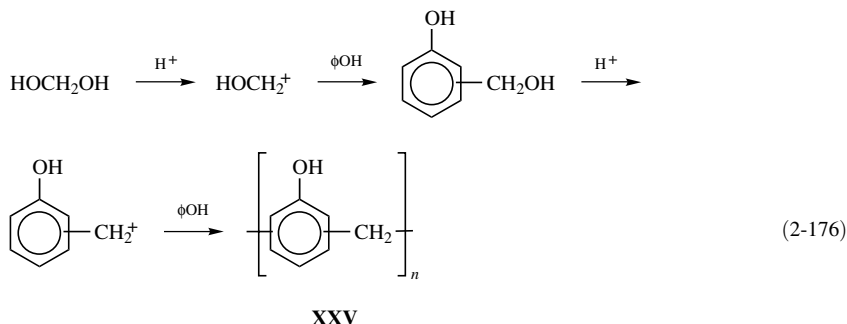


Direct kinetic measurements are not available to show the reactivity of the methylol group in this reaction compared to the initial reaction of formaldehyde. However, the general observation that the amounts of di- and polynuclear compounds present in resole prepolymers differ widely depending on the reaction condition (temperature, pH, specific catalyst used, concentrations of reactants) indicates that the two functional groups of formaldehyde differ in reactivity.

A further complication in the phenol-formaldehyde polymerization is that it may involve a decrease in functional group reactivity with molecular size. This can easily happen in systems that undergo extensive crosslinking. Such systems may cease to be homogeneous solutions before the experimentally determined gel point. The gel point may be preceded by the formation of microgel particles (Sec. 2-2d) which are too small to be visible to the naked eye [Katz and Zwi, 1978]. Functional groups in the microgel particles would be relatively unreactive because of their physical unavailability. Similar considerations would apply for the reaction period subsequent to the gel point. A decrease in reactivity with size may not be due to molecular size but a consequence of steric shielding of ortho or para positions of benzene rings within a chain compared to those positions on rings at the chain ends [Kumar et al., 1980].

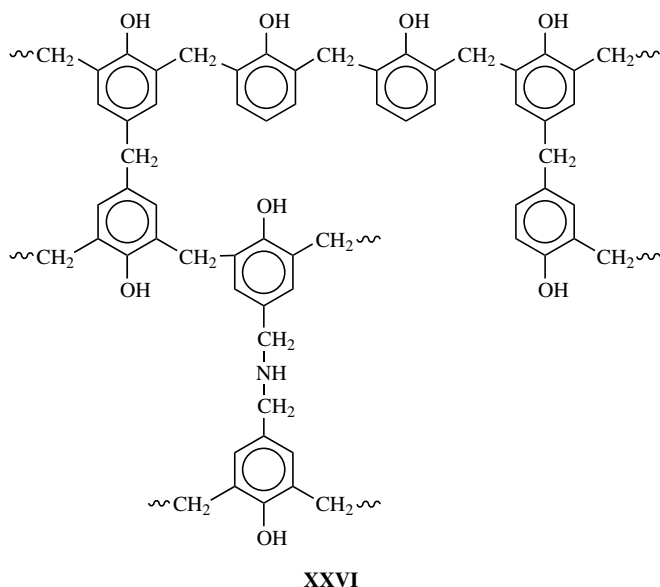
### 2-12b-2 Novolac Phenolics

Phenol-formaldehyde prepolymers, referred to as *novolacs*, are obtained by using a ratio of formaldehyde to phenol of 0.75–0.85 : 1, sometimes lower. Since the reaction system is starved for formaldehyde, only low molecular weight polymers can be formed and there is a much narrower range of products compared to the resoles. The reaction is accomplished by heating for 2–4 h at or near reflux temperature in the presence of an acid catalyst. Oxalic and sulfuric acids are used in amounts of 1–2 and <1 part, respectively, per 100 parts phenol. The polymerization involves electrophilic aromatic substitution, first by hydroxymethyl carbocation and subsequently by benzyl carbocation—each formed by protonation of OH followed by loss of water. There is much less benzyl ether bridging between benzene rings compared to the resole prepolymers.



Some novolacs are synthesized without strong acid present by using a carboxylate salt of zinc, calcium, manganese, cobalt, or other divalent metal ion (2% or more relative to phenol). These novolacs contain a higher degree of ortho substitution on the benzene rings and cure faster compared to the novolacs synthesized with the stronger acids. The mechanism for this ortho effect probably involves simultaneous complexation of the divalent metal ion with the phenol and carbocation hydroxyl groups. Similar effects of divalent ions on the relative amounts of ortho and para substitution are observed in the formation of resol prepolymers on comparison of catalysis by divalent metal hydroxides versus monovalent metal hydroxides.

The reaction mixture is dehydrated at temperatures as high as 160°C (higher temperatures can be tolerated than with resoles). The prepolymer is cooled, crushed, blended with 5–15% hexamethylenetetramine,  $(\text{CH}_2)_6\text{N}_4$ , and sold to the fabricator. Hexamethylenetetramine, referred to as *hexa*, is the product of the reaction of 6 mol of formaldehyde and 4 mol of ammonia. Curing occurs rapidly on heating with the formation of both methylene and benzylamine crosslinking bridges between benzene rings. The crosslinked network is pictured as **XXVI**.



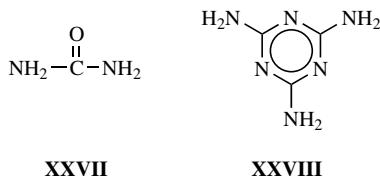
### 2-12b-3 Applications

Phenolic polymers, the first commercial synthetic plastics, were introduced by Leo Baekeland in 1909 through his Bakelite Company. Bakelite dominated this product until 1926 when its patent expired. Phenolic polymers are the largest-volume thermosetting plastics. The United States production of phenolics was about 4.5 billion pounds in 2001. Phenolics have high strength and dimensional stability combined with good resistance to impact, creep, solvents, and moisture. Most phenolics contain fillers or reinforcements. General-grade phenolics are filled with mica, clay, wood or mineral flour, cellulose, and chopped fabric. Engineering-grade phenolics, reinforced with glass or organic fibers, elastomers, graphite, and polytetrafluoroethylene, are rated for continuous use at 150–170°C.

The largest-volume application of phenolic polymers is the adhesive bonding material for the manufacture of plywood, particle board, wafer board, and fiberboard. The phenolic constitutes up to one-third of the weight of such products. Other adhesive applications include the binder for aluminum oxide or silicon carbide in abrasion wheels and disks and contact adhesives, usually blends of rubber and phenolic, used extensively in the furniture, automotive, construction, and footwear industries. Phenolics are used in a variety of coatings applications—baked-on coatings, coatings on cans, drums, metal pipe, electrical insulation, varnishes, and metal primers. The phenolic resins are generally too hard and brittle to be used alone for the coatings applications but blends with alkyds, polyethylene, and epoxy resins perform well. Laminates of cellulose paper, cotton fabric, glass and asbestos cloths, and wood veneer with phenolics are made in various forms (sheet, rod, tubes) that can be machined. These find wide uses as printed-circuit boards, gears, cams and protective and decorative surfaces for tables, furniture, kitchen and bathroom countertops, and walls. Composites containing phenolics are used as the ablative coating for space reentry vehicles, aircraft interiors, and brakes. Other applications of phenolics include molded objects (switches, pump housings, cutlery handles, oven and toaster parts), friction materials (brake lining, transmission bands), foam insulation, carbonless copy paper, and the binder for sand in the manufacture of foundry molds for molded-metal casing.

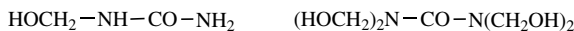
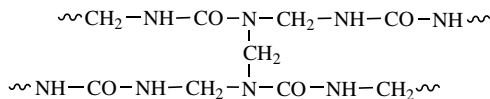
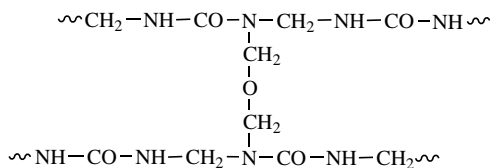
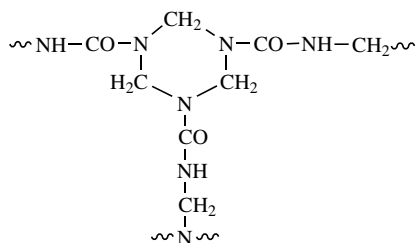
### 2-12c Amino Plastics

The amino resins or plastics, closely related to the phenolics in both synthesis and applications, are obtained by the polymerization of formaldehyde with urea (**XXVII**) ( $f = 4$ ) or melamine (**XXVIII**) ( $f = 6$ ). Synthesis of the amino plastics can be carried out either in alkaline or acidic conditions [Drumm and LeBlanc, 1972; Nair and Francis, 1983; Updegraff, 1985]. Control of the extent of reaction is achieved by pH and temperature control. The prepolymer can be made at various pH levels depending on the reaction temperature chosen. Polymerization is stopped by cooling and bringing the pH close to neutral. Curing of the prepolymer involves heating, usually in the presence of an added acid catalyst.



Polymerization of urea and formaldehyde yields various methylolureas such as **XXIX** and a mixture of higher oligomers as was the case for the phenolic prepolymers. The relative

amounts of the various components is dependent on reaction conditions. The crosslinking reaction involves methylene (**XXX**), methylene ether (**XXXI**), and cyclic (**XXXII**) bridges between urea units [Ebdon and Heaton, 1977; Tomita and Ono, 1979]. As in the

**XXIXa****XXIXb****XXX****XXXI****XXXII**

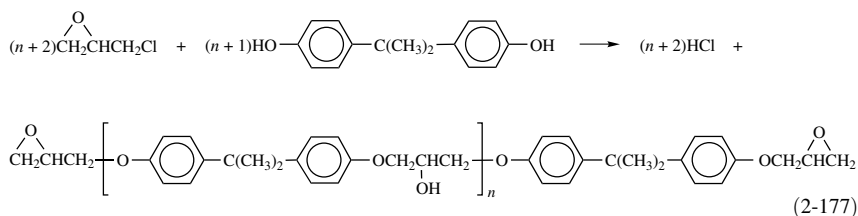
phenol-formaldehyde system, there is considerable evidence that the assumption of equal reactivity of functional groups is invalid for both urea and formaldehyde [Kumar and Katiyar, 1990; Tomita and Hirose, 1977]. The formation and curing of prepolymers from formaldehyde and melamine (2,4,6-triamino-*s*-triazine) follows in a similar manner.

The United States production of amino plastics was more than 3 billion pounds in 2001. The urea-formaldehyde polymers account for slightly more than 85% of the total. The amino plastics are similar in properties to the phenolics but are clearer and colorless. They are also harder but have somewhat lower impact strength and resistance to heat and moisture. The melamine resins are better than the ureas in hardness and resistance to heat and moisture. The melamine and urea resins are rated for continuous use at temperatures of 130–150°C and 100°C, respectively. The general applications of the amino and phenolic plastics are the same but there are uses where the amino plastics are superior. The melamine resins find an important niche due to their combination of clarity and lack of color compared to the phenolics and their superior hardness and heat and moisture resistance compared to

urea resins. Molding and laminating techniques are used to produce colored dinnerware and dinnerware with decorative patterns. A combination of phenolic and melamine plastics are used to produce decorative laminated plastic sheets for tabletop and counters. The combination gives a superior product—a phenolic backing imparts superior mechanical properties while a top melamine layer imparts outstanding clarity and hardness. Amino resins are used to impart crease resistance and wash-and-wear properties to cellulosic fabrics. A garment with its appropriate creases and containing the low-molecular-weight amino resin is heated to achieve curing. Curing involves reaction of the amino resin with hydroxyl groups of the cellulosic fabric, and this “sets” the garment into its shape. Amino resins also find extensive use as automotive paints; the cheaper ureas are used as primers while the melamines are used as topcoats.

## 2-12d Epoxy Resins

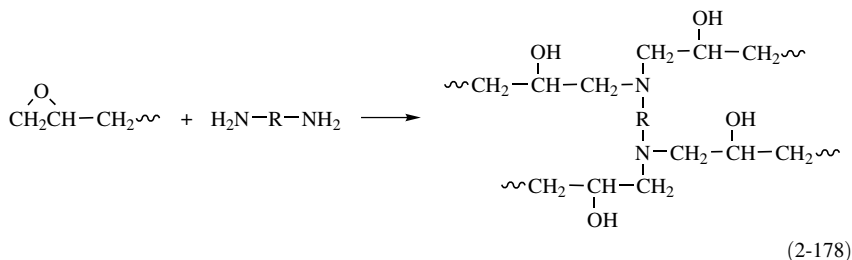
Epoxy resins or plastics are typically formed by the reaction of epichlorohydrin and bisphenol A [Dewprashad and Eisenbraun, 1994; McAdams and Gannon, 1988] (Eq. 2-177).



The reaction actually involves the sodium salt of bisphenol A since polymerization is carried out in the presence of an equivalent of sodium hydroxide. Reaction temperatures are in the range 50–95°C. Side reactions (hydrolysis of epichlorohydrin, reaction of epichlorohydrin with hydroxyl groups of polymer or impurities) as well as the stoichiometric ratio need to be controlled to produce a prepolymer with two epoxide end groups. Either liquid or solid prepolymers are produced by control of molecular weight; typical values of  $n$  are less than 1 for liquid prepolymers and in the range 2–30 for solid prepolymers.

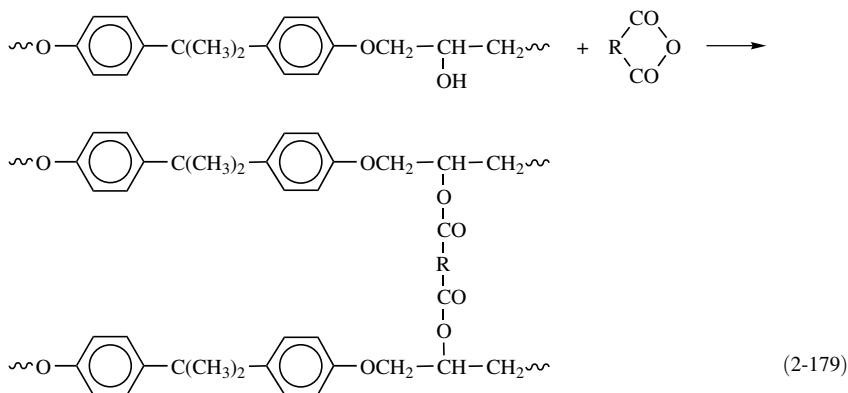
Epichlorohydrin is reacted with a variety of hydroxy, carboxy, and amino compounds to form monomers with two or more epoxide groups, and these monomers are then used in the reaction with bisphenol A [Lohse, 1987]. Examples are the diglycidyl derivative of cyclohexane-1,2-dicarboxylic acid, the triglycidyl derivatives of *p*-aminophenol and cyanuric acid, and the polyglycidyl derivative of phenolic prepolymers. Epoxidized diolefins are also employed (Sec. 9-8).

A variety of coreactants are used to cure epoxy resins, either through the epoxide or hydroxyl groups [Mezzenga et al., 2000; Mijovic and Wijaya, 1994; Trappe et al., 1991]. Polyamines are the most common curing agent with reaction involving ring-opening addition of amine (Eq. 2-178). Both primary and secondary amines are used; primary amines are more reactive than secondary amines [Glover et al., 1988; Zvetkov, 2002]. Since each nitrogen–hydrogen bond is reactive in the curing reaction, primary and secondary amine groups are bi- and monofunctional, respectively. A variety of amines are used as crosslinking agents, including diethylene triamine ( $f = 5$ ), triethylene tetramine ( $f = 6$ ), 4,4'-diaminodiphenylmethane ( $f = 4$ ), and polyaminoamides (e.g., the diamide formed from diethylene triamine



and a dimerized or trimerized fatty acid). Other types of compounds have also been used to cure epoxy resins via the epoxide groups, including polythiols, dicyandiamide (cyanoguanidine), diisocyanates, and phenolic prepolymers. Some of these agents require weak bases such as tertiary amines and imidazole derivatives to accelerate the curing process.

Crosslinking of epoxy plastics through the hydroxyl groups of the repeat unit is used for prepolymers with low epoxide group contents. The most common curing agent is phthalic anhydride although other acid anhydrides such as tetrahydrophthalic, nadic methyl, and chloroendic anhydrides are used in specialty applications:



Curing of epoxy resins can also be achieved by ring-opening polymerization of epoxide groups using either Lewis acids (including those generated photochemically) or Lewis bases (Sec. 7-2).

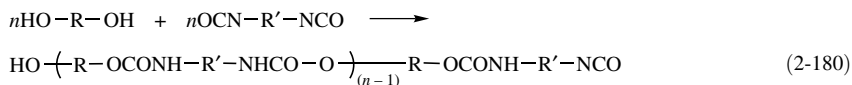
Most epoxy formulations contain diluents, fillers or reinforcement materials, and toughening agents. Diluents may be reactive (mono- and diepoxides) or nonreactive (di-*n*-butyl phthalate). Toughening (flexibilizing) agents such as low-molecular-weight polyesters or 1,3-butadiene-acrylonitrile copolymers with carboxyl end groups or aliphatic diepoxides participate in the crosslinking process.

Epoxy resins possess high chemical and corrosion resistance, toughness and flexibility, good mechanical and electrical behavior, and outstanding adhesion to many different substrates. A wide range of products varying in properties and curing temperature are obtained for specific applications by proper selection of the monomers, additives, and curing agents. Use temperatures are in the range 90–130°C. The United States production of epoxy polymers was about 700 million pounds in 2001. The applications for epoxies fall into two

categories—coatings and structural. Coatings applications include marine, maintenance, drum, and can coatings. Automotive primer coatings involve epoxy resins with ionic charges (either carboxylate or quaternary ammonium ion) that allow for electrodeposition of the resin. Waterborne epoxy coatings have been developed for beer and beverage containers. Structural composites are used in the military (missile casings, tanks), aircraft (rudders, wing skins, flaps), automobiles (leaf springs, drive shafts), and pipe in the oil, gas, chemical, and mining industries. Laminates are used in the electrical and electronics industries (circuit-board substrate, encapsulation of devices such as transistors, semiconductors, coils). Other applications include industrial and terrazzo flooring, repair of highway concrete cracks, coatings for roads and bridges, and a wide range of adhesive applications.

### 2-12e Polyurethanes

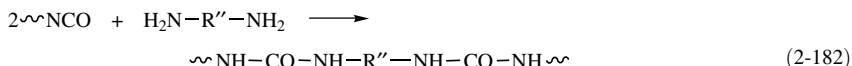
The synthesis of polyurethanes is usually presented as proceeding via the formation of carbamate (urethane) linkages by the reaction of isocyanates and alcohols:



However, this is an oversimplification since other reactions are also usually involved [Backus, 1977; Backus et al., 1988; Occhiello and Corti, 2003]. Foamed products such as seat cushions and bedding are the largest applications of polyurethanes. Water is often deliberately added in the production of flexible polyurethane foams. Isocyanate groups react with water to form urea linkages in the polymer chain with the evolution of carbon dioxide. The



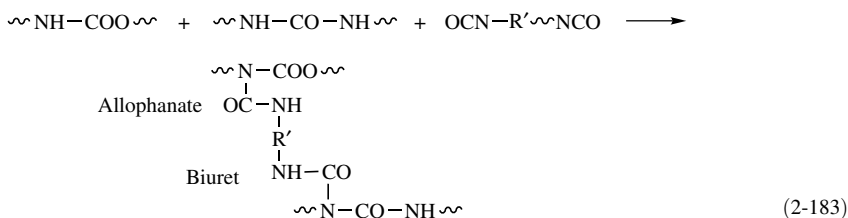
carbon dioxide acts as the *blowing agent* to form the foamed structure of the final product. (Low-boiling solvents such as fluorotrichloromethane are usually added to act as blowing agents in the synthesis of rigid polyurethane foamed products.) Many polyurethanes are synthesized using mixtures of diols and diamines. The diamines react with isocyanate groups to introduce additional urea linkages into the polymer. Thus, the typical polyurethane actually contains both urethane and urea repeat units.



(There are even some instances where only diamines are used in the synthesis. The polymer is then a polyurea although the manufacturer typically refers to it as a *polyurethane*.)

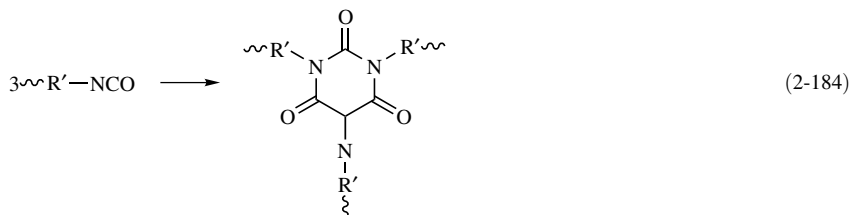
The situation is even more complex since the N—H bonds of both urethane and urea linkages add to isocyanate groups to form allophanate and biuret linkages, respectively. These

reactions result in branching and crosslinking of the polymer. Equation 2-183 shows how a diisocyanate crosslinks the urethane and urea groups from two different polymer chains. The



relative amounts of allophanate and biuret crosslinks in the polymer depend on the relative amounts of urea and urethane groups (which, in turn, depends on the relative amounts of diamine and diol) and reaction conditions. There is a greater tendency to biuret linkages since the urea N—H is more reactive than the urethane N—H.

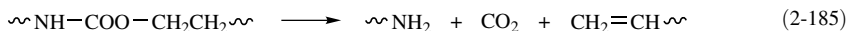
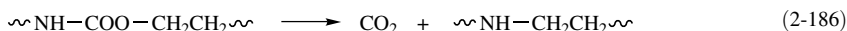
Trimerization of isocyanate groups to form isocyanurates also occurs and serves as an additional source of branching and crosslinking:



These reactions present a complexity in carrying out polymerization. Simultaneously, we have the ability to vary polymer properties over a wide range by control of the relative amounts of reactants and the polymerization conditions. Further control of the final product is achieved by choice of monomers. Most polyurethanes involve a macroglycol (a low-molecular-weight polymer with hydroxyl end groups), diol or diamine, and diisocyanate. The macroglycol (also referred to as a *polyol*) is a polyether or polyester synthesized under conditions that result in two or more hydroxyl end groups. (Details of polyurethane synthesis involving macroglycols are described in Sec. 2-13c.) The diol monomers include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and *p*-di(2-hydroxyethoxy)benzene. The diamine monomers include diethyltoluenediamine, methylenebis(*p*-aminobenzene), and 3,3'-dichloro-4,4'-diaminodiphenylmethane. The diisocyanate monomers include hexamethylene diisocyanate, toluene 2,4- and 2,6-diisocyanates, and naphthalene 1,5-diisocyanate. Alcohol and isocyanate reactants with functionality greater than 2 are also employed.

The extent of crosslinking in polyurethanes depends on a combination of the amount of polyfunctional monomers present and the extent of biuret, allophanate, and trimerization reactions [Dusek, 1987]. The latter reactions are controlled by the overall stoichiometry and the specific catalyst present. Stannous and other metal carboxylates as well as tertiary amines are catalysts for the various reactions. Proper choice of the specific catalyst result in differences in the relative amounts of each reaction. Temperature also affects the extents

of the different reactions. Polymerization temperatures are moderate, often near ambient and usually no higher than 100–120°C. Significantly higher temperatures are avoided because polyurethanes undergo several different types of degradation reactions, such as



as well as decomposition back to the alcohol and isocyanate monomers. Overall control in the synthesis of polyurethane foamed products also requires a balance between the polymerization–crosslinking and blowing processes. An imbalance between the chemical and physical processes can result in a collapse of the foamed structures (before solidification by crosslinking and/or cooling) or imperfections in the foam structures, which yields poor mechanical strength and performance.

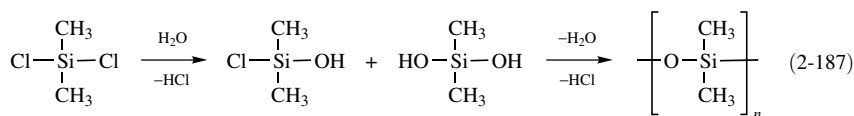
The wide variations possible in synthesis give rise to a wide range of polyurethane products including flexible and rigid foams and solid elastomers, extrusions, coatings, and adhesives. Polyurethanes possess good abrasion, tear, and impact resistance coupled with oil and grease resistance. The global production of polyurethanes was more than 15 billion pounds in 1997. Flexible foamed products include upholstered furniture and auto parts (cushions, backs, and arms), mattresses, and carpet underlay. Rigid foamed products with a closed-cell morphology possess excellent insulating properties and find extensive use in commercial roofing, residential sheathing, and insulation for water heaters, tanks, pipes, refrigerators, and freezers. Solid elastomeric products include forklift tires, skateboard wheels, automobile parts (bumpers, fascia, fenders, door panels, gaskets for trunk, windows, windshield, steering wheel, instrument panel), and sporting goods (golf balls, ski boots, football cleats). Many of these foam and solid products are made by reaction injection molding (RIM), a process in which a mixture of the monomers is injected into a mold cavity where polymerization and crosslinking take place to form the product. Reaction injection molding of polyurethanes, involving low-viscosity reaction mixtures and moderate reaction temperatures, is well suited for the economical molding of large objects such as automobile fenders. (Many of the elastomeric polyurethane products are *thermoplastic elastomers*; see Sec. 2-13c.)

## 2-12f Polysiloxanes

Polysiloxanes, also referred to as *silicones*, possess an unusual combination of properties that are retained over a wide temperature range (–100 to 250°C). They have very good low-temperature flexibility because of the low  $T_g$  value (–127°C). Silicones are very stable to high temperature, oxidation, and chemical and biological environments, and possess very good low-temperature flexibility because of the low  $T_g$  values (–127°C for dimethylsiloxane), a consequence of the long Si–O bond (1.64 Å compared to 1.54 Å for C–C) and the wide Si–O–Si bond angle (143° compared to 109.5° for C–C–C). The Si–O bond is stronger than the C–C bond (~450 vs. 350 kJ/mol) and siloxanes are very stable to high temperature, oxidation, chemical and biological environments, and weathering, and also possess good dielectric strength, and water repellency. The United States production of polysiloxane fluids, resins, and elastomers was about 800 million pounds in 2001. Fluid applications include fluids for hydraulics, antifoaming, water-repellent finishes for textiles,

surfactants, greases, lubricants, and heating baths. Resins are used as varnishes, paints, molding compounds, electrical insulation, adhesives, laminates, and release coatings. Elastomer applications include sealants, caulks, adhesives, gaskets, tubing, hoses, belts, electrical insulation such as automobile ignition cable, encapsulating and molding applications, fabric coatings, encapsulants, and a variety of medical applications (antiflatulents, heart valves, encasing of pacemakers, prosthetic parts, contact lenses, coating of plasma bottles to avoid blood coagulation). Silicone elastomers differ markedly from other organic elastomers in the much greater effect of reinforcing fillers in increasing strength properties.

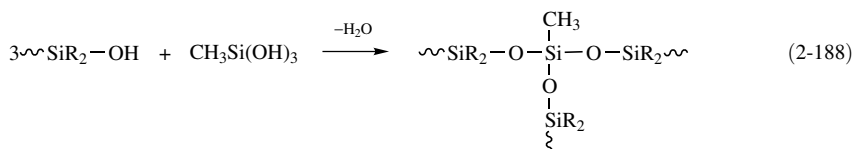
Polysiloxane fluids and resins are obtained by hydrolysis of chlorosilanes such as dichlorodimethyl-, dichloromethylphenyl-, and dichlorodiphenylsilanes [Brydson, 1999; Hardman and Torkelson, 1989]. The chlorosilane is hydrolyzed with water to a mixture of chlorohydroxy and dihydroxysilanes (referred to as *silanols*), which react with each other by dehydration and dehydrochlorination. The product is an equilibrated mixture of approximately equal



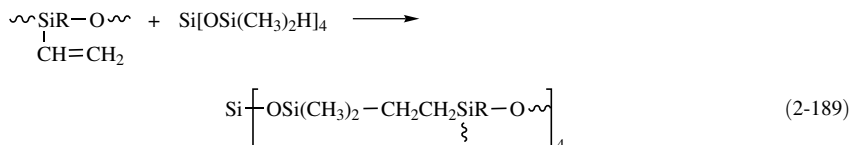
amounts of cyclic oligomers and linear polysiloxanes. The amount of cyclics can vary from 20 to 80% depending on reaction conditions. The major cyclic oligomer is the tetramer with progressively decreasing amounts of higher cyclics. After the initial equilibration, a disiloxane-terminating agent such as  $[(\text{CH}_3)_3\text{Si}]_2\text{O}$  is added to stabilize the reaction mixture by termination of the linear species. The process may be carried out under either acidic or basic conditions depending on the desired product molecular weight. Basic conditions favor the production of higher molecular weight. Mixtures of cyclic oligomers and linear polymer may be employed directly as silicone fluids, or the cyclic content may be decreased prior to use by devolatilization (heating under vacuum). The synthesis of silicone resins proceeds in a similar manner, except that the reaction mixture includes trichlorosilanes to bring about more extensive polymerization with crosslinking. Typically, the polymer product will be separated from an aqueous layer after the hydrolytic step, heated in the presence of a basic catalyst such as zinc octanoate to increase the polymer molecular weight and decrease the cyclic content, cooled, and stored. The final end-use application of this product involves further heating with a basic catalyst to bring about more extensive crosslinking.

Silicone elastomers are either *room-temperature vulcanization* (RTV) or *heat-cured silicone rubbers* depending on whether crosslinking is accomplished at ambient or elevated temperature. (The term *vulcanization* is a synonym for crosslinking. *Curing* is typically also used as a synonym for crosslinking but often refers to a combination of additional polymerization plus crosslinking.) RTV and heat-cured silicone rubbers typically involve polysiloxanes with degrees of polymerizations of 200–1500 and 2500–11,000, respectively. The higher-molecular-weight polysiloxanes cannot be synthesized by the hydrolytic step polymerization process. This is accomplished by ring-opening polymerization using ionic initiators (Sec. 7-11a). “One-component” RTV rubbers consist of an airtight package containing silanol-terminated polysiloxane, crosslinking agent (methyltriacetoxysilane, and catalyst (e.g., dibutyltin laurate). Moisture from the atmosphere converts the crosslinking agent to the

corresponding silanol (acetic acid is a by-product),  $\text{CH}_3\text{Si}(\text{OH})_3$ , which brings about further polymerization combined with crosslinking of the polysiloxane:

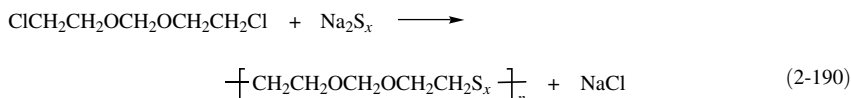


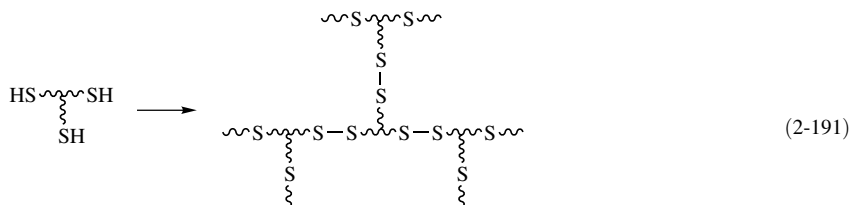
Two-component RTV formulations involve separate packages for the polysiloxane and crosslinking agent. Hydrosilation curing involves the addition reaction between a polysiloxane containing vinyl groups (obtained by including methylvinylchlorosilane in the original reaction mixture for synthesis of the polysiloxane) and a siloxane crosslinking agent that contains Si—H functional groups, such as 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (Eq. 2-189). The reaction is catalyzed by chloroplatinic acid or other soluble Pt compound. Hydride functional siloxanes can also crosslink silanol-terminated polysiloxanes. The reaction is catalyzed by tin salts and involves  $\text{H}_2$  loss between Si—H and Si—O—H groups. Heat curing of silicone rubbers usually involves free-radical initiators such as benzoyl peroxide (Sec. 9-2c). Hydrosilation at 50–100°C is also practiced.



## 2-12g Polysulfides

Polysulfide elastomers are produced by the reaction of an aliphatic dihalide, usually bis-(2-chloroethyl)formal, with sodium polysulfide under alkaline conditions [Brydson, 1999; Ellerstein, 1988] (Eq. 2-190). The reaction is carried out with the dihalide suspended in an aqueous magnesium hydroxide phase. The value of  $x$  is slightly above 2. The typical polymerization system includes up to 2% 1,2,3-trichloropropane. The polymerization readily yields a polymer with a very high molecular weight, but this is not desirable until its end-use application. The molecular weight is lowered and the *polysulfide rank* (value of  $x$ ) is simultaneously brought close to 2 by reductive treatment with NaSH and  $\text{Na}_2\text{SO}_3$  followed by acidification. The result is a liquid, branched polysulfide with terminal thiol end groups and a molecular weight in the range 1000–8000. Curing to a solid elastomer is accomplished by oxidation of thiol to disulfide links by oxidants such as lead dioxide and *p*-quinone dioxime (Eq. 2-191).

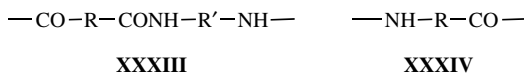




Polysulfides, often referred to as *thiokols*, are not produced in high volumes. These are specialty materials geared toward a narrow market. The annual production of polysulfides in the United States exceeds 50 million pounds. The advantages and disadvantages of polysulfides both reside in the disulfide linkage. They possess low temperature flexibility and very good resistance to ozone, weathering, oil, solvent (hydrocarbons as well as polar solvents such as alcohols, ketones, esters), and moisture. However, polysulfides have poor thermal stability and creep resistance, have low resilience, and are malodorous. (Aromatic polysulfides do not have the same deficiencies; see Sec. 2-14d.) The major applications of polysulfides are as sealants, caulks, gaskets, O-rings, and cements for insulating glass and fuel tanks, in marine applications, and in gasoline and fuel hose.

## 2-13 STEP COPOLYMERIZATION

It should be apparent that step polymerization is a versatile means of synthesizing a host of different polymers. The chemical structure of a polymer can be varied over a wide range in order to obtain a product with a particular combination of desirable properties. One can vary the functional group to produce a polyester, polyamide, or some other class of polymer as desired. Further, for any specific class of polymer, there is a considerable choice in the range of structures that can be produced. Consider, for example, that polyamides with either of the general structures **XXXIII** and **XXXIV** can be synthesized depending on whether one uses the reaction of a diamine with a diacid or the self-reaction of an amino acid. A range of different polyamides can be obtained by varying the choice of the R and R' groups in structure **XXXIII** and the R group in structure **XXXIV**. Thus, for example, one can produce nylon 6/6 and nylon 6/10 by the reactions of hexamethylene diamine with adipic and sebacic acids, respectively. Nylon 6/10 is more flexible and moisture-resistant than nylon 6/6 because of the longer hydrocarbon segment derived from sebacic acid.



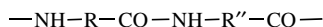
### 2-13a Types of Copolymers

Further variation is possible in the polymer structure and properties by using mixtures of the appropriate reactants such that the polymer chain can have different R and R' groups. Thus polyamide structures of types **XXXV** and **XXXVI** are possible variations on structures **XXXIII** and **XXXIV**, respectively. A polymer such as **XXXV** or **XXXVI** has two different repeat units and is referred to as a *copolymer*; the process by which it is synthesized is

referred to as a *copolymerization*. Polymers with structures **XXXIII** and **XXXIV**, each containing a single repeat unit, may be referred to as *homopolymers* to distinguish them from copolymers.

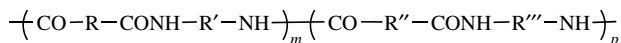


**XXXV**



**XXXVI**

Different types of copolymers are possible with regard to sequencing of the two repeating units relative to each other. Thus a copolymer with an overall composition indicated by **XXXV** could have the *alternating copolymer* structure shown in **XXXV**, in which the R, R', R'', and R''' groups alternate in that order over and over again along the polymer chain; or the *block copolymer* structure **XXXVII**, in which blocks of one type of homopolymer structure are attached to blocks of another type of homopolymer structure; or the *statistical copolymer* structure, in which there is an irregular (statistical) distribution of R and R'' groups as well as R' and R''' groups along the copolymer chain. Similarly, one can have alternating, block, and statistical copolymers for the overall composition **XXXVI**.



**XXXVII**

For the statistical copolymer the distribution may follow different statistical laws, for example, Bernoullian (zero-order Markov), first- or second-order Markov, depending on the specific reactants and the method of synthesis. This is discussed further in Secs. 6-2 and 6-5. Many statistical copolymers are produced via Bernoullian processes wherein the various groups are randomly distributed along the copolymer chain; such copolymers are *random copolymers*. The terminology used in this book is that recommended by IUPAC [Ring et al., 1985]. However, most literature references use the term *random copolymer* independent of the type of statistical distribution (which seldom is known).

The alternating and statistical copolymer structures can be symbolized as

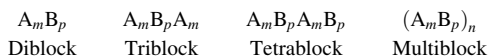


Alternating copolymer



Statistical copolymer

where A and B represent two different repeating units. Different block copolymers are distinguished by the number of blocks per molecule, for example



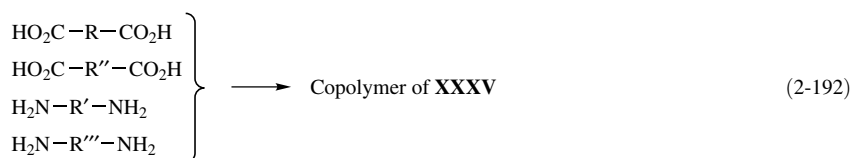
which are referred to as AB diblock, ABA triblock, ABAB tetrablock, and AB multiblock copolymers, respectively. For the various block copolymers the values of  $m$  and  $p$  as well



## 2-13b Methods of Synthesizing Copolymers

### 2-13b-1 Statistical Copolymers

The copolymerization of a mixture of monomers offers a route to statistical copolymers; for instance, a copolymer of overall composition **XXXV** is synthesized by copolymerizing a mixture of the four monomers

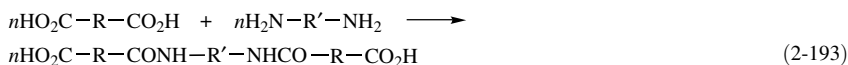


It is highly unlikely that the reactivities of the various monomers would be such as to yield either block or alternating copolymers. The quantitative dependence of copolymer composition on monomer reactivities has been described [Korshak et al., 1976; Mackey et al., 1978; Russell et al., 1981]. The treatment is the same as that described in Chap. 6 for chain copolymerization (Secs. 6-2 and 6-5). The overall composition of the copolymer obtained in a step polymerization will almost always be the same as the composition of the monomer mixture since these reactions are carried out to essentially 100% conversion (a necessity for obtaining high-molecular-weight polymer). Further, for step copolymerizations of monomer mixtures such as in Eq. 2-192 one often observes the formation of random copolymers. This occurs either because there are no differences in the reactivities of the various monomers or the polymerization proceeds under reaction conditions where there is extensive interchange (Sec. 2-7c). The use of only one diacid or one diamine would produce a variation on the copolymer structure with either  $\text{R} = \text{R}'$  or  $\text{R}' = \text{R}'''$  [Jackson and Morris, 1988].

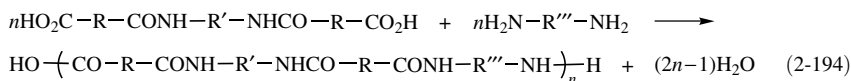
Statistical copolymers containing repeating units each with a different functional group can be obtained using appropriate mixture of monomers. For example, a polyesteramide can be synthesized from a ternary mixture of a diol, diamine, and diacid or a binary mixture of a diacid and amine-alcohol [East et al., 1989].

### 2-13b-2 Alternating Copolymers

The alternating copolymer of composition **XXXV** cannot be synthesized. However, it is possible to synthesize an alternating copolymer in which  $\text{R}'' = \text{R}$  by using a two-stage process [Ueda, 1999]. In the first stage, a diamine is reacted with an excess of diacid to form a trimer

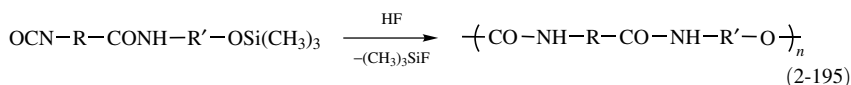
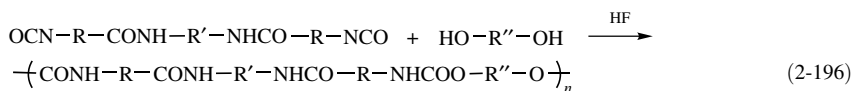


The trimer is then reacted with an equimolar amount of a second diamine in the second stage:



Alternating copolymers with two different functional groups are similarly synthesized by using preformed reactants [Adduci and Amone, 1989; Gopal and Srinivasan, 1986; Liou and

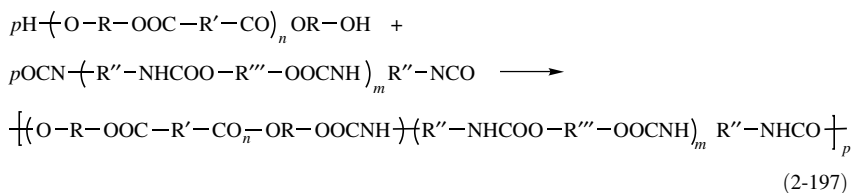
Hsiao, 2001b; Mormann et al., 1989]. For example, polyamideurethanes analogous to **XXXIV** and **XXXV** are obtained by the polymerizations



The silyl ether derivative of the alcohol is used in Eq. 2-195 since the corresponding alcohol  $\text{OCN-R-CONH-R'-OH}$  cannot be isolated because of the high degree of reactivity of isocyanate and alcohol groups toward each other.

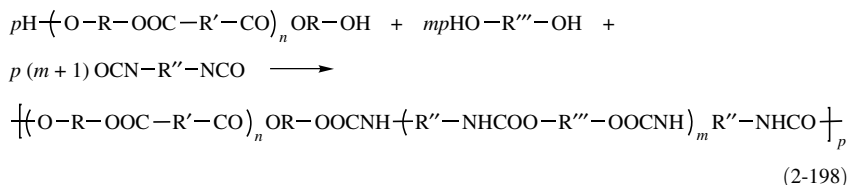
### 2-13b-3 Block Copolymers

There are two general methods for synthesizing block copolymers [Gaymans et al., 1989; Hadjichristidis, 2002; Hedrick et al., 1989; Klein et al., 1988; Leung and Koberstein, 1986; Reiss et al., 1985; Speckhard et al., 1986]. The two methods, referred to here as the *one-prepolymer* and *two-prepolymer* methods, are described below for block copolymers containing different functional groups in the two repeat units. They are equally applicable to block copolymers containing the same functional group in the two repeating units. The two-prepolymer method involves the separate synthesis of two different prepolymers, each containing appropriate end groups, followed by polymerization of the two prepolymers via reaction of their end groups. Consider the synthesis of a polyester-*block*-polyurethane. A hydroxy-terminated polyester prepolymer is synthesized from  $\text{HO-R-OH}$  and  $\text{HOOC-R'-COOH}$  using an excess of the diol reactant. An isocyanate-terminated polyurethane prepolymer is synthesized from  $\text{OCN-R''-NCO}$  and  $\text{HO-R'''-OH}$  using an excess of the diisocyanate reactant. The  $\alpha,\omega$ -dihydroxypolyester and  $\alpha,\omega$ -diisocyanatopolyurethane prepolymers, referred to as *macrodiol* and *macrodiisocyanate* respectively, are subsequently polymerized with each other to form the block copolymer.



The block lengths  $n$  and  $m$  can be varied separately by adjusting the stoichiometric ratio  $r$  of reactants and conversion in each prepolymer synthesis. In typical systems the prepolymers have molecular weights in the range 500–6000. The molecular weight of the block copolymer is varied by adjusting  $r$  and conversion in the final polymerization. A variation of the two-prepolymer method involves the use of a coupling agent to join the prepolymers. For example, a diacyl chloride could be used to join together two different macrodiols or two different macrodiamines or a macrodiol with a macrodiamine.

The one-prepolymer method involves one of the above prepolymers with two "small" reactants. The macrodiol is reacted with a diol and diisocyanate



The block lengths and the final polymer molecular weight are again determined by the details of the prepolymer synthesis and its subsequent polymerization. An often-used variation of the one-prepolymer method is to react the macrodiol with excess diisocyanate to form an isocyanate-terminated prepolymer. The latter is then *chain-extended* (i.e., increased in molecular weight) by reaction with a diol. The one- and two-prepolymer methods can in principle yield exactly the same final block copolymer. However, the dispersity of the polyurethane block length ( $m$  is an average value as are  $n$  and  $p$ ) is usually narrower when the two-prepolymer method is used.

The prepolymers described above are one type of *telechelic polymer*. A telechelic polymer is one containing one or more functional end groups that have the capacity for selective reaction to form bonds with another molecule. The functionality of a telechelic polymer or prepolymer is equal to the number of such end groups. The macrodiol and macrodiisocyanate telechelic prepolymers have functionalities of 2. Many other telechelic prepolymers were discussed in Sec. 2-12. (The term *functional polymer* has also been used to describe a polymer with one or more functional end groups.)

### 2-13c Utility of Copolymerization

There has been enormous commercial success in the synthesis of various copolymers. Intense research activity continues in this area of polymer science with enormous numbers of different combinations of repeating units being studied. Copolymer synthesis offers the ability to alter the properties of a homopolymer in a desired direction by the introduction of an appropriately chosen second repeating unit. One has the potential to combine the desirable properties of two different homopolymers into a single copolymer. Copolymerization is used to alter such polymer properties as crystallinity, flexibility,  $T_m$ , and  $T_g$ . The magnitudes, and sometimes even the directions, of the property alternations differ depending on whether statistical, alternating, or block copolymers are involved. The crystallinity of statistical copolymers is lower than that of either of the respective homopolymers (i.e., the homopolymers corresponding to the two different repeating units) because of the decrease in structural regularity. The melting temperature of any crystalline material formed is usually lower than that of either homopolymer. The  $T_g$  value will be in between those for the two homopolymers. Alternating copolymers have a regular structure, and their crystallinity may not be significantly affected unless one of the repeating units contains rigid, bulky, or excessively flexible chain segments. The  $T_m$  and  $T_g$  values of an alternating copolymer are in between the corresponding values for the homopolymers. Block copolymers often show significantly different behavior compared to alternating and statistical copolymers. Each type of block in a block copolymer shows the behavior (crystallinity,  $T_m$ ,  $T_g$ ) present in the corresponding homopolymer as long as the block lengths are not too short. This behavior is typical since A blocks from different polymer molecules aggregate with each other and, separately, B blocks from

different polymer molecules aggregate with each other. This offers the ability to combine the properties of two very different polymers into one block copolymer. The exception to this behavior occurs infrequently—when the tendency for cross-aggregation between A and B blocks is the same as for self-aggregation of A blocks with A blocks and B blocks with B blocks.

Most commercial utilizations of copolymerization fall into one of two groups. One group consists of various statistical (usually random) copolymers in which the two repeating units possess the same functional group. The other group of commercial copolymers consists of block copolymers in which the two repeating units have different functional groups. There are very few commercial statistical copolymers in which the two repeating units have different functional groups. The reasons for this situation probably reside in the difficulty of finding one set of reaction conditions for simultaneously performing two different reactions, such as amidation simultaneously with ether formation. Also, the property enhancements available through this copolymerization route are apparently not significant enough in most systems to motivate one to overcome the synthetic problem by the use of specially designed monomers. The same synthetic and property barriers probably account for the lack of commercial alternating copolymers in which the two repeating units have different functional groups. Similar reasons account for the general lack of commercial block copolymers in which the two repeating units have the same functional group. The synthetic problem here is quite different. Joining together blocks of the same type of repeat unit is not a problem, but preventing interchange (Sec. 2-7c) between the different blocks is often not possible. Scrambling of repeating units via interchange is also a limitation on producing alternating copolymers in which both repeating units have the same functional group. With all the present research activity in copolymer synthesis, one might expect the situation to be significantly different in the future.

### 2-13c-1 Statistical Copolymers

Statistical copolymerization is practiced in many of the polymerization systems discussed in Secs. 2-8 and 2-12. Mixtures of phenol with an alkylated phenol such as cresol or bisphenol A are used for producing specialty phenolic resins. Trifunctional reactants are diluted with bifunctional reactants to decrease the crosslink density in various thermosetting systems. Methylphenyl-, diphenyl-, and methylvinylchlorosilanes are used in copolymerization with dimethyldichlorosilane to modify the properties of the polysiloxane. Phenyl groups impart better thermal and oxidative stability and improved compatibility with organic solvents. Vinyl groups introduce sites for crosslinking via peroxides (Sec. 9-2c). Polysiloxanes with good fuel and solvent resistance are obtained by including methyltrifluoropropylchlorosilane. Flame retardancy is imparted to the polycarbonate from bisphenol A (Eq. 2-127) by statistical or block copolymerization with a tetrabromo derivative of bisphenol A.

Statistical copolymerization of ethylene glycol and 1,4-butanediol with dimethyl terephthalate results in products with improved crystallization and processing rates compared to poly(ethylene terephthalate). *Polyarylates* (trade names: *Ardel*, *Arylon*, *Durel*), copolymers of bisphenol A with iso- and terephthalate units, combine the toughness, clarity, and processibility of polycarbonate with the chemical and heat resistance of poly(ethylene terephthalate). The homopolymer containing only terephthalate units is crystalline, insoluble, sometimes infusible, and difficult to process. The more useful copolymers, containing both tere- and isophthalate units, are amorphous, clear, and easy to process. Polyarylates are used in automotive and appliance hardware and printed-circuit boards. Similar considerations in the copolymerization of iso- and terephthalates with 1,4-cyclohexanedimethanol or hexamethylene diamine yield clear, amorphous, easy-to-process copolyesters or copolyamides,

respectively, which are used as packaging film for meats, poultry, and other foods. The use of a mixture of unsaturated and saturated diacids or dianhydrides allows one to vary the crosslink density (which controls hardness and impact strength) in unsaturated polyesters (Sec. 2-12a). The inclusion of phthalic anhydride improves hydrolytic stability for marine applications.

### 2-13c-2 Block Copolymers

Polyurethane multiblock copolymers of the type described by Eqs. 2-197 and 2-198 constitute an important segment of the commercial polyurethane market. The annual global production is about 250 million pounds. These polyurethanes are referred to as *thermoplastic polyurethanes* (TPUs) (trade names: *Estane*, *Texin*). They are among a broader group of elastomeric block copolymers referred to as *thermoplastic elastomers* (TPEs). Crosslinking is a requirement to obtain the resilience associated with a rubber. The presence of a crosslinked network prevents polymer chains from irreversibly slipping past one another on deformation and allows for rapid and complete recovery from deformation.

Crosslinking in conventional elastomers is chemical; it is achieved by the formation of chemical bonds between copolymer chains (Sec. 9-2). Crosslinking of thermoplastic elastomers occurs by a physical process as a result of their microheterogeneous, two-phase morphology. This is a consequence of morphological differences between the two different blocks in the multiblock copolymer [Manson and Sperling, 1976]. One of the blocks, the polyester or polyether, is flexible (*soft*) and long while the other block, the polyurethane, is rigid (*hard*) and short. The rigidity of the polyurethane blocks is due to crystallinity (and hydrogen bonding). (For other thermoplastic elastomers such as those based on styrene and 1,3-dienes, the rigidity of the hard polystyrene blocks is due to their glassy nature; see Sec. 5-4a.) The hard blocks from different copolymer molecules aggregate together to form rigid domains at ambient temperature. These rigid domains comprise a minor, discontinuous phase dispersed in the major, continuous phase composed of the rubbery blocks from different copolymer chains. The rigid domains act as *physical crosslinks* to hold together the soft, rubbery domains in a network structure. Physical crosslinking, unlike chemical crosslinking, is thermally reversible since heating over the  $T_m$  of the hard blocks softens the rigid domains and the copolymer flows. Cooling reestablishes the rigid domains, and the copolymer again behaves as a crosslinked elastomer.

Thermoplastic elastomers have the important practical advantage over conventional elastomers that there is no need for the additional chemical crosslinking reaction, which means that fabrication of objects is achieved on conventional equipment for thermoplastics. The transition from a molten polymer to a solid, rubbery product is much faster and takes place simply on cooling. There are significant advantages in recycle times, the ability to recycle scrap, and overall production costs. However, thermoplastic elastomers generally are not as effective as chemically crosslinked elastomers in solvent resistance and resistance to deformation at high temperature. TPE is not used in applications such as automobile tires, where these properties are important. Thermoplastic polyurethanes are used in applications such as wire insulation, automobile fascia, footwear (lifts, ski boots, football cleats), wheels (industrial, skateboard), and adhesives, where such properties are not important. Two types of macrodiols are used in the synthesis of TPU—polyesters, as described in Eqs. 2-197 and 2-198, and  $\alpha,\omega$ -dihydroxypolyethers obtained by ring-opening polymerizations (Chap. 7) of ethylene and propylene oxides and tetrahydrofuran (THF). The polyester-based TPU is tougher and has better oil resistance while the polyether-based TPU shows better low temperature flexibility and better hydrolytic stability. *Spandex* (trade name: *Lycra*) fibers are

multiblock polyurethanes similar to TPU. Spandex typically differs from TPU in containing urea linkages instead of urethane in the hard blocks. These are obtained by using a diamine (instead of diol) to chain-extend isocyanate-terminated polyurethane prepolymers (synthesized from macroglycol and excess diisocyanate). Spandex fibers can undergo large, reversible deformations and are used in the manufacture of undergarments. The various multiblock polyurethanes are often referred to as *segmented polyurethanes*.

Other important thermoplastic elastomers are the multiblock polyetheresters (trade names: *Hytrel*, *Lomod*) and polyetheramides (trade names: *Pebax*, *Estamid*, *Grilamid*).

### 2-13c-3 Polymer Blends and Interpenetrating Polymer Networks

*Polymer blends* and *interpenetrating polymer networks* (IPNs) are different from copolymers but like copolymers are used to bring together the properties of different polymers [Paul et al., 1988]. The total of all polymer blends (produced by both step and chain reactions) is estimated at about 3% of the total polymer production—about 3 billion pounds per year in the United States. There is considerable activity in this area since “new” products can be obtained and markets expanded by the physical mixing together of existing products. No new polymer need be synthesized.

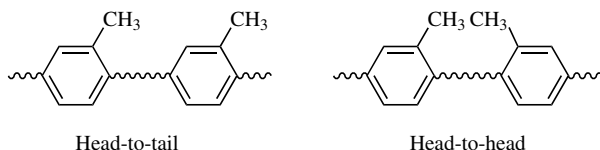
Polycarbonate is blended with a number of polymers including PET, PBT, acrylonitrile–butadiene–styrene terpolymer (ABS) rubber, and styrene–maleic anhydride (SMA) copolymer. The blends have lower costs compared to polycarbonate and, in addition, show some property improvement. PET and PBT impart better chemical resistance and processability, ABS imparts improved processability, and SMA imparts better retention of properties on aging at high temperature. Poly(phenylene oxide) blended with high-impact polystyrene (HIPS) (polybutadiene-*graft*-polystyrene) has improved toughness and processability. The impact strength of polyamides is improved by blending with an ethylene copolymer or ABS rubber.

The interpenetrating polymer network is a blend of two different polymer networks without covalent bonds between the two networks. An IPN is obtained by the simultaneous or sequential crosslinking of two different polymer systems [Kim et al., 1986; Klempner and Berkowski, 1987; Sperling, 1981, 1986, 1997]. IPN synthesis is the only way of achieving the equivalent of a physical blend for systems containing crosslinked polymers. A simultaneous IPN, referred to as *SIN*, is produced by reacting a mixture of the monomers, crosslinking reagents, and catalysts for the two crosslinking systems. A sequential IPN (SIPN) is produced by reacting a mixture of one crosslinked polymer and the ingredients for the other crosslinking system. *Semi*-IPN and *pseudo*-IPN refer to sequential and simultaneous synthesis, respectively, of interpenetrating polymer networks in which one of the polymers is not crosslinked. Interpenetrating polymer networks are possible for a pair of step polymerization systems, a pair of chain polymerization systems, or the combination of step and chain polymerization systems.

There are a number of commercial interpenetrating polymer networks, although they seldom are identified as IPNs. The inclusion of a thermoplastic with an unsaturated polyester decreases the amount of shrinkage of the latter on crosslinking. The inclusion of a polyurethane makes the unsaturated polyester tougher and more resilient. Other examples of useful IPNs are epoxy resin–polysulfide, epoxy resin–polyester, epoxy resin–polyurethane, polyurethane–poly(methyl methacrylate), polysiloxane–polyamide, and epoxy resin–poly(diallyl phthalate). Many of these are not “pure” IPNs as defined above because of the presence of grafting and crosslinking between the two components. This is usually an advantage in producing an IPN with minimal phase separation.

### 2-13c-4 Constitutional Isomerism

The previous discussions pertain to symmetric reactants such as adipic acid and hexamethylenediamine. The situation is more complicated for unsymmetric reactants such as tolylene 2,4-diisocyanate since the reactant can be incorporated into the polymer chain in two different ways. Unsymmetric reactants can be considered as having two different ends, a *head* (the more substituted end) and a *tail* (the less substituted end). The polymer has a *head-to-tail* (H-T) microstructure if successive monomer units are incorporated in the same way. The microstructure is *head-to-head* (H-H) whenever successive monomer units add in opposite ways. The H-H and H-T microstructures are constitutional isomers. The typical step polymerization is not regioselective and yields a random copolymer; specifically, H-T and H-H structures are randomly arranged in the polymer chain because the two functional groups do not differ sufficiently in reactivity and, more importantly, equilibration usually occurs between H-T and H-H units. There has been some recent success in synthesizing ordered polyamides and polyurethanes, all H-T and all H-H, by using preformed reactants [Li et al., 2001; Nishio et al., 2001; Ueda, 1999]. Some property differences between the ordered and random polymers have been observed, but the differences do not appear to be of major practical importance.



## 2-14 HIGH-PERFORMANCE POLYMERS

The driving force in polymer synthesis is the search for new polymers with improved properties to replace other materials of construction. Polymers are lightweight and can be processed easily and economically into a wide range of shapes and forms. The major synthetic efforts at present are aimed at polymers with *high temperature*, *liquid crystal*, *conducting*, and *non-linear optical* properties [Maier et al., 2001; Sillion, 1999]. There is an interrelationship between these efforts as will become apparent.

### 2-14a Requirements for High-Temperature Polymers

There has been a continuing and strong effort since the late 1950s to synthesize *high-temperature polymers*. The terms *heat-resistant* and *thermally stable polymer*, used synonymously with *high-temperature polymer*, refer to a *high-performance polymer* that can be utilized at higher use temperatures; that is, its mechanical strength and modulus, stability to various environments (chemical, solvent, UV, oxygen), and dimensional stability at higher temperatures match those of other polymers at lower temperatures. The impetus for heat-resistant polymers comes from the needs in such technological areas as advanced air- and spacecraft, electronics, and defense as well as consumer applications. The advantages of heat-resistant polymers are the weight savings in replacing metal items and the ease of processing polymeric materials into various configurations. Lightweight polymers possessing high strength, solvent and chemical resistance, and serviceability at temperatures in excess of 250°C would find a variety of potential uses, such as automotive and aircraft components

(including electrical and engine parts), nonstick and decorative coatings on cookware, structural components for aircraft, space vehicles, and missiles (including adhesives, gaskets, composite and molded parts, ablative shields), electronic and microelectronic components (including coatings, circuit boards, insulation), and components such as pipes, exhaust filter stacks, and other structural parts for the chemical and energy-generating (nuclear, geothermal) plants. The synthetic routes studied have involved inorganic and semiinorganic as well as organic systems. The efforts to date have been much more fruitful in the organic systems, which will be discussed in this section. Inorganic and semiinorganic systems will be considered separately in Sec. 2-15.

Both chemical and physical factors determine the heat resistance of polymers [Cassidy, 1980; Critchley et al., 1983; Hedrich and Labadie, 1996; Hergenrother, 1987; Marvel, 1975]. The strengths of the primary bonds in a polymer are the single most important determinant of the heat resistance of a polymer structure. This is especially critical with respect to the bonds in the polymer chain. Breakage of those bonds results in a deterioration of mechanical strength due to the drop in molecular weight. Bond breakages in pendant (side) groups on the polymer chain may not be as disastrous (unless it subsequently results in main-chain breakage). Aromatic ring systems (carbocyclic and heterocyclic) possess the highest bond strengths due to resonance stabilization and form the basis of almost all heat-resistant polymers. The inclusion of other functional groups in the polymer chain requires careful choice to avoid introducing weak links into an otherwise strong chain. Certain functional groups (ether, sulfone, imide, amide,  $\text{CF}_2$ ) are much more heat-resistant than others (alkylene, alicyclic, unsaturated,  $\text{NH}$ ,  $\text{OH}$ ).

A number of other factors weaken or strengthen the inherent heat resistance of a polymer chain. Polymer chains based on aromatic rings are desirable not only because of the high primary bond strengths but also because their rigid (stiff) polymer chains offer increased resistance to deformation and thermal softening. *Ladder* or *semiladder* polymer structures are possible for chains constructed of ring structures. A ladder polymer has a double-strand structure with an uninterrupted sequence of rings in which adjacent rings have two or more atoms in common (see structure **VII** in Sec. 1-2c). A semiladder structure has single bonds interconnecting some of the rings. The ladder polymer is more desirable from the viewpoint of obtaining rigid polymer chains. Also, the ladder polymer may be more heat-resistant since two bond cleavages (compared to only one bond cleavage for the semiladder structure) in the same ring are required before there is a large drop in chain length and mechanical strength. Ladder polymers have been synthesized but have no practical utility because of a complete lack of processability. High molecular weight and crosslinking are desirable for the same reason. Strong secondary attractive forces (including dipole-dipole and hydrogen bond interactions) improve heat resistance. Crystallinity increases heat resistance by serving as physical crosslinks that increase polymer chain rigidity and the effective secondary attractions. Branching lowers heat resistance by preventing close packing of polymer chains.

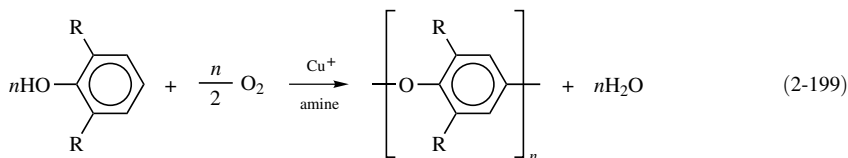
The factors that lead to increased heat resistance also present problems with respect to the synthesis of polymers and their utilization. Rigid polymer chains lead to decreased polymer solubility, and this may present a problem in obtaining polymer molecular weights sufficiently high to possess the desired mechanical strength. Low-molecular-weight polymers may precipitate from the reaction mixture and prevent further polymerization. Polymers with highly rigid chains may also be infusible and intractable, which makes it difficult to process them by the usual techniques into various shapes, forms, and objects. The synthesis of heat-resistant polymers may then require a compromise away from polymer chains with maximum rigidity in order to achieve better solubility and processing properties. There are two general approaches to this compromise. One approach involves the introduction of some

flexibilizing linkages, such as isopropylidene, C=O, and SO<sub>2</sub>, into the rigid polymer chain by using an appropriate monomer or comonomer. Such linkages decrease polymer chain rigidity while increasing solubility and processability. The other approach involves the synthesis of reactive telechelic oligomers containing functional end groups capable of reacting with each other. The oligomer, possessing a molecular weight of 500–4000 and two functional end groups, is formed into the desired end-use object by the usual polymer-processing techniques. Subsequent heating of the oligomer results in reaction of the functional end groups with each other. The oligomer undergoes polymerization to higher molecular weight (referred to as *chain extension*). Crosslinking may also occur depending on the functionality of the A groups.

A number of the polymers considered previously—polycarbonate, aramid, and polyarylate—were among the first commercial successes in the efforts to synthesize polymers with increasingly high use temperatures. In the following sections we will discuss some of the other commercially available heat-resistant polymers followed by a consideration of research efforts to move further up in the temperature scale.

## 2-14b Aromatic Polyethers by Oxidative Coupling

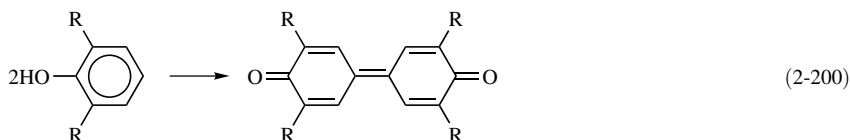
The *oxidative coupling* polymerization of many 2,6-disubstituted phenols to form aromatic polyethers is accomplished by bubbling oxygen through a solution of the phenol in an organic solvent (toluene) containing a catalytic complex of a cuprous salt and amine [Ayccock et al., 1988; Finkbeiner et al., 1977; Hay, 1998, 1999; Jayakannan and Ramakrishnan, 2001; Kobayashi and Higashimura, 2003]. Amine complexes of other oxidants such as cobalt and manganese salts are also useful.



Amines such as diethylamine, morpholine, pyridine, and *N,N,N',N'*-tetramethylethylenediamine are used to solubilize the metal salt and increase the pH of the reaction system so as to lower the oxidation potential of the phenol reactant. The polymerization does not proceed if one uses an amine that forms an insoluble metal complex. Some copper–amine catalysts are inactivated by hydrolysis via the water formed as a by-product of polymerization. The presence of a desiccant such as anhydrous magnesium sulfate or 4-Å molecular sieve in the reaction mixture prevents this inactivation. Polymerization is terminated by sweeping the reaction system with nitrogen and the catalyst is inactivated and removed by using an aqueous chelating agent.

Polymerization proceeds rapidly under mild conditions (25–50°C) for phenols containing small substituents. Phenols with one or more bulky *o*-substituents, such as isopropyl or *t*-butyl, undergo dimerization instead of polymerization (Eq. 2-200). Dimerization is also the major reaction for phenols with two *o*-methoxy substituents. The amine : cuprous ion ratio and the reaction temperature determine the extent of carbon–oxygen coupling (polymerization) relative to carbon–carbon coupling (dimerization), probably by affecting the nature of the complex formed among cuprous ion, amine, and reaction intermediate. Higher amine : cuprous ratios and lower reaction temperatures favor polymerization while dimerization is

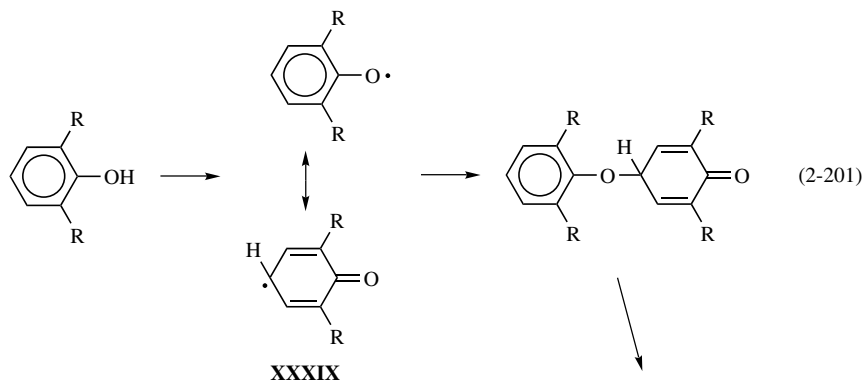
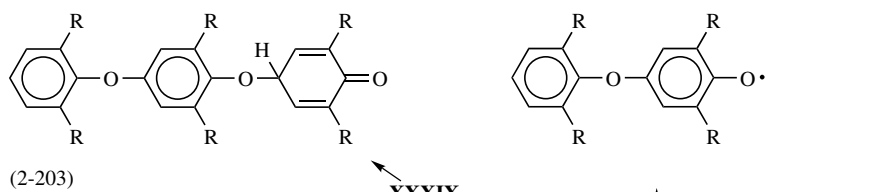
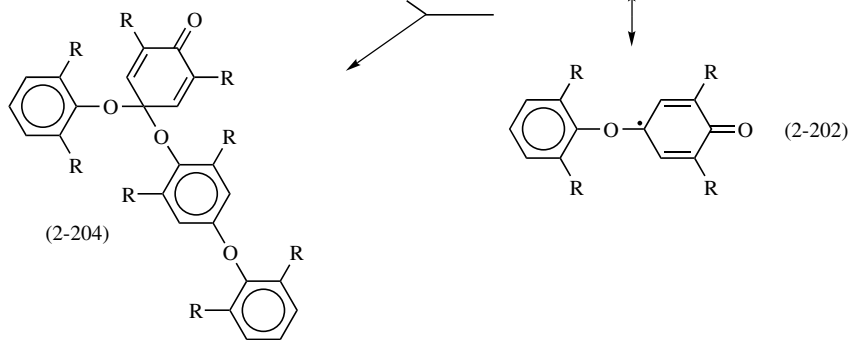
avored by higher temperatures and lower amine : cuprous ratios. Phenols with only one ortho substituent undergo branching during polymerization. Polymerization of phenols with only one ortho substituent, and even phenol itself, has been achieved by using sterically hindered amine ligands for the cuprous ion or other catalytic oxidant [Almou et al., 1999; Higashimura et al., 2000a].



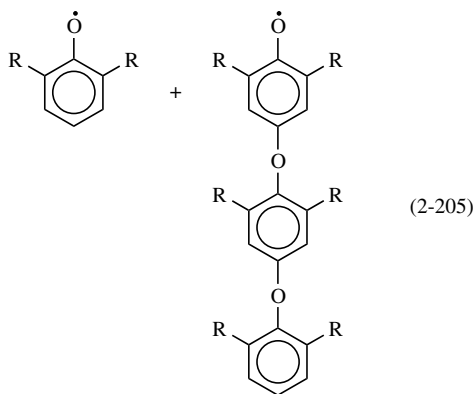
The mechanism of oxidative coupling polymerization of phenols involves the reaction sequence in Eqs. 2-201 through 2-205. The copper–amine complex functions as a catalyst for the oxidation by oxygen of the phenol to the monomeric phenoxy radical **XXXIX**. The phenoxy radical then undergoes dimerization by carbon–oxygen coupling (Eq. 2-201). Polymerization proceeds by oxidation of the dimer to the corresponding phenoxy radical (Eq. 2-202) followed by carbon–oxygen coupling reactions with monomeric phenoxy radical (Eq. 2-203) and itself (Eq. 2-204). The trimer continues to grow by repeating the oxidation-coupling sequence; the tetramer continues its growth by dissociation (Eq. 2-205) into two phenoxy radicals (a monomer and a trimer) that can undergo coupling reactions. Growth to high-molecular-weight polymer proceeds by successive oxidation-coupling sequences.

The polymer from 2,6-dimethylphenol is the commercial product referred to as *poly(p-phenylene oxide)* or PPO. The IUPAC name is poly(oxy-2,6-dimethyl-1,4-phenylene). PPO possesses very little measurable crystallinity ( $T_m = 262\text{--}267^\circ\text{C}$ ,  $T_g = 205\text{--}210^\circ\text{C}$ ). There is very little neat PPO used commercially because its high melt viscosity makes processing too difficult. The commercially available products are blends of PPO with high-impact polystyrene (HIPS) (polybutadiene-*graft*-polystyrene). (Some blends with other rubbery polymers are also available.) Blending overcomes the processing problem by lowering the melt viscosity and also increases the impact strength. However, the continuous use temperature for the blend, referred to as *modified PPO* (trade name: *Noryl*), is decreased to the  $80\text{--}110^\circ\text{C}$  range with the specific use temperature depending on the relative amount of polystyrene. Modified PPO has close to the lowest water absorption of all engineering plastics, and this imparts excellent electrical properties over a considerable humidity range. It has excellent resistance to aqueous environments, including acids, bases, and oxidants, but this is not matched by its resistance to organic solvents. The resistance of PPO to organic solvents is not as good as that of PET and is much poorer than the resistance of polyamides such as nylon 6/6. PPO has better resistance to aromatic, halogenated, and polar organic solvents compared to polycarbonate.

More than 350 million pounds of modified PPO were produced in the United States in 2001. As with all engineering plastics, the applications for modified PPO include both filled (including reinforced) and unfilled grades. The continuous use temperatures of  $80\text{--}110^\circ\text{C}$  indicated above are the maximum use temperatures and these require reinforced grades (e.g., reinforced with fiber glass or carbon-black-filled). A wide range of applications are found for modified PPO: automotive (dashboard, wheel covers, metalized grilles, and trim), electrical (radomes, fuse boxes, wiring splice devices), consumer and business (refrigerator door liners, computer housing, keyboard frame, steam iron), and liquid handling (pipe, valves, pump housing, impellers).

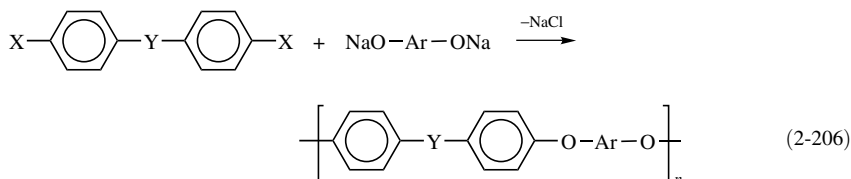


(2-204)



## 2-14c Aromatic Polyethers by Nucleophilic Substitution

*Polyetherketones* and *polyethersulfones*, also referred to as *polyketones* and *polysulfones*, are synthesized by nucleophilic aromatic substitution between aromatic dihalides and bisphenolate salts [Cassidy, 1980; Clagett, 1986; Critchley et al., 1983; Harris and Johnson, 1989; Jayakannan and Ramakrishnan, 2001; Matsumura et al., 2001; May, 1988]. This is shown in Eq. 2-206, where X is halogen and Y is C=O or SO<sub>2</sub>:

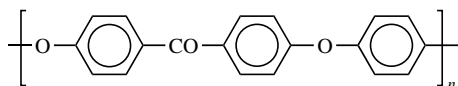


Although aromatic halides are typically not reactive toward nucleophilic substitution, polymerization is rather facile in these systems because of the electron-withdrawing sulfone and carbonyl groups. The bisphenolate salt is formed in situ by the addition of the bisphenol and sodium or other alkali metal carbonate or hydroxide. Polysulfones are typically synthesized from aromatic dichlorides in a polar aprotic solvent such as 1-methyl-2-pyrrolidinone (NMP) or dimethyl sulfoxide. The polar aprotic solvent increases the nucleophilicity of the phenoxide anion by preferential solvation of cations but not anions. Reaction temperatures of 130–160°C are used mainly because of the poor solubility of the diphenolate salt. An excess of monohydric phenol or monochloroalkane is used to control the polymer molecular weight. A dry reaction system is required for polymerization to yield high-molecular-weight polymer. The presence of water hydrolyzes the phenolate salt, generating sodium hydroxide, which reacts with the aromatic dichloride and alters the stoichiometric ratio of reacting functional groups. Polymerization is carried out in the absence of oxygen to prevent oxidation of the bisphenolate. Polyketones are typically synthesized from aromatic difluorides in diphenyl sulfone at temperatures of 200–350°C. The higher reaction temperatures compared to polysulfone synthesis are needed to keep the polymer from premature precipitation, which would limit the polymer molecular weight. There are efforts to use variations on the synthetic scheme to allow lower polymerization temperatures. For example, phase-transfer catalysts such as crown ethers or quaternary ammonium salts allow lower reaction temperatures by complexation with the counterion of the phenolate reactant, increasing its nucleophilicity and also its solubility in less polar medium [Hoffman et al., 1994; Sillion, 1999].

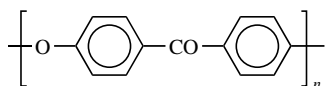
Other reactions have been studied for synthesizing these polymers, including the electrophilic aromatic substitution of acyl and sulfonyl halides on aromatic reactants and the nickel-catalyzed aromatic coupling of aromatic dihalides [Yonezawa et al., 2000].

Polymers **XL–XLIII** are commercially available. **XL** and **XLI** are referred to as *polyetheretherketone* (PEEK) and *polyetherketone* (PEK), respectively. **XLII** and **XLIII** are known as *bisphenol A polysulfone* and *polyethersulfone*, respectively. Polymers **XLI** and **XLIII** can be synthesized not only using the combination of A–A and B–B reactants, but also by the self-polymerization of appropriate A–B reactants.

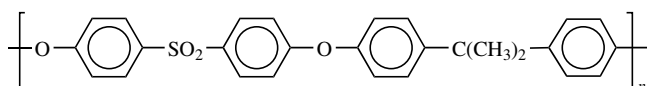
The polysulfones are transparent, amorphous polymers but possess good mechanical properties due to the rigid polymer chains. The glass transition temperatures are in the 180–230°C range, and polysulfones are rated for continuous use in the 150–200°C range.



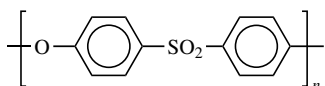
XL



XLI



XLII



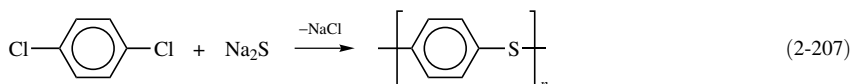
XLIII

The resistance of polysulfones to aqueous environments, including acids, bases, and oxidants, is excellent. Their resistance to aromatic and halogenated organic solvents is comparable to PPO; PPO is better toward polar solvents but poorer toward aliphatics. Bisphenol A polysulfone differs from the other members of the polysulfone family because of the isopropylidene group. It has lower glass transition and use temperatures and is less resistant to organic solvents. More than 20 million pounds of polysulfones are produced annually in the United States. The very good thermal and hydrolytic stability of polysulfones makes them useful for microwave cookware and in medical, biological, and food-processing and service applications that require repeated cleaning with hot water or steam. Other applications include circuit breakers, electrical connectors, switch and relay bases, radomes, battery cases, camera bodies, aircraft interior parts, and membrane supports for reverse osmosis. Outdoor use is somewhat limited because of relatively low UV stability.

The polyketones are partially crystalline (approximately 35%). PEEK and PEK, respectively, have glass transition temperatures of 143 and 165°C and melting temperatures of 334 and 365°C. Both polyketones have excellent resistance to a wide range of aqueous and organic environments. Their resistance to organics matches that of the polyamides, while their resistance to aqueous environments matches that of the polysulfones. PEEK and PEK are rated for continuous service at temperatures of 240–280°C. These relatively new engineering plastics have an annual production in the United States of about one million pounds. The polyketones are finding applications in parts subjected to high temperature and aggressive environments: automotive (bearing, piston parts), aerospace (structural components), oil and chemical (pumps, compressor valve plates), and electrical–electronic (cable, insulation) applications.

## 2-14d Aromatic Polysulfides

Poly (*p*-phenylene sulfide) [IUPAC: poly(sulfanediyl-1,4-phenylene) (trade name: *Ryton*) (PPS) is synthesized by the reaction of sodium sulfide with *p*-dichlorobenzene in a polar solvent such as 1-methyl-2-pyrrolidinone (NMP) at about 250°C and 1.1 MPa (160 psi) [Fahey and Geibel, 1996; Hill and Brady, 1988; Lopez and Wilkes, 1989]. The reaction may be more complicated than a simple nucleophilic aromatic substitution [Koch and Heitz, 1983]. PPS undergoes a slow curing process when heated above the melting point in air. Curing involves chain extension, oxidation, and crosslinking, but is poorly understood. There is spectroscopic evidence for crosslinking via sulfur, oxygen, and aromatic bridges between polymer chains [Hawkins, 1976].

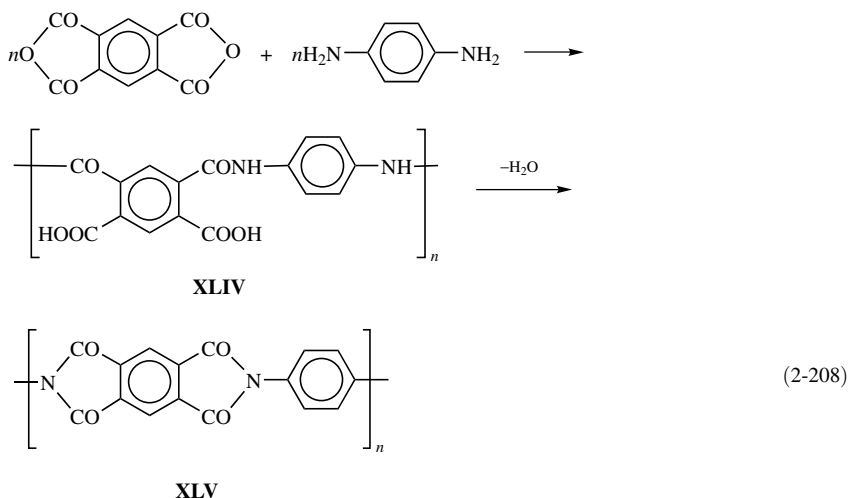


Uncrosslinked PPS is a highly (~60%) crystalline polymer with  $T_m = 285^\circ\text{C}$  and  $T_g = 85^\circ\text{C}$ . It is rated for continuous service at 200–240°C, placing PPS between the polysulfones and the polyketones. It has inherent flame resistance, and its stability toward both organic and aqueous environments is excellent. PPS is comparable to polysulfones and polyketones in resistance to acids and bases but is somewhat less resistant to oxidants. The resistance of PPS to organic solvents is comparable to that of polyamides and polyketones. More than 20 million pounds of PPS are produced annually in the United States. Applications of PPS include automotive (components requiring heat and fluid resistance, sockets and reflectors for lights), consumer (microwave oven components, hair-dryer grille), industrial (oilfield downhole components, motor insulation, pumps and valves), blends with fluorocarbon polymers (release coating for cookware, appliances, molds), and protective coatings (valves, pipe, heat exchangers, electromotive cells). PPS is an alternative to traditional thermosetting plastics in some of these applications.

## 2-14e Aromatic Polyimides

Aromatic polyimides are synthesized by the reactions of dianhydrides with diamines, for example, the polymerization of pyromellitic anhydride with *p*-phenylenediamine to form poly(pyromellitimido-1,4-phenylene) (XLV) [de Abajo, 1988, 1999; Hergenrother, 1987; Johnston et al., 1987; Maier, 2001]. Solubility considerations sometimes result in using the half acid-half ester of the dianhydride instead of the dianhydride.

The direct production of high-molecular-weight aromatic polyimides in a one-stage polymerization cannot be accomplished because the polyimides are insoluble and infusible. The polymer chains precipitate from the reaction media before high molecular weights are obtained. Polymerization is accomplished by a two-stage process. The first stage involves an amidation reaction carried out in a polar aprotic solvent such as NMP or *N,N*-dimethylacetamide (DMAC) to produce a high-molecular-weight poly(amic acid) (XLIV). Processing of the polymer can be accomplished only prior to the second stage, at which point it is still soluble and fusible. It is insoluble and infusible after the second stage of the process. The poly(amic acid) is formed into the desired physical form of the final polymer product (e.g., film, fiber, laminate, coating) and then the second stage of the process is performed. The poly(amic acid) is cyclodehydrated to the polyimide (XLV) by heating at temperatures above 150°C.



The poly(amic acid) is kept in solution during the amidation by using mild temperatures, no higher than 70°C and usually lower than 30°C, to keep the extent of cyclization to a minimum. Less polar, more volatile solvents than NMP and DMAC are sometimes used to facilitate solvent evaporation in the second stage reaction. This requires the use of an acidic or basic catalyst since the reaction rate is decreased in a less polar solvent. The poly(amic acid) is prone to hydrolytic cleavage and has relatively poor storage stability unless kept cold and dry during storage. Temperatures as high as 300°C are used for the second-stage solid-state cyclization reaction, although the use of vacuum or dehydrating agents such as acetic anhydride-pyridine allow lower cyclization temperatures.

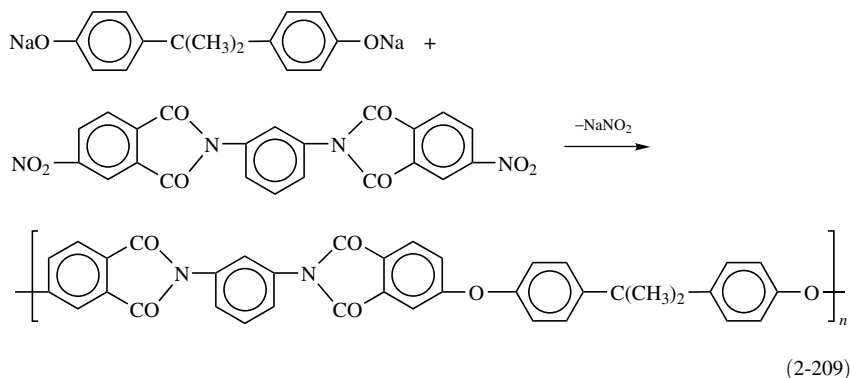
Polyimides (PIs) are mostly amorphous materials with high glass transition temperatures. The resistance of PI to organic solvents is excellent. Polyimides show good oxidation resistance and hydrolytic stability toward acidic environments, comparable to PET and better than nylon 6/6. However, PI undergoes hydrolytic degradation in strongly alkaline environments, comparable to polycarbonate and poorer than PET and nylon 6/6. The high temperature resistance of polyimides is excellent with continuous use temperatures of 300–350°C possible, especially for structures containing only aromatic rings. Wholly aromatic polyimides are generally too stiff for most applications, and their processability is limited by poor solubility and lack of melt flow at accessible temperatures.

One of the first commercial polyimides was the polymer obtained from 4,4'-diaminodiphenyl ether and pyromellitic dianhydride (trade names: Kapton, Vespel). This and other similar polyimides are available in the form of poly(amic acid) solutions that are used as high-temperature wire enamels and insulating varnishes and for coating fiber glass and other fabrics. Polyimide films find applications as insulation for electric motors and missile and aircraft wire and cable. There is also some processing of PI by powder technology (low-temperature forming followed by sintering) and compression molding (requiring higher pressures than normal) to form such automotive and aircraft engine parts as bushings, seals, piston rings, and bearings.

The lack of easy processability initially limited the utilization of this high-performance material. Several different modifications of the polyimide system have successfully produced

materials that are more readily processable at the fully imidized state. Appropriate dianhydrides and diamines are used to increase solubility and melt processability by decreasing molecular order and packing. This is done by introducing flexible segments [aliphatic, O, S, C=O, SO<sub>2</sub>, C(CH<sub>3</sub>)<sub>2</sub>, C(CF<sub>3</sub>)<sub>2</sub>] into the polyimide chains or bulky side groups (phenyl, *t*-butyl) or using 1,3-disubstituted reactants instead of 1,4 reactants [de Abajo, 1999; Sillion, 1999; Yokota et al., 2001].

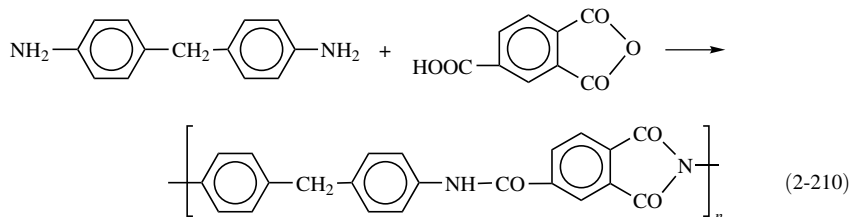
*Polyetherimides* (PEI) are polyimides containing sufficient ether as well as other flexibilizing structural units to impart melt processability by conventional techniques, such as injection molding and extrusion. The commercially available PEI (trade name: *Uitem*) is the polymer synthesized by nucleophilic aromatic substitution between 1,3-bis(4-nitrophthalimido) benzene and the disodium salt of bisphenol A (Eq. 2-209) [Clagett, 1986]. This is the same reaction as that used to synthesize polyethersulfones and polyetherketones (Eq. 2-206) except that nitrite ion is displaced instead of halide. Polymerization is carried out at 80–130°C in a polar solvent (NMP, DMAC). It is also possible to synthesize the same polymer by using the diamine–dianhydride reaction. Everything being equal (cost and availability of pure reactants), the nucleophilic substitution reaction is probably the preferred route due to the more moderate reaction conditions.



PEI is amorphous with a glass transition temperature of 215°C and continuous-use temperature of 170–180°C. The solvent and chemical resistance of PEI is comparable to that of polyimides as described above, except that it is soluble in partially halogenated organic solvents. Processability by conventional techniques coupled with a wide range of desirable properties has resulted in fast growth for this new polymer. PEI also has the advantage of not having any volatiles (water) produced during processing as occurs during the second-stage cyclization of poly(amic acids). Voids and strains can be generated as volatiles are lost during processing. PEI presently accounts for a major fraction of all polyimides. PEI resins are used in many industries: electrical–electronic (circuit boards, radomes, high-temperature switches), transportation (fuel system components, transmission and jet engine components, lamp sockets), medical (surgical instrument handles, trays, and other items requiring sterilization by steam, ethylene oxide, chemical means, or  $\gamma$  radiation), and consumer and business (microwave cookware, curling irons, food packaging, memory disks, fans for computer and other equipment).

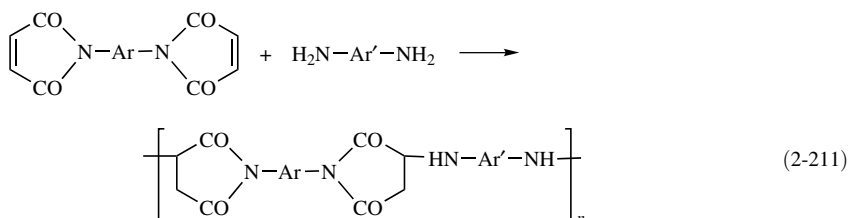
*Polyamideimides* (PAIs) (trade name: *Torlon*), containing both amide and imide functional groups in the polymer chain, are produced by the reaction of trimellitic anhydride (or a derivative) with various diamines (Eq. 2-210). PAI resins are amorphous polymers

with glass transition temperatures of 270–285°C and continuous-use temperatures of 220–230°C. Polyamideimides have excellent resistance to organic solvents. PAI has good resistance to acids, bases, and oxidants but is attacked by bases at high temperature. Polyamideimides are used in various aircraft (jet engine, generator, and compressor components),

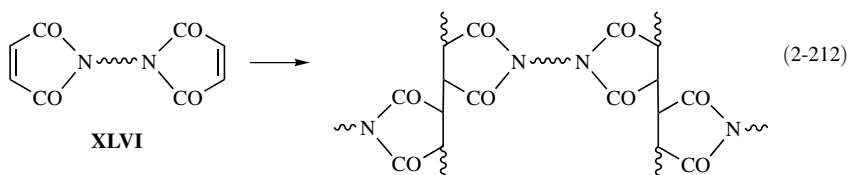


automotive (universal joints, transmission seal rings and washers), and industrial (machine gears and other mechanical components, nonstick and low-friction coatings) applications. *Polyesterimides* have been commercialized using reactants that possess combinations of imide or imide-forming groups together with carboxyl and hydroxyl groups [Lienert, 1999].

*Bismaleimide* (BMI) polymers are produced by reaction of a diamine and a bismaleimide (Eq. 2-211) [de Abajo, 1988, 1999; Mison and Sillion, 1999]. Polymerization is carried out with the bismaleimide in excess to produce maleimide end-capped telechelic oligomers (**XLVI**). Heating at temperatures of 180°C and higher results in crosslinking via radical chain



polymerization (Chap. 3) of the maleimide carbon–carbon double bonds (Eq. 2-212). The properties of the thermoset product can be varies by changing the Ar and Ar' groups and the crosslink density. The latter depends on the bismaleimide : diamine ratio. (Further variations are possible by radical copolymerization (Chap. 6) of **XLVI** with alkene monomers.) A variety of other end-capping reactants (including allyl, alkyne, and cyanate functionalities) have been used to allow subsequent crosslinkng [Enoki et al., 1995; Mison and Sillion, 1999; Wright and Schorzman, 2001].



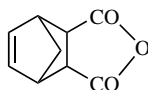
BMI polymers have glass transition temperatures in excess of 260°C and continuous-use temperatures of 200–230°C. BMI polymers lend themselves to processing by the same techniques used for epoxy polymers. They are finding applications in high-performance structural composites and adhesives (e.g., for aircraft, aerospace, and defense applications) used at temperatures beyond the 150–180°C range for the epoxies. *Bisnadimide* (BNI) polymers are similar materials based on bisnadimides instead of bismaleimides.

## 2-14f Reactive Telechelic Oligomer Approach

We noted several successful alternatives—PEI, PAI, and BMI—used to overcome the inherent lack of processability of polyimides. The BMI approach can be considered a precursor of the *reactive telechelic oligomer* approach (also referred to as the *polymeric monomer reactants* approach) for overcoming processability problems in many of the more advanced heat-resistant polymer systems [Mison and Sillion, 1999; Yokota et al., 2001]. The polymer chains in those materials, consisting of heterocyclic and carbocyclic rings, often show poor processability. Even for systems where processability is not a problem, including previously discussed polymers such as polyketone and polysulfone, the reactive telechelic oligomer approach introduces the ability to form thermoset products in addition to thermoplastics. The reactive telechelic oligomer approach will be specifically described in this section for the polyimides, but it has been practiced for a large number of different polymers.

The reactive telechelic oligomer approach is relatively simple. Polymerization is carried out in the usual manner except that one includes a monofunctional reactant to stop reaction at the oligomer stage, generally in the 500–3000 molecular weight range. The monofunctional reactant not only limits polymerization but also end-caps the oligomer with functional groups capable of subsequent reaction to achieve curing of the oligomer (i.e., chain extension as well as crosslinking in most cases). Many different functional groups have been used for this purpose—alkyne, 5-norbornene (bicyclo[2.2.1]hept-4-ene), maleimide, biphenylene, nitrile, [2.2]paracyclophane, and cyanate. Maleimide end-capped oligomers are cured by heating as described above for the BMI polymers. Maleimide end groups can be introduced into polyimide oligomers simply by carrying out polymerization with a mixture of diamine, dianhydride, and maleic anhydride. An alternate approach is to polymerize the dianhydride in the presence of excess diamine to form an amine end-capped polyimide, which is then reacted with maleic anhydride [Lyle et al., 1989].

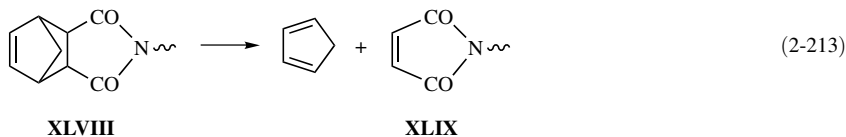
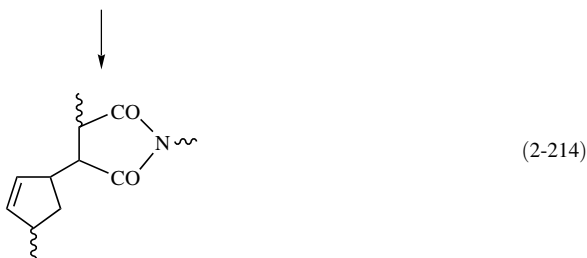
5-Norbornene end-capped polyimide oligomers (trade name: *LARC*) are obtained by including 5-norbornene-2,3-dicarboxylic anhydride (nadic anhydride) (**XLVII**) in the polymerization reaction between a dianhydride and diamine [de Abajo, 1988; Hergenrother, 1987]. Heating the oligomer at 270–320°C results in a thermoset product. The main reaction



**XLVII**

responsible for crosslinking probably involves a reverse (*retro*) Diels–Alder reaction of the 5-norbornene system to yield cyclopentadiene and maleimide end-capped oligomer (Eq. 2-213). This is followed by radical copolymerization of cyclopentadiene with the carbon–carbon double bond of maleimide (Eq. 2-214). Crosslinking appears to be more

complex, with additional reactions occurring simultaneously and to different extents depending on the cure temperature—copolymerization of cyclopentadiene with **XLVIII** as well as **XLIX**, Diels–Alder reaction of cyclopentadiene and **XLVIII** to form an adduct that copolymerizes with **XLVIII** and/or **XLIX** [Hay et al., 1989].

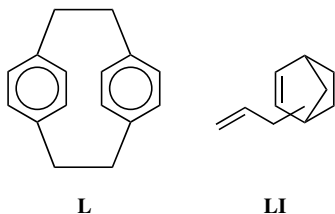


Alkyne end-capped polyimide oligomers are obtained by including an amine or anhydride that contains a triple bond in the polymerization mixture of diamine and dianhydride. Curing to a thermoset product takes place on heating with cyclotrimerization to an aromatic system (Eq. 2-215) as the crosslinking reaction. However, cyclotrimerization is not complete, and the



details of the process are not well understood [Hergenrother, 1985; Takeichi and Stille, 1986; Yokota et al., 2001]. Nitrile ( $\text{—C}\equiv\text{N}$ ) and cyanate ( $\text{—O—C}\equiv\text{N}$ ) groups also undergo cyclotrimerization, but the thermoset structures are not as stable as those formed using alkyne functional groups [Harrys and Spinelli, 1985; Temin, 1982–1983].

Many other functional groups been studied, including [2.2]paracyclophane (**L**) and allyl 5-norbornene (**LI**) [Renner and Kramer, 1989; Tan and Arnold, 1988; Upshaw and Stille, 1988]. The curing process due to [2.2]paracyclophane units probably occurs from an initial homolytic breakage at the bond connecting the two methylene groups followed by various radical–radical coupling reactions. Curing due to allyl 5-norbornene units involves both Diels–Alder and ene reactions.



## 2-14g Liquid Crystal Polymers

*Liquid crystal polymers* (LCP) are polymers that exhibit liquid crystal characteristics either in solution (*lyotropic* liquid crystal) or in the melt (*thermotropic* liquid crystal) [Ballauf, 1989; Finkelmann, 1987; Morgan et al., 1987]. We need to define the *liquid crystal* state before proceeding. Crystalline solids have three-dimensional, long-range ordering of molecules. The molecules are said to be ordered or oriented with respect to their centers of mass and their molecular axes. The physical properties (e.g., refractive index, electrical conductivity, coefficient of thermal expansion) of a wide variety of crystalline substances vary in different directions. Such substances are referred to as *anisotropic* substances. Substances that have the same properties in all directions are referred to as *isotropic* substances. For example, liquids that possess no long-range molecular order in any dimension are described as isotropic.

Not all crystalline substances lose all long-range molecular order on melting. Some crystalline substances retain one- or two-dimensional long-range molecular order above the crystalline melting point. Such substances are then described as being in the liquid crystal state. They show the flow behavior of isotropic liquids but appear to possess some kind of long-range molecular order greater than the isotropic liquid state but less than the true crystal state. Heating a thermotropic liquid crystal eventually results in its transformation to the liquid state at some temperature,  $T_{lc,i}$ , referred to as the *liquid crystal–isotropic phase transformation temperature for thermotropic liquid crystals*.

Our understanding of lyotropic liquid crystals follows in a similar manner. The action of solvent on a crystalline substance disrupts the lattice structure and most compounds pass into solution. However, some compounds yield liquid crystal solutions that possess long-range ordering intermediate between solutions and crystal. The lyotropic liquid crystal can pass into the solution state by the addition of more solvent and/or heating to a higher temperature. Thermotropic and lyotropic liquid crystals, both turbid in appearance, become clear when they pass into the liquid and solution states, respectively.

Liquid crystal behavior is due chiefly to molecular rigidity that excludes more than one molecule occupying a particular volume, rather than intermolecular attractive forces. The requirement for a substance to exhibit liquid crystal behavior is molecular shape anisotropy, which is not affected by conformational changes. Some biological molecules (e.g., tobacco mosaic virus, polypeptides, and cellulose) are liquid crystals because of their rigid helical rod conformations. This is not the case for synthetic polymers. The typical polymer liquid crystal is a rigid-rod molecule. (Theoretical studies indicate the molecular length must exceed the diameter by a factor greater than 6 [Flory and Ronca, 1979].) Other anisotropic molecular shapes (e.g., disks) also show liquid crystal behavior but these are much more rare for polymers. Polymer liquid crystals typically show either *smectic* or *nematic* liquid crystal behavior. These are shown in Fig. 2-20, where each line (—) represents a polymer molecule. There is a parallel arrangement of the long molecular axes in both nematic and smectic liquid crystals. Smectic liquid crystals are more ordered than nematic liquid crystals as a result of differences in the orientation of their molecular chain ends. Molecular chain ends are coterminous (i.e., lined up next to each other) in smectics but are out of register (i.e., have no particular orientation) in nematics. Another difference between smectic and nematic liquid crystals is that smectics are layered while nematics are seldom layered. (A third type of liquid crystal, *cholesteric*, involves nematic packing in planes with the molecular axes in each plane turned at an angle relative to those in the next plane, but is rarely observed in polymers.) Smectic liquid crystals, being more ordered, are more viscous than nematics (everything else being equal). Microscopic observations are of prime importance in distinguishing nematic and smectic structures [Demus and Richter, 1978].

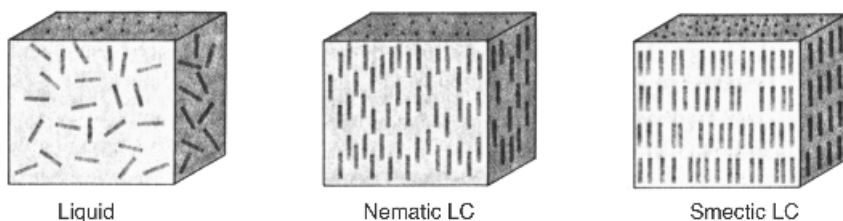


**Fig. 2-20** Molecular ordering in nematic and smectic liquid crystals compared to liquid. After Brown and Crooker [1983] (by permission of American Chemical Society, Washington, DC).

Rigid-rod liquid crystal polymer molecules result from having rigid groups either within the polymer chain or as side groups on the polymer chain. These two types of LC polymers, referred to as *main-chain* and *side-chain* LC polymers, respectively, are depicted in Fig. 2-21. The rigid groups are referred to as *mesogens* or *mesogenic* groups. The mesogens are shown as rigid-rod groups, but other shapes (e.g., disks) are also possible. The collection of mesogenic units results in a molecule that is a rigid rod with molecular shape anisotropy and liquid crystal behavior.

Liquid crystal behavior in polymers has practical consequences. Liquid crystal melts or solutions have lower viscosities than melts or solutions of random-coil polymers and are easier to process. More importantly, the extension and orientation of polymer chains during processing yields highly crystalline products with high modulus and high strength. The moduli and strengths of chain-extended LC polymers is considerably higher than those of

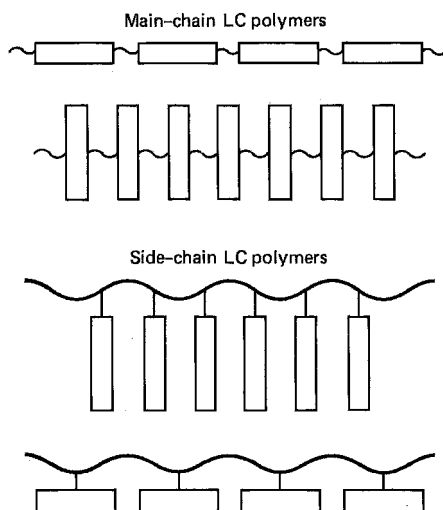
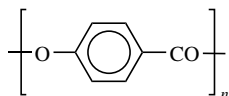


**Fig. 2-21** Main-chain and side-chain liquid crystal polymers.

the chain-folded crystalline polymers formed from non-LC polymers. LC polymers also have significantly increased crystalline melting temperatures as a result of the extended-chain morphology. Thus, the synthetic guidelines are the same for synthesis of heat-resistant and LC polymers—build rigid polymer chains.

Poly(1,4-oxybenzoyl) (**LII**) [IUPAC: poly(oxy-1,4-phenylenecarbonyl)], obtained by self-reaction of *p*-hydroxybenzoic acid, and the various aramids (Sec. 2-8f) were among the first LC polymers studied. The experience in commercializing poly(1,4-oxybenzoyl) and the



**LII**

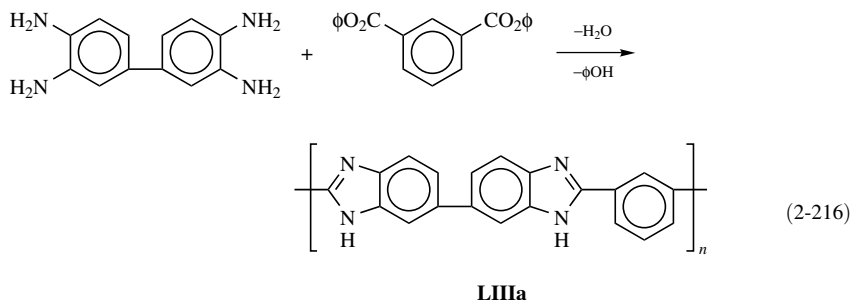
aramids illustrates that one can have “too much of a good thing.” None of these polymers can be melt processed since they undergo decomposition before melting ( $T_m > 500^\circ\text{C}$ ). The aramids are spin processed into fibers using lyotropic solutions in sulfuric acid. It would be preferable to melt-process the polymers or, at least, to use a less aggressive or less dangerous solvent, but these options do not exist. Poly(1,4-oxybenzoyl) (*Ekonol*) has found limited utility due to a lack of easy processability. It does not have sufficient solubility even in an aggressive solvent to allow solution processing. It can be processed by plasma spraying or powder sintering.

There is a need to decrease the crystalline melting temperature in such very-high-melting LC polymers to achieve a degree of processability. Copolymerization is used to alter the polymer chains in the direction of decreased rigidity but one needs to do it carefully to retain as high modulus, strength, and  $T_m$  as possible. Chain rigidity can be lowered by reducing molecular linearity by incorporating a less symmetric comonomer unit (*o*- and *m*- instead of *p*- or naphthalene rings, other than 1,4-disubstituted, instead of the 1,4-phenylene unit), a comonomer containing a flexible spacer (single bond, oxygen, or methylene between mesogenic monomer units) or a comonomer with flexible side groups [Jin and Kang, 1997; Yamana et al., 1999]. This approach has been successfully applied to poly(1,4-oxybenzoyl). Two copolyesters are commercial products. *Vecta* is a copolymer of *p*-hydroxybenzoic acid with 6-hydroxy-2-naphthoic acid; *Xydar* is a copolymer of *p*-hydroxybenzoic acid with *p,p'*-biphenol and terephthalic acid. These polymers have continuous service temperatures up to  $240^\circ\text{C}$  and find applications for microwave ovenware, automotive components, components for chemical pumps and distillation towers, and electronic devices.

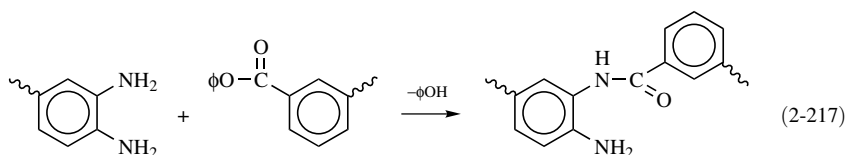
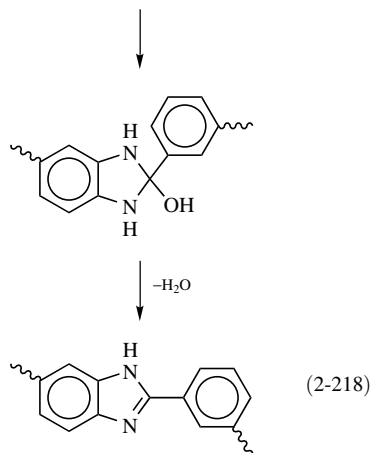
Many of the polymers discussed in the following sections exhibit liquid crystal behavior.

## 2-14h 5-Membered Ring Heterocyclic Polymers

Polyimides are obtained from amine and carboxyl reactants when the ratio of amine to acid functional groups is 1:2. If reactants with the reverse ratio of amine to acid functional groups are employed, polybenzimidazoles (PBI) are produced; for instance, polymerization of 3,3'-diaminobenzidine and diphenyl isophthalate yields poly[(5,5'-bi-1*H*-benzimidazole]-2,2'-diyl)-1,3-phenylene] (**LIIIa**) (Eq. 2-216) [Buckley et al., 1988; Hergenrother, 1987;



Marvel, 1975; Ueda et al., 1985]. The reaction probably proceeds by a sequence of two nucleophilic reactions: a nucleophilic substitution to form an amine–amide (Eq. 2-217) followed by cyclization via nucleophilic addition (Eq. 2-218).

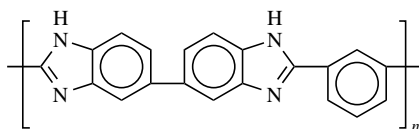
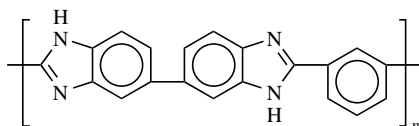


Polymerization is often carried out as a two-stage melt polymerization. Oxygen is removed from the reaction system by vacuum and the system purged with nitrogen to avoid loss of stoichiometry by oxidation of the tetramine reactant. The reaction mixture is heated to about 290°C in the first stage with the reaction starting soon after the reactants form a melt (150°C). The high-volume foam produced in this stage is removed, cooled, and crushed to a fine powder. The second-stage reaction involves heating of the powder at 370–390°C under nitrogen.

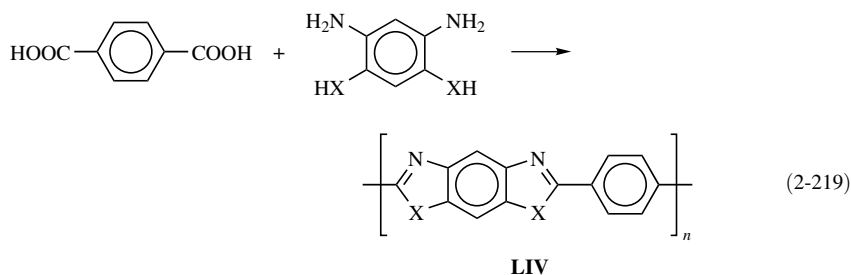
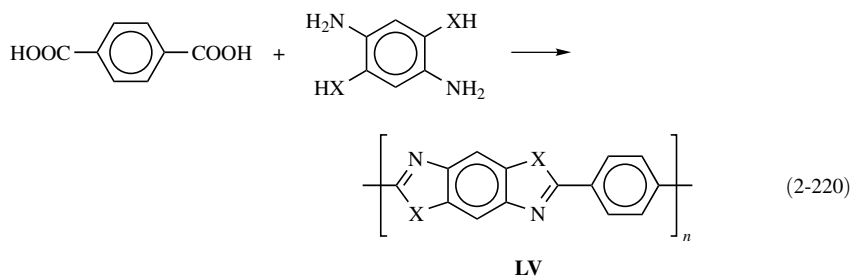
Considerable efforts have centered on carrying out the synthesis of polybenzimidazoles at more moderate temperatures. Polymerization of the isophthalic acid or its diphenyl ester have been successfully carried out in polyphosphoric acid or methanesulfonic acid–phosphorous pentoxide at 140–180°C, but the reaction is limited by the very low solubilities (<5%) of the reactants in that solvent. The lower reaction temperature is a consequence of activation of the carboxyl reactant via phosphorylation. Lower reaction temperatures are also achieved in hot molten nonsolvents such as sulfolane and diphenyl sulfone, but the need to remove such solvents by a filtration or solvent extraction is a disadvantage.

The PBI in Eq. 2-216 is commercially available in the form of fiber, composite resin, and formed objects (trade name: *Celazole*). It has good stability and mechanical behavior up to 300°C and higher (about 25°C higher than the most stable polyimides), does not burn and is self-extinguishing. PBI has better hydrolytic stability than aromatic polyamides and polyimides. It has been used to make flight suits for *Apollo*, *Skylab*, MIR, and ISS astronauts and cosmonauts, and escape suits for Space Shuttle astronauts. Fiber is spun from PBI using lyotropic solutions of the polymer in solvents such as *N,N*-dimethylacetamide, in which it is reasonably soluble at the processing temperature of 250°C. Sulfonated PBI has potential for clothes for firefighters. PBI itself is not appropriate for such use since it undergoes extensive shrinkage when exposed to flames. Sulfonation of PBI (on the aromatic rings) greatly reduces this shrinkage problem. Other applications include bushings in injection-molding equipment, electrical connectors in aircraft engines, and ball valve seats in hot-fluid-handling piping.

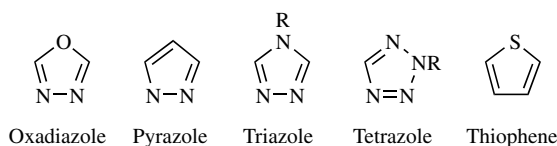
It should be noted that structure **LIIfa** is an oversimplification for the polymer formed from 3,3'-diaminobenzidine and diphenyl isophthalate. Dehydration after ring closure can occur toward either of the two nitrogens, and one would expect more or less random placements of the carbon–nitrogen double bonds. Thus, the PBI structure is a random copolymer of repeating units **LIIfa**, **LIIfb**, and **LIIfc**.

**LIIfb****LIIfc**

Polybenzoxazoles (PBO) and polybenzthiazoles (PBT) are related to and synthesized in a manner similar to polybenzimidazoles [Chow et al., 1989; Evers et al., 1981; Hergenrother, 1987; Krause et al., 1988; Maier, 2001; Maruyama et al., 1988; So et al., 1998; Wolfe, 1988]. Synthesis of PBO (**LIV**) and PBT (**LV**) is accomplished by the reactions of a dicarboxyl reactant with a bis-*o*-aminophenol ( $X = O$ ) and bis-*o*-aminothiophenol ( $X = S$ ), respectively (Eqs. 2-219 and 2-220).

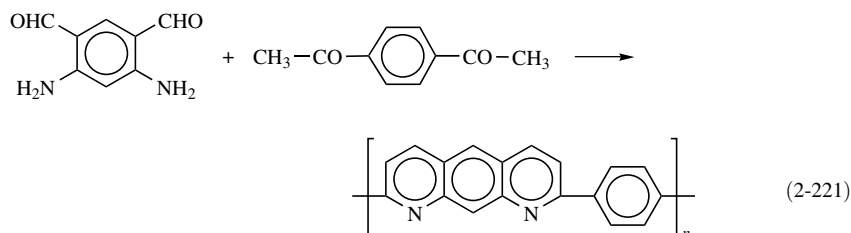


A wide range of polymers based on other heterocyclic 5-membered rings have been investigated, including oxadiazole, pyrazole, triazole, tetrazole, and thiophene [Bass et al., 1987; Briffaud et al., 2001; Cassidy, 1980; Critchley et al., 1983; Gebben et al., 1988; Ueda and Sugita, 1988].



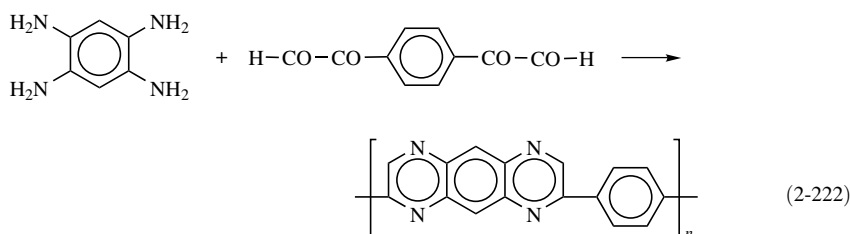
## 2-14i 6-Membered Ring Heterocyclic Polymers

Polyquinolines (PQ) are obtained by the Friedlander reaction of a bis-*o*-aminoaromatic aldehyde (or ketone) with an aromatic bisketomethylene reactant [Concilio et al., 2001; Stille, 1981]. The quinoline ring is formed by a combination of an aldol condensation and imine formation (Eq. 2-221). Polymerization is carried out at 135°C in *m*-cresol with poly(phosphoric acid) as the catalyst. The reaction also proceeds under base catalysis, but there



are more side reactions. There has been a considerable effort to use the reactive telechelic oligomer approach to producing crosslinking polyquinolines [Sutherland and Stille, 1986]. PQs in the repeating unit have been obtained by reactions other than the Friedlander reaction [Moore and Robello, 1986; Ruan and Litt, 1988].

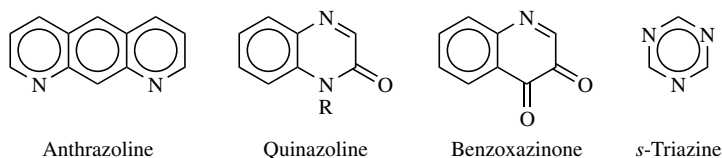
Polyphenylquinoxalines (PPQ) are obtained by the polymerization of aromatic bis- $\alpha$ -diamine and bis- $\alpha$ -ketoaldehyde reactants in *m*-cresol at  $\sim 80^\circ\text{C}$  [Hergenrother, 1988; Klein et al., 2001]:



Reaction temperatures above  $100^\circ\text{C}$  are avoided to prevent branching. PPQs can also be synthesized from monomers that contain the quinoxaline ring [Maier, 2001].

Most PQ and PPQ polymers are amorphous, although a few show some crystalline behavior. PQ and PPQ are promising materials as they possess a very good combination of properties: excellent thermal and oxidative stability, resistance to acids and bases, high glass transition temperature, and high strength and modulus. These properties are coupled with a significant ability to be processed. This is especially the case for PPQ polymers. There is a considerable range between the glass transition temperature and the decomposition temperature, which allows for thermoplastic processing. Also, PPQ is soluble in phenolic and chlorinated solvents, although PQ is soluble only in phenolic solvents. The favorable combination of properties has resulted in considerable efforts to explore the synthetic and practical limits of the PQ and PPQ systems. A number of ladder PQ and PPQ polymers have been studied, but the results have been disappointing, as is the case with other ladder polymers. Nonladder PQ and PPQ polymers in the form of films, composites, and adhesives show good high-temperature properties, but their utilization is impeded by high costs.

Many other 6-membered ring systems have been explored as the basis for high-temperature polymers, including anthrazoline, quinoxaline, benzoxazinone, and *s*-triazine [Cassidy, 1980; Critchley et al., 1983].



## 2-14j Conjugated Polymers

There has been a large effort to synthesize organic conjugated polymers [Aldissi, 1989; Fromer and Chance, 1986; Kraft et al., 1998; Maier, 2001; Potember et al., 1987; Pron

and Rannou, 2002; Yamamoto, 2002] because such polymers have potential as semiconducting, conducting, and light-emitting (optoelectronic) materials. Organic polymers offer potential advantages over the traditional inorganic and nonpolymeric materials used for these purposes. First, processing of organic conjugated polymers by molding and other plastics processing techniques into various electrical, electronic, and optoelectronic devices and forms is potentially easier and more economical compared to processes used for inorganic and nonpolymeric materials. Second, the lightweight property of polymer materials would make certain types of applications more practical and economical.

One potential application for conjugated polymers is lightweight rechargeable batteries for portable devices and vehicles. Conducting polymers would serve both current-carrying and ion conduction functions by replacing traditional electrode and electrolyte substances. Another area of application for conducting polymers is their use in building circuitry elements, both passive (conducting circuits) and active ( $p$ - $n$  and Schottky junctions). Other potential applications include transparent antistatic coatings for metals and electronic devices, electromagnetic shielding, light-emitting diodes (LEDs), electrodes, biosensors, transistors, and ultrathin, flexible screens for computer and TV monitors.

The structural requirement for a conducting polymer is a conjugated  $\pi$ -electron system. The typical polymers studied are based on a  $\pi$ -conjugated electron system constituting the polymer backbone, but conducting polymers are also possible when the  $\pi$ -conjugated electron system is present as side chains. Polymers with conjugated  $\pi$ -electron systems display unusual electronic properties, including high electron affinities and low ionization potentials. Such polymers are easily oxidized or reduced by charge-transfer agents (*dopants*) that act as electron acceptors or electron donors, respectively. This could result in poly(radical-cation)- or poly(radical-anion)-doped conducting materials ( $p$ -type and  $n$ -type, respectively) with near-metallic conductivity in some cases. Electrons are removed from or added to the conjugated  $\pi$ -electron system to form extra holes or electrons, respectively, which carry current by wandering through the polymer chain. The dopant plays an additional role other than bringing about oxidation or reduction. It acts as the bridge or connection for carrying current between different polymer chains. Oxidative dopants include  $\text{AsF}_5$ ,  $\text{I}_2$ ,  $\text{AlCl}_3$ , and  $\text{MoCl}_5$ . Sodium, potassium, and lithium naphthalides are reductive dopants. The dopant, necessary to impart electrical conduction, often decreases but does not eliminate the processability of a polymer.

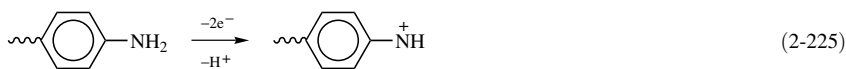
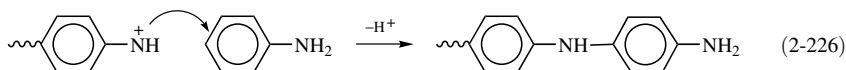
A number of other characteristics are required in order to ensure a viable polymeric conductor. Chain orientation is needed to enhance the conducting properties of a polymeric material, especially the intermolecular conduction (i.e., conduction of current from one polymer molecule to another). This is a problem with many of the polymers that are amorphous and show poor orientation. For moderately crystalline or oriented polymers, there is the possibility of achieving the required orientation by mechanical stretching. Liquid crystal polymers would be especially advantageous for electrical conduction because of the high degree of chain orientation that can be achieved. A problem encountered with some doped polymers is a lack of stability. These materials are either oxidants or reductants relative to other compounds, especially water and oxygen.

The first polymer shown to have conducting behavior was polyacetylene (Sec. 8-6c). Some of the polymers investigated as heat-resistant polymers have conjugated  $\pi$ -electron systems and offer potential as conducting polymers. Among the polymers we have covered up to this point, poly( $p$ -phenylene sulfide), polyquinoline, and polyquinoxaline have shown some promise as conducting polymers. We now consider a number of other polymers which are more promising as conducting polymers.

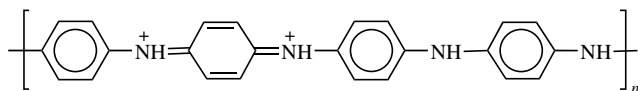
### 2-14j-1 Oxidative Polymerization of Aniline

Passage of current through a solution results in oxidation (electron loss) at the anode and reduction (electron gain) at the cathode. This process is referred to as *electrochemical polymerization* when polymer is formed. Polyaniline [IUPAC: poly(imino-1,4-phenylene)] is obtained by the oxidative polymerization of aniline in aqueous HCl solution, either by electrochemical polymerization or by using a chemical oxidant such as ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  [Macdiarmid et al., 1987; Mav and Zignoni, 2001; Tejskal and Gilbert, 2002; Wei, 2001; Wei et al., 1989, 1990]. Polymerization proceeds by a chain polymerization mechanism, but is included in this section on conjugated polymers for convenience.

Initiation involves a loss of two electrons and one proton from aniline to form a nitrenium ion (Eq. 2-223), which subsequently attacks aniline by electrophilic substitution (Eq. 2-224). Propagation proceeds in a similar manner by oxidation of the primary amine end of a growing polymer chain (Eq. 2-225) followed by electrophilic substitution (Eq. 2-226). The process has been referred to as *reactivation chain polymerization* to highlight the fact that the chain end formed after each addition of aniline must be reactivated to the nitrenium



ion by oxidation and proton loss. The product formed directly from oxidative polymerization is not the neutral structure shown in Eq. 2-226. The polymer has the positively charged structure **LVI**, which is referred to as *emeraldine salt*, and it is the conducting form of polyaniline. Other forms of polyaniline can be obtained after synthesis by varying the applied voltage and pH [Sherman et al., 1994]. Polyaniline offers considerable promise for commercialization. There have been extensive studies using substituted anilines alone or in copolymerization with aniline to alter the conducting and optoelectronic properties of the polymer as well as their solubility characteristics.



**LVI**

Oxidative polymerizations of thiophene and pyrrole and their derivatives are also under study to obtain polymers with conducting and optoelectronic properties [Jin et al., 2000;

Kraft et al., 1998; Lowen and Van Dyke, 1990; Wei and Tian, 1993]. Reactions other than oxidative polymerization are also being studied for producing polyaniline and polythiophene [Kraft et al., 1998; Loewe et al., 2001]. An example is the Pd-catalyzed dehydrohalogenation between aryl dihalides and aryl primary diamines to synthesize polyanilines [Kanbara et al., 2000].

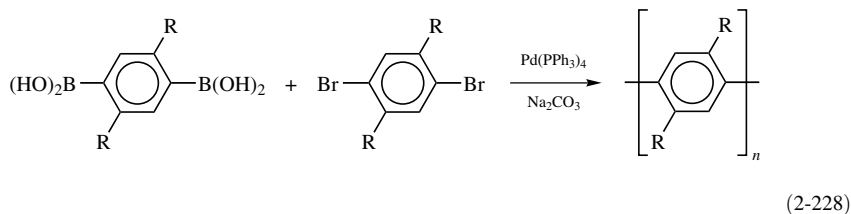
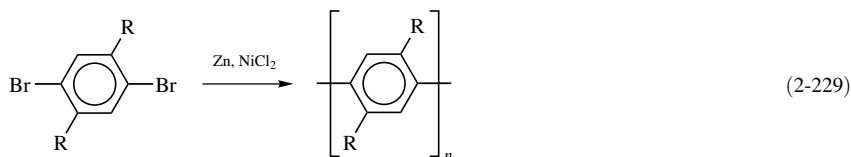
### 2-14j-2 Poly(*p*-phenylene)

One of the earliest attempts to synthesize heat-resistant polymers was the oxidative polymerization of benzene to poly(*p*-phenylene) [IUPAC: poly(1,4-phenylene)] (Eq. 2-227) [Jones

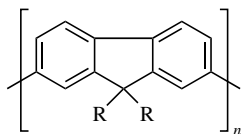


and Kovacic, 1987; Kovacic and Jones, 1987]. The reaction requires the presence of both a Lewis acid catalyst and an oxidant, such as aluminum chloride and cupric chloride. Poly(*p*-phenylene) is of interest not only for heat resistance but also as a conducting polymer. Unfortunately, the oxidative route yields an insoluble and intractable product of low molecular weight and irregular structure (a mixture of *o* and *p* substitution). Similar results have been found for polymerization of biphenyl, *p*-terphenyl, and naphthalene.

Alternate approaches to the poly(*p*-phenylene) system have been more successful [Kraft et al., 1998; Schluter, 2001]. The emphasis in these approaches has been on substituted poly(*p*-phenylene)s with suitable side groups that solubilize the polymer. Also of interest are chromophores as side groups to impart light-emitting properties for specific wavelengths of light. One of the reactions successfully employed is the *Suzuki coupling* between arylboronic acids (or their esters) and aryl bromides (Eq. 2-228) [Hu, 2003; Schluter and Wegner, 1993]. Another useful reaction is the coupling of aryl dihalides with zinc (Eq. 2-229). These



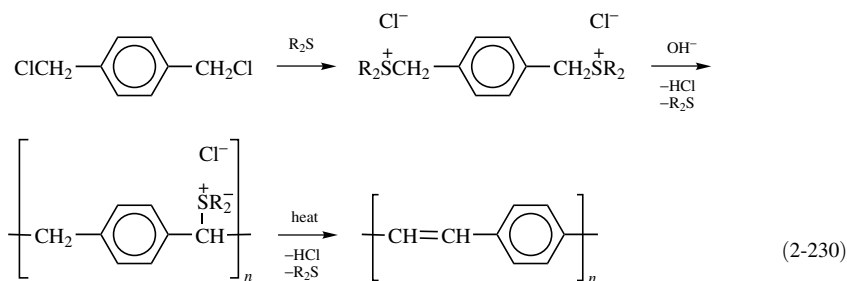
reactions have been adapted for synthesis of other conjugated polyaromatic polymers, for example, polyfluorenes (**LVII**).



LVII

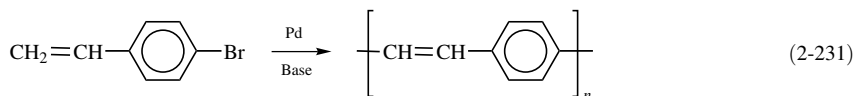
### 2-14j-3 Poly(*p*-phenylene Vinylene)

Poly(*p*-phenylene vinylene) [IUPAC: poly(1,4-phenyleneethene-1,2-diyl)] (PPV) (**LVIII**) is obtained by the sequence in Eq. 2-230 involving successive base- and heat-induced

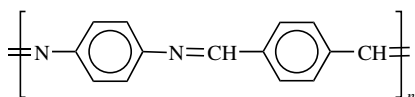


LVIII

eliminations of dialkyl sulfide and hydrogen halide [Cho, 2002; Kraft et al., 1998; Lenz et al., 1988; van Breemen et al., 2001]. PPV can also be synthesized by the *Heck coupling* of aryl halides with alkenes (Eq. 2-231).



The corresponding azomethine polymers (**LIX**) have been synthesized by the reaction of the appropriate diamine and dialdehyde [Farcas and Grigoras, 2001; Gutch et al., 2001; Morgan et al., 1987].



LIX

## 2-15 INORGANIC AND ORGANOMETALLIC POLYMERS

The drive for heat-resistant polymers has led to an exploration of polymers based on inorganic elements since bond energy considerations indicate that such polymers should be superior to organic polymers in thermal stability [Allcock et al., 2003; Archer, 2001; Manners, 1996; Nguyen et al., 1999; Ray, 1978]. Both *inorganic and organometallic* polymers have been studied. Inorganic polymers are polymers containing no organic groups, while organometallic polymers contain a combination of inorganic and organic groups. Inorganic and organometallic polymers would have potential for a variety of uses—as partial or complete substitutes for organic fibers, elastomers, and plastics where flame and heat resistance are important; as marine antifoulants, bactericides, medicinals, fungicides, adhesives, photoresists, photosensitizers, photostabilizers; and as conducting polymers. In general much of this potential is unrealized, although significant exceptions exist—the polysiloxanes (Secs. 2-12f and 7-11a), poly(*p*-phenylene sulfide) (Sec. 2-14d), polyphosphazenes (Sec. 7-11b), and polysilanes (Sec. 2-15b-3) are commercial polymers.

### 2-15a Inorganic Polymers

The synthesis of high-molecular-weight inorganic polymers is more difficult than that of organic polymers. Chain polymerization through multiple bonds is routinely used for organic monomers such as ethylene. This route is not readily available for inorganic polymers because monomers with multiple bonds between inorganic elements are generally unstable. Chain polymerization of cyclic monomers (ring-opening polymerization) offers more promise and is discussed in Chap. 7. Step polymerization using monomers with two different functional groups, relatively easy to accomplish with organic molecules, is more difficult for synthesizing inorganic polymers. The chemistry of inorganic functional groups is not well understood, and monomers of high purity are difficult to prepare. Thus, it is difficult to achieve the polymer molecular weights needed to obtain materials with sufficient mechanical strength for fabrication into plastic, elastomers, and fibers.

With almost no exceptions attempts to synthesize inorganic polymers that can directly substitute for organic polymers have been unsuccessful. Although the intrinsic thermal stability is often good, a variety of difficulties must be overcome before a usable polymer is obtained. Inorganic polymers typically suffer from various combinations of poor hydrolytic stability, low polymer molecular weights, and low chain flexibility. For example, inorganic polymers with high molecular weights and good hydrolytic stability are often highly inflexible. A large deficiency for many polymers is their intractability to current techniques of fabricating polymers into products such as film, fiber, tubing, and other objects. This does not mean that inorganic polymers are useless. Inorganic polymers comprise many of the materials that are employed at home, industry, and elsewhere. Let us briefly consider some of those materials. [Several wholly inorganic polymers, polysulfur, polyselenium, polythiazyl, and poly(dichlorophosphazene), are discussed in Chap. 7.]

#### 2-15a-1 Minerals

A variety of mineral-type materials are inorganic polymers [Ray, 1978]. Silica [ $(\text{SiO}_2)_n$ ] is found in nature in various crystalline forms, including sand, quartz, and agate. The various crystalline forms of silica consist of three-dimensional, highly crosslinked polymer chains composed of  $\text{SiO}_4$  tetrahedra where each oxygen atom is bonded to two silicon atoms and each silicon atom is bonded to four oxygen atoms. *Silicates*, found in most clay, rocks, and

soils, are also based on  $\text{SiO}_4$  tetrahedra. However, they differ from silica in having Si : O ratios under 1 : 2 (compared to 1 : 2 for silica) and contain  $\text{Si}-\text{O}^-$  groups with associated metal cations. Single-strand, double-strand (ladder), sheet (composed of multiple-double-strand sheets analogous to graphite), and three-dimensional polymer chains occur depending on the Si : O ratio, cation : Si ratio, and charge on the cation. Talc contains magnesium and possesses a sheet silicate structure. Tremolite, an asbestos mineral, has a double-strand structure and contains calcium and magnesium. The silicates, similar to silica itself, are highly rigid materials because of their ladder, sheet, and three-dimensional structure. Even the single-strand chains are rigid since the cations act to hold together adjacent polymer chains.

### 2-15a-2 Glasses

Silicate *glasses* are produced by melting and rapidly cooling silica or a mixture of silica with other materials [Thornton and Colangelo, 1985]. The product is an amorphous glass since molten silica has a strong tendency to supercool. (Special procedures with regard to heating and cooling rates are required to achieve crystallization.) Silica glass differs from crystalline silica in that there is less than full coordination of all silicon and oxygen atoms; that is, not every silicon is coordinated to four oxygens, and not every oxygen is coordinated to two silicons. *Fused-silica glass*, consisting of virtually pure silica, is the most chemically resistant of glasses and exhibits the maximum continuous service temperature ( $900^\circ\text{C}$ ). Its relatively high cost limits its use to special applications such as the fiber optics used in information and image transmission and medical fiberoscopes for internal examination of humans and animals. The most commonly encountered glass, referred to as *soda-lime glass*, is made by incorporating various amounts of calcium, sodium, and potassium into the silicate by adding the appropriate compounds, such as sodium and calcium carbonates or oxides, to molten silica. The properties of the glass (e.g., hardness, softening temperature) are varied by varying the relative amounts of the different cations. This is the glass used for windows, light-bulbs, bottles, and jars. Optical glass is similar to soda-lime glass but is much harder because it contains less sodium and more potassium. Colored glasses are obtained by the addition of appropriate compounds; for example, chromium(III) and cobalt(II) oxides yield green and blue glasses, respectively. Photochromic glasses, which darken reversibly on exposure to light, are obtained by including silver halide in the glass formulation. Vitreous enamels on metal objects and glazes on pottery are glass coatings obtained by covering the item with a paste of the appropriate oxides and heating to a high temperature.

*Borosilicate* and *aluminosilicate* glasses are produced by adding  $\text{B}_2\text{O}_3$  (borax) and  $\text{Al}_2\text{O}_3$  (alumina), respectively, to molten silica. This produces a structure where boron and aluminum atoms, respectively, replace some silicon atoms in the silicate polymer chain. Laboratory glassware is manufactured from borosilicate glass, which additionally contains sodium and calcium (trade name: *Pyrex*). The very low coefficient of thermal expansion of borosilicate glasses makes them far less prone to breakage on heating and cooling and especially useful for volumetric glassware. This glass also has very good chemical resistance. Greater chemical resistance, when required, is obtained by using borosilicate glasses with a very high (99.6%) silica content. Pyrex-type borosilicate glasses contain 70–80% silica. (Quartz glassware is used for very special applications.) Aluminosilicate glasses containing calcium and magnesium are used for cookware. There are many naturally occurring aluminosilicate minerals, such as feldspars and zeolites, which contain various combinations of sodium, potassium, and calcium.

A variety of other glassy inorganic polymers are known [Ray, 1978]. *Polymetaphosphates* are linear polymers produced by heating an alkali dihydrogen phosphate (Eq. 2-232).

*Polyultraphosphates*, the corresponding branched and crosslinked analogs, are obtained by having phosphoric acid present in the reaction mixture. *Chalcogenide glasses* are crosslinked polymers formed by the fusion of a chalcogen (S, Se, Te) with one or more of various polyvalent elements (e.g., As, Cd, Ge, P, Si, Sn). Some of these polymers are useful as infrared transparent windows in applications such as infrared detectors and for encapsulating photo-sensitive transistors.



### 2-15a-3 Ceramics

*Ceramic* materials have higher heat resistance than do their corresponding glass compositions. The *traditional ceramics*, such as brick, pottery, and porcelain, are aluminosilicates derived from clay as the main raw material [Jastrzebski, 1976; Thornton and Colangelo, 1985]. These are heterogeneous materials in which microcrystals are embedded in a glass matrix. Clays are produced by the weathering of the mineral feldspar, an aluminosilicate containing sodium and potassium ions. Weathering of feldspar produces kaolinite, empirical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , in the form of small thin platelets. Clays are mixtures of kaolinite with small amounts of feldspar, sand, and other minerals. Most clays are reddish because of the presence of iron(III) oxide as an impurity. Ceramic objects are made by working a mixture of clay with water. Other silicate materials are often added depending on the desired properties in the final product. The presence of water renders the mixture pliable as kaolinite platelets can slide over one another. *Firing* (heating) of the shaped object results in a complex set of reaction. Water is lost during the process, and the kaolinite platelets can no longer slip past one another. In addition, an aluminosilicate glassy network with its associated cations is formed. The resulting ceramic consists of kaolinite platelets distributed in a glassy aluminosilicate matrix. The partially crystalline nature of these ceramics results in denser materials with higher strength, heat conduction, and heat resistance compared to glasses. Traditional ceramics find a range of applications: pottery, construction bricks, whitewares (porcelain coatings on various household items, and spark plugs, ovenware), and refractory (furnace bricks, mortar, liners, coatings). Most of these applications require the heat-resistant properties inherent in the ceramic materials. However, the strength requirements are not very high in such applications. A second group of ceramic materials, often referred to as *new ceramics* or *high-performance ceramics*, have been developed in more recent years [Baldus and Jansen, 1997; Corriu, 2000; Segal, 1991]. These include various pure and mixed oxides, carbides, nitrides, borides, and silicides, (e.g., BeO, ZrO,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\alpha\text{-SiC}$ ,  $\text{B}_4\text{C}$ , TiC, BN, AlN,  $\text{Si}_3\text{N}_4$ ,  $\text{ZrB}_2$ ,  $\text{TaB}_2$ ; empirical formulas). The new ceramics are used in applications requiring high strength at high temperature, such as parts for gas and jet engines, nuclear plants, high-temperature chemical plants and abrasives, cutting tools, and dies for high-speed machining of metals. Silicon carbide is used for the heat-resistant tiles that protect the space shuttle during reentry into the earth's atmosphere. Many of the new ceramics are close to being completely crystalline materials. Others consist of crystalline material embedded in a glassy matrix, but the amount of crystalline phase is typically greater than that for the traditional ceramics. Synthesis of the various materials used for the newer ceramics typically requires high-temperature processes; for instance, SiC is produced by the reaction of silica and

anthracite coal or coke in an electric resistance furnace. The production of objects from the newer ceramics follows in the same manner as the traditional ceramics but with higher firing temperatures (800–1800°C). The firing process at these higher temperatures is referred to as *sintering*.

The formation of objects from glass and ceramic (especially the new ceramic) materials is achieved only at very high temperatures where there are considerable limitations on the manipulative techniques available to form desired shapes and forms. Two new methods hold considerable promise for producing glass and ceramic objects more easily and at much more moderate temperatures. The key to both methods is the use of very different chemical reactions, based on organic derivatives of the inorganic element, to form the glass or ceramic compound(s). The *preceramic polymer* method is described in Sec. 2-15b-3. The *sol-gel* method involves the in situ generation of silica by the base- or acid-catalyzed hydrolysis of tetramethoxy- or tetraethoxysilane in an alcohol–water mixture (Eq. 2-233) [Brinker et al., 1984; Celzard and Mareche, 2002; Corriu, 2000; Corriu and Leclercq, 1996; Hench and West, 1990]. The polymerization conditions (temperature, reactant and catalyst concentrations) may be varied to yield reaction times from minutes to hours or days for completion. Polymerization generally involves initial reaction at ambient temperature followed by an aging process at 50–80°C to develop a controlled network structure. The acid-catalyzed process is slower and easier to control compared to the base-catalyzed process. Tetraacetoxysilanes have also been used as the silica precursor.



The reaction mixture consists of a silica gel swollen with solvent (alcohol and water) after aging. Densification occurs by a drying step in which solvent is evaporated from the reaction mixture. The product after densification is a microporous, low-density silica referred to as a *xerogel* or *aerogel* depending on the conditions of solvent removal. Normal solvent evaporation of the open (to the atmosphere) reaction mixture results in a xerogel. Bleeding solvents slowly from a closed reaction mixture kept under conditions where the solvents are above their critical conditions results in an aerogel. The aerogel is generally lower in density than the xerogel, but both have very low densities and offer potential as lightweight thermal insulators and perhaps even as materials of construction. The last phase of densification may involve temperatures considerably in excess of 100°C to complete the polymerization reaction and drive off the last amounts of solvent. Fabrication of the silica gel, such as by coating onto some object or device or pouring into a mold, can be carried out at various times during the overall process depending on the specific application. A variety of mixed silicate glasses can be obtained by including other compounds in the reaction mixture. Borosilicate, aluminosilicate, and mixed boroaluminosilicate glasses containing various additional cations (e.g., sodium, barium, potassium) are produced by polymerizing a mixture of tetraalkoxysilane with the appropriate alkoxides, acetates, or nitrates of the other metals.

*Nonhydrolytic sol-gel* synthesis is a more recent variation on the sol-gel method. A metal halide is reacted with an oxygen derivative of the metal (Eq. 2-234). The reaction is catalyzed by Lewis acids such as FeCl<sub>3</sub> and alkyl halide is a by-product [Hay and Raval, 2001]. The reaction has been used to produce alumina (Al<sub>2</sub>O<sub>3</sub>) and titania (TiO<sub>2</sub>) as well as silica [Corriu and Leclercq, 1996].



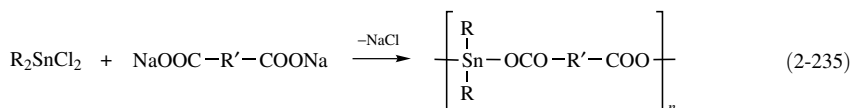
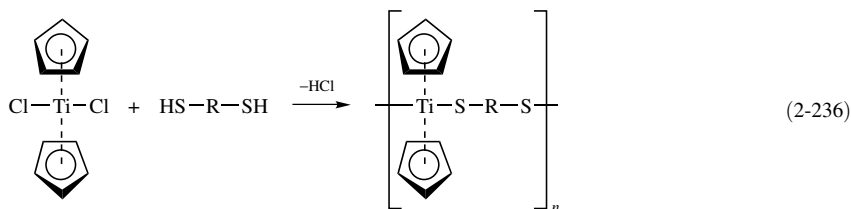
## 2-15b Organometallic Polymers

Although inorganic polymers find important applications as glasses and ceramics, their high rigidity make them unsuitable for replacement of organic polymers. Organometallic polymers, a compromise between inorganic and organic polymers, have been studied in the effort to achieve the goal of heat-resistant polymers processable by the techniques used for organic polymers. The general approach involves decreasing the extent of ladder, sheet, and three-dimensional structures as well as bridging between different chains through cation–oxygen anion interactions by replacing some of the oxygen linkages to metal atoms by organic linkages. The model for this approach is the polysiloxane system, where the presence of two organic groups attached to each silicon atom greatly changes chain rigidity compared to silica. Although many systems have and are being investigated, commercial success in this field is limited at present.

### 2-15b-1 Polymerization via Reaction at Metal Bond

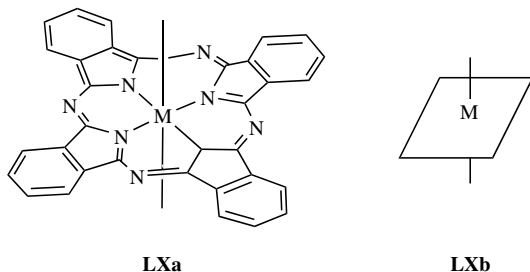
Many polymerizations used to synthesize organometallic polymers involve cleavage of a bond to the metal atom of one reactant followed by attachment at that metal of a fragment derived from a second reactant [Carraher et al., 1978; Kaliyappan and Kannan, 2000; Manners, 1996; Nguyen et al., 1999; Pittman et al., 1987; Sheets et al., 1985].

A wide range of reactions have been used, but only a few are illustrated here. Carboxylate and sulfide groups have been used to obtain organometallic polymers (Eqs. 2-235 and 2-236). These types of reactions have been used to synthesize organometallic polymers of a wide variety of other metals (e.g., Zr, Hf, Si, Ge, Pb, As, Sb, Bi, Mn, B, Se). The polymer obtained

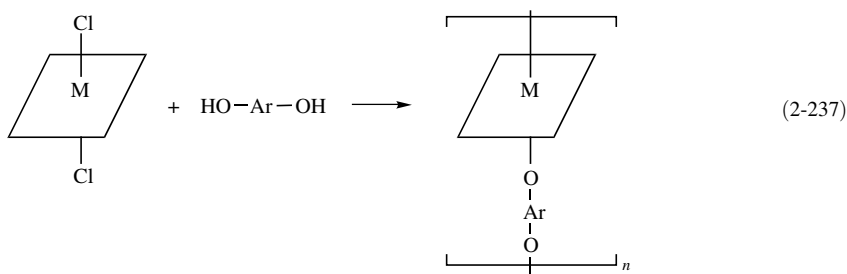


in Eq. 2-236 contains the titanocene group in which two cyclopentadienyl ligands are coordinated to titanium. Organometallic polymers containing coordinate-bonded metal atoms are referred to as *coordination polymers*.

The phthalocyanine moiety (**LXa**), where M represents a coordinated metal, has been incorporated into polymer structures. **LXa** is abbreviated by structure **LXb**. One reaction

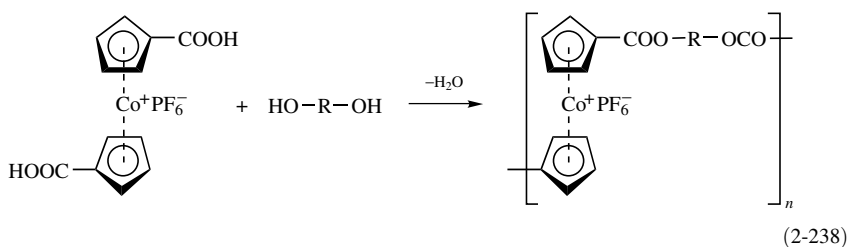


used for this purpose is the nucleophilic substitution on a phthalocyanine dichloride by a diphenol reactant (Eq. 2-237) [Snow and Griffith, 1988].



### 2-15b-2 Polymerization without Reaction at Metal Bond

An alternate synthetic approach to organometallic polymers is to perform reactions where the metal atom is not the reaction site. An example is a polyesterification between an organometallic monomer containing two carboxyl groups and a diol (Eq. 2-238). Reaction of the diacid with a diamine would yield an organometallic polymer via polyamidation. A wide range of other reactions covered in this chapter can be used to synthesize organometallic polymers.



### 2-15b-3 Polysilanes

*Polysilanes* are polymers in which there is catenation of silicon, that is, where silicon atoms are bonded to each other in a continuous manner. Synthesis of polysilanes involves the *Wurtz coupling* of diorganodichlorosilanes with sodium metal (Eq. 2-239) [Baldus and Jansen, 1997; Corriu, 2000; Manners, 1996; Miller and Michl, 1989; West, 1986; West and Maxka,

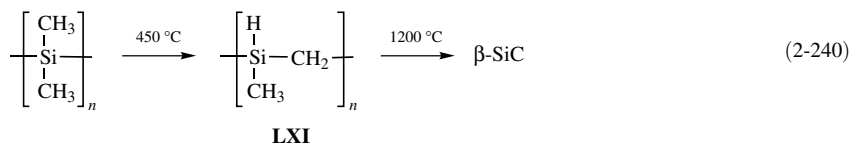


1988; Yajima et al., 1978]. The reaction is typically carried out in a hydrocarbon solvent such as toluene, xylene, or octane at temperatures above 100°C. Polymerization can be achieved at ambient temperature in the presence of ultrasound, which produces high temperature and

pressures locally for short bursts [Kim and Matyjaszewski, 1988]. The mechanism for this reaction is not established, but most evidence indicates polymerization is a complex process involving some combination of radical, anionic, and silylene (the Si analog of carbene) intermediates [Gauthier and Worsfold, 1989; Matyjaszewski et al., 1988]. Furthermore, although included in this chapter, the polymerization is probably a chain reaction. It is included here because of its technological importance in complementing the sol-gel process for producing ceramics. The corresponding polystannanes and polygermanes (Sn and Ge in place of Si) have also been synthesized by the Wurtz coupling reaction.

Polysilanes have been synthesized with various combinations of alkyl and aryl substituents. Polysilanes, such as polydimethylsilane or polydiphenylsilane, with symmetric substitution are highly crystalline and show little or no solubility in a range of organic solvents. (The IUPAC names of the two polymers are poly(dimethylsilanediy) and poly(diphenylsilanediy), respectively. They have also been referred to as *polydimethylsilylene* and *polydiphenylsilylene*.) Crystallinity is decreased and solubility increased when R and R' are different or for copolymers derived from two different symmetrically substituted dichlorosilanes. There is considerable interest in polysilanes from several viewpoints. Many of the interesting properties of polysilanes result from the relative ease of delocalization of the electrons in the catenated Si-Si  $\sigma$ -bonds as evidenced by the strong ultraviolet absorption at 300–400 nm. Polysilanes undergo photolytic radical cleavage with a high quantum yield and offer potential as radical initiators and positive photoresists. (In a positive photoresist application, the portions of a polymer not protected by a mask are degraded by irradiation and then dissolved by solvent or photovolatilized.) Polysilanes also offer potential as semiconductor, photoconductor and nonlinear optical materials.

The greatest interest in polysilanes is probably in their use as *preceramic polymers*. The normal powder metallurgy techniques for processing ceramic materials limits the complexity of the objects that can be produced. Polysilane chemistry offers an alternate with good potential for making a variety of objects, including fiber. Thermolysis of a polysilane in an inert atmosphere at 450°C yields a polycarbosilane through a complex rearrangement process. For example, poly(dimethylsilanediy) yields poly(methylsilanediy)methylene) (**LXI**) (Eq. 2-240). A soluble portion of the polycarbosilane is isolated by fractional precipitation from *n*-hexane and used as a ceramic precursor. The soluble polycarbosilane can be formed into objects (including fibers) and then pyrolyzed at 1200°C to yield the corresponding crystalline  $\beta$ -silicon carbide ceramic objects. Other organometallic polymers are being studied for use as precursor polymers for other ceramic systems, such as polysilazanes for silicon nitride [Baldus and Jansen, 1997; Baney and Chandra, 1988].



The use of a monoalkyltrichlorosilane in the Wurtz-type polymerization is reported to yield  $(\text{RSi})_n$  referred to as polyalkylsilyne [Bianconi et al., 1989]. The elemental composition and NMR spectra of the polymer suggest a three-dimensional crosslinked structure.

## 2-16 DENDRITIC (HIGHLY BRANCHED) POLYMERS

There is an ongoing effort to synthesize different, well-defined polymer architectures. A considerable thrust in this direction has been the synthesis of *dendritic* polymers [Bosman et al.,

1999; Fischer and Vogtle, 1999; Frechet and Tomalia, 2002; Kim, 1998; Newkome et al., 1999, 2001; Tomalia, 2001; Tomalia et al., 1990; Vogtle et al., 2000; Voit, 2000]. Dendritic polymers are highly branched polymers—polymers with treelike branching, where there are branches on branches on branches, and so on. Dendritic polymers differ considerably from linear (and also from lightly branched) polymers in their molecular shapes. Dendritic polymers have globular shapes, whereas linear polymers have elongated shapes. The term *globular shape* indicates that the dimensions of the polymer molecule are about the same in all directions, whereas the term *elongated shape* indicates that the dimensions are much greater in one direction than the other directions. [In the extreme, the globular shape is illustrated by a sphere or ellipsoid (where no axis is much longer than the other axes) and the elongated shape, by a cylinder (where the length of the cylinder is much greater than the diameter)].

The difference in molecular shape leads to differences in the attractive secondary forces present in linear and dendritic polymer molecules. The attractive secondary forces are greater for linear (elongated) polymers because the molecules pack together and attract each other over a larger surface area than is possible for dendritic (globular) polymer molecules. Also, dendritic polymer molecules do not undergo chain entanglements as do linear polymers. Thus, unlike linear polymers, dendritic polymers rarely have sufficient strength to be useful as fibers, rubbers, and plastics. However, because of their low secondary forces, dendritic polymers have higher solubility and miscibility with other materials, including other polymers. The globular shape of dendritic polymers also results in lower hydrodynamic volume and lower viscosity compared to linear polymers. Dendritic polymers have potential for use as additives to polymers and oils to modify their viscosity, melt behavior, and lubricating properties; and to aid in compatibilizing mixtures of different materials. The difference between linear and dendritic polymers has an analogy in nature. For example, there are globular and elongated (more often called *fibrous*) proteins. The fibrous proteins have strong secondary attractive forces and are used to construct such materials as bone, skin, and nails. Globular protein molecules do not attract each other strongly and are soluble in aqueous media, and this fits their biological functions. Globular proteins perform catalytic, transport, regulatory, hormonal, and other functions that require their solubility in blood and the other aqueous media of cells and tissues.

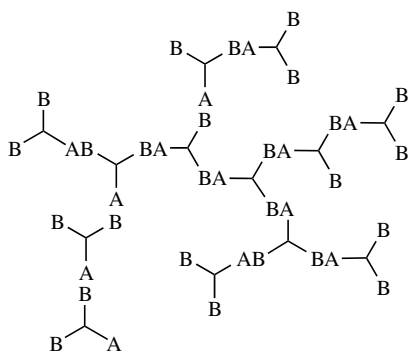
Another (obvious) difference between linear and dendritic polymers is that dendritic polymers have a much larger number of chain ends. The interesting situation arises when the dendritic polymers are synthesized by methods that result in functional groups such as  $\text{NH}_2$ ,  $\text{OH}$ , or  $\text{COOH}$  at the chain ends. Such polymers carry a large number of derivitizable functional groups and hold promise as carrier molecules for drug delivery, gene therapy, catalysis, and sensors [Frechet and Tomalia, 2002; Stiriba et al., 2002].

Two types of dendritic polymers have been developed: hyperbranched polymers and dendrimers.

## 2-16a Random Hyperbranched Polymers

*Hyperbranched* polymers are produced in a one-pot synthesis using a multifunctional monomer such as  $\text{AB}_f$  where  $f$  is 2 or greater [Bolton and Wooley, 2002; Galina et al., 2002; Kim, 1998; Voit, 2000]. Hyperbranched polymers are more correctly called *random hyperbranched* polymers because the branching occurs in a random manner. For an  $\text{AB}_2$  multifunctional monomer such as a diamino or dihydroxy carboxylic acid,  $f = 2$  and the product has a structure described by **LXII**. With increasing conversion  $\text{AB}_2$  adds to **LXII** to produce higher  $\bar{X}_n$  polymer. The random hyperbranched polymer at every stage of its growth has a single

unreacted A group. The number of unreacted B groups is given by Eq. 2-241 [Kim, 1998]. **LXII** has  $\bar{X}_n = 13$  and 14 unreacted B groups. The number of unreacted B groups increases with increasing  $\bar{X}_n$  and  $f$ .



**LXII**

$$\text{Unreacted B groups} = [1 + \bar{X}_n(f - 1)] \quad (2-241)$$

A hyperbranched polymer is often characterized by the degree of branching DB [Holter et al., 1997; Jo and Lee, 2001; Kim, 1998; Lee et al., 2000]. For the hyperbranched polymer produced from  $AB_2$ , there are three different types of repeat units: dendritic, linear, and terminal units defined as units having two, one, and no B groups reacted, respectively. The degree (fraction) of branching (DB) is given by

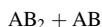
$$DB = \frac{D + T}{D + T + L} \quad (2-242)$$

where  $D$ ,  $L$ , and  $T$  are the mole fractions of dendritic, linear, and terminal units. For high molecular weight polymers,  $D$ ,  $L$ , and  $T$  have limiting values of 0.25, 0.25, and 0.50, respectively, and DB is 0.50. (For linear polymers, DB is zero. DB is 1 for dendrimers—Sec. 2-16b.)

Hyperbranched polymers are similar to linear polymers in that they show molecular weight polydispersity. There is also polydispersity due to constitutional isomerism, resulting from the different placements of monomer units. For example, **LXII** has many isomers, such as those arising from placement of the lower leftmost  $AB_2$  unit at any of the other positions around the perimeter of the molecule. The synthesis of hyperbranched polymers has inherent difficulties which limit molecular weight or shape. One is the occurrence of intramolecular cyclization, which decreases the functional groups available for polymerization. Another difficulty is the steric crowding that occurs within and/or at the periphery of hyperbranched molecules with increasing conversion and molecular size. (This steric crowding effect, discussed extensively for dendrimers, is called *de Gennes dense packing* [de Gennes and Hervet, 1983].) Although steric crowding may not limit polymer molecular weight (as it does for dendrimers), it will affect molecular shape. Functional groups in some regions become inaccessible for reaction, but growth proceeds in other regions where functional groups are accessible. Steric crowding in a region is relieved by an increase of linear (one unreacted

B group) units and fewer dendritic (no unreacted B groups) units. The polydispersity in molecular weight and isomerism, the intramolecular cyclization, and the molecular shape variations due to steric crowding contribute to the random nature of hyperbranched polymers.

Hyperbranched polymers can also be synthesized from the following systems [Jikei and Kakimoto, 2001]:



The  $AB_2 + AB$  system is equivalent to  $AB_2$  except that  $AB_2$  units are separated from each other by  $AB$  units. The  $AB_2 + B_3$  system modifies the  $AB_2$  system by using  $B_3$  as a central core from which polymerization radiates and offers greater control of molecular shape. The  $A_2 + B_3$  system is one of the standard systems used to produce crosslinked polymers (Sec. 2-10). It is useful for synthesizing hyperbranched polymers only when crosslinking is minimized by limiting conversion and/or diluting the reactants with solvent.

Hyperbranched polymers can also be synthesized by chain polymerization, ring-opening polymerization, and combinations of ring-opening and step polymerization [Kim, 1998; Voit, 2000] (Secs. 3-6e, 3-15b-4, 3-15b-5, 3-15c, 5-4c).

## 2-16b Dendrimers

*Dendrimers* are dendritic (highly branched) polymers with a more controlled structure than the hyperbranched polymers [Bosman et al., 1999; Fischer and Vogtle, 1999; Grayson and Frechet, 2001; Hecht, 2003; Newkome et al., 1999; Simanek and Gonzalez, 2002; Tomalia, 2001; Tomalia and Frechet, 2002; Vogtle et al., 2000]. Other terms have also been used to describe various dendritic polymers—*arborol*, *cascade*, *cauliflower*, *starburst*. The synthesis of dendrimers differs greatly from the one-pot process for hyperbranched polymers. Dendrimers are synthesized by more complicated processes involving sequential reactions. There are two different methods: divergent and convergent. The *divergent* method starts with a core molecule and builds outward by attaching to the core successive layers (or generations) of monomer units one at a time. A large variety of reactions (organometallic as well as organic) have been used in synthesizing dendrimers.

The divergent method is illustrated in Fig. 2-22 for the synthesis of polyamidoamine (PAMAM) dendrimers [Tomalia et al., 1990]. A repetitive sequence of two reactions are used—the Michael addition of an amine to an  $\alpha,\beta$ -unsaturated ester followed by nucleophilic substitution of ester by amine. Ammonia is the starting core molecule. The first step involves reaction of ammonia with excess methyl acrylate (MA) to form **LXIII** followed by reaction with excess ethylenediamine (EDA) to yield **LXIV**. **LXV** is a schematic representation of the dendrimer formed after four more repetitive sequences of MA and EDA.

Dendrimers are characterized by the number of *generations*, the number of layers or shells of repeat units, analogous to the layering of an onion. The number of generations is the number of repetitive sequences of the Michael addition and nucleophilic substitution reactions. **LXIV** and **LXV** correspond to generations 1 and 5, respectively. **LXIV** has three arms or three  $NH_2$  groups. Each generation doubles the number of arms or  $NH_2$  groups. The fifth-generation dendrimer (**LXV**) has 48 arms or  $NH_2$  groups.

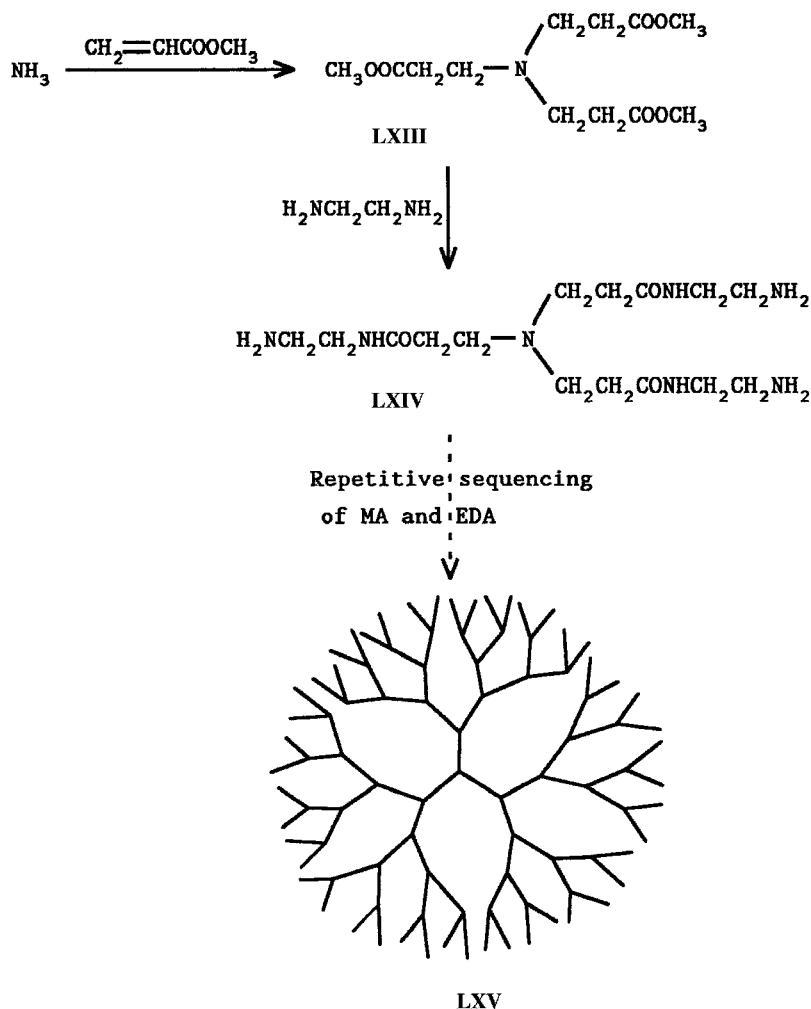


Fig. 2-22 Divergent synthesis of PAMAM dendrimer. Generation is 1 for LXIV and 5 for LXV.

The *convergent* method of dendrimer synthesis is shown in Fig. 2-23 for a dendrimer of five generations. Dendrimeric fragments are synthesized by repetitive reactions, and then several (three for the dendrimer in Fig. 2-23) are joined together in the last step by using a central core molecule to form the dendrimer. The method requires the use of appropriate reactants and chemical reactions. The functional group Z has an identity such that smaller fragments can be linked together to form a larger fragment, either by direct reaction with each other or with a coupling agent. The larger fragment also has a Z group because of the choice of appropriate reactants or coupling agent, and the linking of fragments continues in a repetitive manner. In some systems Z is a protected functional group that is deprotected at the appropriate time.

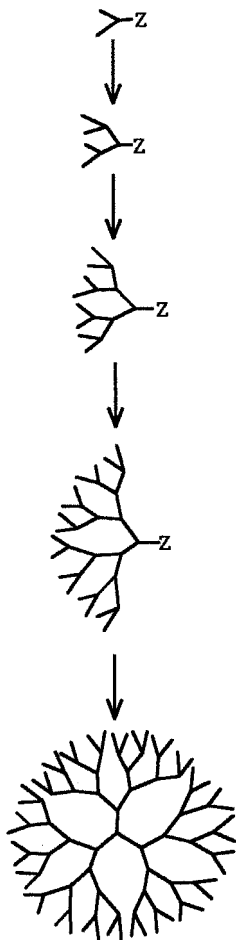


**Fig. 2-23** Convergent synthesis of dendrimer.

The convergent method also allows the synthesis of dendrimers of regular shapes other than spheres. Ellipsoid- and rod-shaped dendrimers can be synthesized by using appropriate core molecules [Tomalia, 2001].

Dendrimers have the potential for greater structural regularity and narrower molecular weight distribution than hyperbranched polymers. However, there are problems inherent in dendrimer synthesis that must be controlled to achieve this potential. There are many reactions to carry out, and each reaction includes physical manipulations to wash the product free of reagents. Each of these reactions and physical manipulations must be carried out with 100% efficiency to achieve a monodisperse product. For example, if a fraction of the second generation dendrimer is not perfect, that is, if some functional groups are unreacted, this imperfection is carried through each subsequent generation, and new imperfections in subsequent generations accumulate and carry forward to the higher generations. This is less of a problem for the convergent method than for the divergent method since the latter requires the

carrying out of a much greater number of reactions on a single molecule. The application of solid-phase synthetic techniques (Sec. 9-14) appears useful for increasing the efficiency of dendrimer synthesis [Lebreton et al., 2001].

It becomes progressively more difficult to form each new generation in the divergent synthetic method because of the de Gennes dense packing effect. The steric crowding within a dendrimer molecule and among its peripheral functional groups increases progressively for higher-generation dendrimers. This results in structural defects by distorting the shape of the dendrimer molecule and preventing complete reaction of all functional groups. Steric crowding becomes quite significant after about five generations, and the purity of higher-generation dendrimers decreases fairly rapidly. There are very few reports of dendrimers containing more than 10–15 generations. Steric crowding would appear at first glance to be not as important in the convergent synthetic method because the dendrimer fragments are relatively small compared to the dendrimer molecule. However, steric crowding is present when a number of dendrimer fragments (e.g., three for the synthesis described in Fig. 2-23) need to be joined together by reaction with a central core molecule to form the dendrimer. The steric crowding can be relieved by using a larger and more flexible central core molecule.

How do dendrimers and hyperbranched polymers compare from an industrial viewpoint? Dendrimers offer the potential for producing polymers whose molecular size and structure are more regular and less polydisperse. Hyperbranched polymers are easier and cheaper to synthesize—a one-pot synthesis compared to the multipot synthesis for dendrimers. However, not too many  $AB_f$  monomers are readily available, and this may modify the overall economics. Hyperbranched polymers will probably find use in larger-scale or commodity applications where lower cost is a necessity and dendrimers in specialty applications where higher cost is justified.

## 2-17 MISCELLANEOUS TOPICS

### 2-17a Enzymatic Polymerizations

#### 2-17a-1 *In Vivo (within Living Cells)*

Plants and animals synthesize a number of polymers (e.g., polysaccharides, proteins, nucleic acids) by reactions that almost always require a catalyst. The catalysts present in living systems are usually proteins and are called *enzymes*. Reactions catalyzed by enzymes are called *enzymatic reactions*; polymerizations catalyzed by enzymes are *enzymatic polymerizations*. Humans benefit from naturally occurring polymers in many ways. Our plant and animal foodstuffs consist of these polymers as well as nonpolymeric materials (e.g., sugar, vitamins, minerals). We use the polysaccharide cellulose (wood) to build homes and other structures and to produce paper.

Various microorganisms, such as yeast and bacteria, have been used in industrial bioreactors to produce a host of important products, including alcoholic beverages, penicillin, and carbohydrates (including polysaccharides such as starch). More recently, proteins have been produced for therapeutic purposes by *recombinant DNA technology* [Blei and Odian, 2000]. Diabetics who lack insulin have until now taken insulin derived from other animals such as pigs and beef. Pig and beef insulins are close to but not exactly the same in structure as human insulin. The bacterium *Escherichia coli* has been used to produce human insulin by recombinant DNA technology. The bacterial DNA is altered in the laboratory to contain the gene for human insulin and then inserted into the organism by various techniques

(chemical or thermal shock, viral vectors, microinjection). The *E. coli* are fooled into using the altered DNA to produce the desired human protein. The protein is then harvested by breaking the bacterial cell walls and using an appropriate separation technique. This approach offers much potential for producing a host of therapeutic proteins.

There has been an effort to use microorganisms to produce commodity polymers for use as plastics, elastomers, and fibers as a supplement to the polymers produced by the traditional methods such as those described throughout this chapter. Some species of bacteria produce poly(hydroxyalkanoate) (PHA) storage (reserve) polymers when growth is restricted by some nutrient other than their carbon-containing food source [Jung et al., 2000; Shah et al., 2000]. (This is analogous to the storage in higher animals of carbohydrates and lipids as glycogen and triacylglycerols, respectively [Blei and Odian, 2000].) Bacterial cultures such as *Pseudomonas oleovorans* and *Ralstonia eutropha* have been used to produce PHA polymers in the laboratory. The polyester structure can be varied to some extent by controlling the organic feed. *Biopol* is a small-scale commercial product—a copolymer of 3-hydroxybutanoate and 3-hydroxypentanoate repeat units. Such polymers are of interest because they are environmentally degradable and offer an alternative to recycling the large volumes of non-degradable polymer wastes.

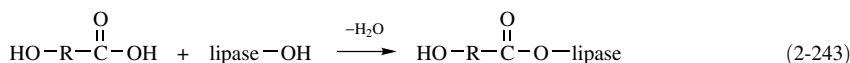
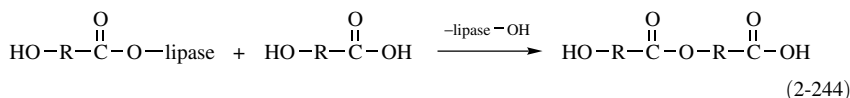
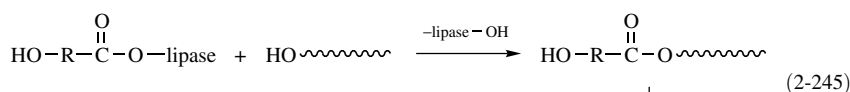
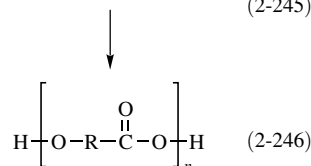
The mechanism for bacterial synthesis of PHA is not the simple dehydration reaction between alcohol and carboxyl groups. It is more complicated and involves the coenzyme A thioester derivative of the hydroxyalkanoic acid monomer (produced from the organic feedstock available to the bacteria) [Kamachi et al., 2001]. Growth involves an acyl transfer reaction catalyzed by the enzyme *PHA synthase* (also called a *polymerase*) [Blei and Odian, 2000]. The reaction is not a step polymerization but is a chain polymerization with the characteristics of a living polymerization [Su et al., 2000] (Secs. 3-15, 5-2g, Chap. 7).

### 2-17a-2 *In Vitro (outside Living Cells)*

The *in vivo* production of commodity polymers has been limited by the difficulties of controlling these processes, including the control of the reaction conditions required to maintain a bacterial culture and the conditions needed to harvest the polymer product. In addition, the *in vivo* method, although applicable for a few polymers, is not useful for the full range of polymers produced by the typical chemical processes. An alternate to the *in vivo* method is the use of enzymes to catalyze *in vitro* polymerizations. *In vitro enzymatic polymerizations* are enzyme-catalyzed polymerizations taking place outside cells, that is, taking place in glass and metal reactors. Biochemists carry out *in vitro* enzymatic polymerizations using the same reactants present in living cells for the purpose of understanding the reactions within living cells [Kamachi et al., 2001]. For polymer chemists, the major effort is the use of enzymes extracted from living cells to carry out *in vitro* polymerizations of nonnatural substrates to produce polymers for industrial use [Gross et al., 2001; Kobayashi, 1999; Kobayashi et al., 2001].

*Lipases* are enzymes that catalyze the *in vivo* hydrolysis of lipids such as triacylglycerols. Lipases are not used in biological systems for ester synthesis, presumably because the large amounts of water present preclude ester formation due to the law of mass action which favors hydrolysis. A different pathway (using the coenzyme A thioester of a carboxylic acid and the enzyme *synthase* [Blei and Odian, 2000]) is present in biological systems for ester formation. However, lipases do catalyze the *in vitro* esterification reaction and have been used to synthesize polyesters. The reaction between alcohols and carboxylic acids occurs in organic solvents where the absence of water favors esterification. However, water is a by-product and must be removed efficiently to maximize conversions and molecular weights.

The reaction mechanism for the polymerization of a hydroxyalkanoic acid (Eqs. 2-243 through 2-246) is a chain polymerization, often called an *activated monomer polymerization*. The active site of lipase is its serine  $\alpha$ -amino acid unit, which contains a hydroxyl group. The acyl carbon of the hydroxyalkanoic acid undergoes nucleophilic attack by the hydroxyl group of serine to form lipase-activated monomer (Eq. 2-243). Initiation consists of reaction



between monomer and lipase-activated monomer by nucleophilic attack of the hydroxyl group of monomer on the acyl carbon of lipase activated monomer, with regeneration of lipase (Eq. 2-244). Propagation proceeds in a similar manner—nucleophilic attack by the hydroxyl end group of a propagating chain on the acyl carbon of lipase-activated monomer, with regeneration of lipase. The reaction can also be considered as an *acyl transfer* reaction to emphasize the transfer of an acyl group from lipase-activated monomer to the hydroxyl group of the propagating chain. Lipases also produce polyesters when anhydrides or esters are used as reactants in place of acids. Ring-opening polymerizations catalyzed by enzymes have also been studied (Sec. 7-5).

Among other in vitro enzymatic polymerizations that have been studied are the oxidative polymerizations of 2,6-disubstituted phenols to poly(*p*-phenylene oxide)s (Sec. 2-14b) catalyzed by horseradish peroxidase [Higashimura et al., 2000b] and the polymerization of  $\beta$ -cellubiosyl fluoride to cellulose catalyzed by cellulase [Kobayashi, 1999; Kobayashi et al., 2001].

In vitro enzymatic polymerizations have the potential for processes that are more regio-selective and stereoselective, proceed under more moderate conditions, and are more benign toward the environment than the traditional chemical processes. However, little of this potential has been realized. A major problem is that the reaction rates are slow compared to non-enzymatic processes. Enzymatic polymerizations are limited to moderate temperatures (often no higher than 50–75°C) because enzymes are denatured and deactivated at higher temperatures. Also, the effective concentrations of enzymes in many systems are low because the enzymes are not soluble. Research efforts to address these factors include enzyme immobilization to increase enzyme stability and activity, solubilization of enzymes by association with a surfactant or covalent bonding with an appropriate compound, and genetic engineering of enzymes to tailor their catalytic activity to specific applications.

### 2-17b Polymerization in Supercritical Carbon Dioxide

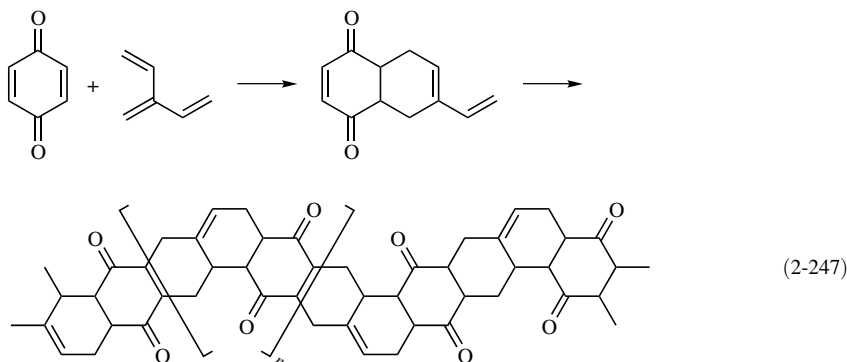
A supercritical fluid (SCF) is a substance above its critical temperature and critical pressure. The *critical temperature* is the highest temperature at which a substance can exist as a gas. The *critical pressure* is the pressure needed at the critical temperature to liquify a gas. Above the critical temperature and critical pressure, a substance has a density characteristic of a liquid but the flow properties of a gas, and this combination offers advantages as a reaction solvent. The liquidlike density allows the supercritical fluid to dissolve substances, while the gaslike flow properties offer the potential for fast reaction rates. Supercritical carbon dioxide (scCO<sub>2</sub>) has a critical temperature of 31°C and critical pressure of 73 atm.

Supercritical carbon dioxide has found uses in a number of applications. These applications take advantage of the safety and ease of removal of carbon dioxide compared to organic compounds. Decaffeination processes for coffee and tea now use scCO<sub>2</sub> instead of methylene chloride, which is a carcinogen. Supercritical carbon dioxide is also used to extract the flavors and fragrances from lemons, nutmeg, and other spices. Other applications include auto bumper coating and dry cleaning. DuPont has recently announced it will use scCO<sub>2</sub> technology to produce some fluorinated polymers (Sec. 3-14e).

Supercritical carbon dioxide has been studied as a solvent for various polymerizations, including step, chain, and ring-opening polymerization [Kendall et al., 1999; Wells and DeSimone, 2001]. Three results to date indicate that scCO<sub>2</sub> will probably not find widespread utilization in polymerizations, primarily because scCO<sub>2</sub> is not a good solvent for most polymers (even though it is a good solvent for many small molecules). However, this does not preclude applications in specific polymerizations such as those producing polysiloxanes and fluorinated polymers, which show significant solubility in scCO<sub>2</sub>, or in applications involving low-molecular-weight polymers.

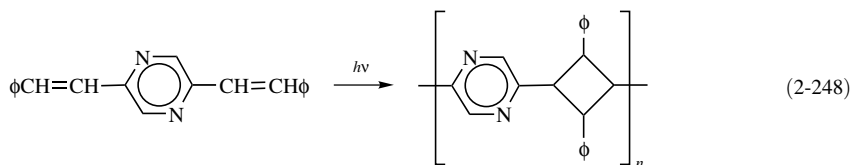
### 2-17c Cycloaddition (Four-Center) Polymerization

The Diels–Alder reaction, involving the [4 + 2]-cycloaddition of an unsaturated group (dienophile) to a 1,3-diene, has been studied for the synthesis of ladder polymers, such as the reaction of 2-vinyl-1,3-butadiene with benzoquinone [Bailey, 1972] (Eq. 2-247). Related polymerizations are those utilizing the [2 + 2]-cycloaddition reaction [Dilling, 1983]. While [4 + 2]-cycloaddition reactions are thermally induced, [2 + 2]-cycloaddition reactions are



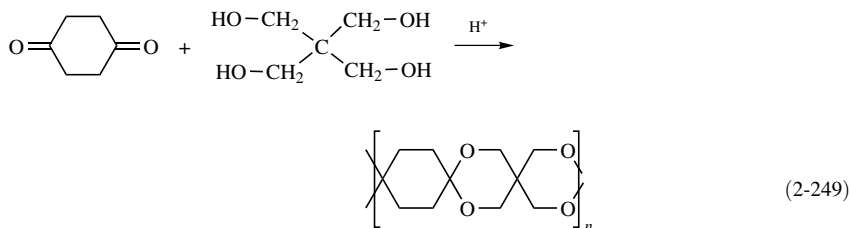
photochemically induced. The self-addition of alkene double bonds is the most extensively studied [2 + 2]-cycloaddition reaction, such as the polymerization of 2,5-distyrylpyrazine

(Eq. 2-248) [Braun and Wegner, 1983; Hasegawa et al., 1988, 1998]. This polymerization is a solid-state reaction involving irradiation of crystalline monomer with ultraviolet or ionizing radiation. The reaction is a *topochemical* or *lattice-controlled* polymerization in which reaction proceeds either inside the monomer crystal or at defect sites where the product structure and symmetry are controlled by the packing of monomer in the lattice or at defect sites, respectively.



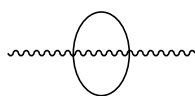
### 2-17d Spiro Polymers

Polymer chains based on *spiro structures* have been studied as another route to heat-resistant polymers [Kurita et al., 1979]. A spiro structure is a double-strand structure (Sec. 1-2c) in which the uninterrupted sequence of rings have one atom in common between adjacent rings. (Adjacent rings in ladder polymers have two or more atoms in common.) An example of a spiro polymer is the polyspiroketal synthesized from 1,4-cyclohexanedione and pentaerythritol (Eq. 2-249). The low solubility and intractability of spiro polymers makes it difficult to synthesize or utilize high-molecular-weight polymers.

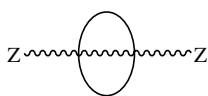


### 2-17e Pseudopolyrotoxanes and Polyrotoxanes

*Pseudopolyrotoxanes* and *polyrotoxanes* are polymers composed of a linear polymer chain threaded through one or more cyclic species [Gibson and Mahan, 2000; Raymo and Stoddart, 1999]. Synthesis of pseudopolyrotoxanes and polyrotoxanes involves polymerization of monomer(s) in the presence of the cyclic species. Cyclodextrins, crown ethers, paraquots, and other macrocyclics are used as the cyclic component. Both step and chain polymerizations have been successfully used.



Pseudopolyrotoxane



Polyrotoxane

There is a statistical extent of threading of the linear polymer chain through the macrocyclics present in the reaction system. The extent of threading is greater for larger macrocyclics. Threading is reversible and is dependent on enthalpic and entropic factors. The difference between pseudopolyrotoxanes and polyrotoxanes is the placement of bulky groups (Z), referred to as *stoppers*, along the linear polymer for polyrotoxanes. The stoppers prevent unthreading of the macrocyclics from the linear polymer chain.

There are many variations on the structures possible for polyrotoxanes. One variation is the number of macrocyclics per linear polymer chain. Another is the placement of the stopper groups. One may have stopper groups only at the two chain ends of the polymer. Alternately, there may be many stopper groups distributed randomly along the polymer chain between different cyclic species. In step polymerization, one may achieve the first situation by adding a reactant with the stopper groups at the end of the polymerization—to end-cap the linear polymer. The second situation can be achieved by including a monomer with stopper groups as part of the reaction system at the beginning of polymerization. In chain polymerization, the two different situations can be achieved by using appropriate initiators and terminating agents, or monomers containing the stopper groups.

Another variation for both pseudopolyrotoxanes and polyrotoxanes is the placement of the cyclic component on linear side chains during a graft polymerization process.

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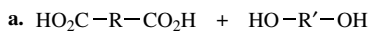
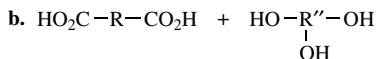
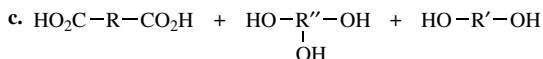
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## PROBLEMS

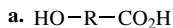
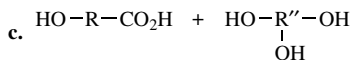
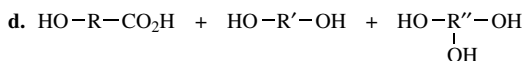
- 2-1** Derive an expression for the rate of polymerization of stoichiometric amounts of adipic acid and hexamethylene diamine. Indicate the assumptions inherent in the derivation. Derive an expression for the rate of polymerization of nonstoichiometric amounts of the two reactants.
- 2-2** A 21.3-g sample of poly(hexamethylene adipamide) is found to contain  $2.50 \times 10^{-3}$  mol of carboxyl groups by both titration with base and infrared spectroscopy. From these data the polymer is calculated to have a number-average molecular weight of 8520. What assumption is made in the calculation? How can one experimentally obtain the correct value of  $\bar{M}_n$ ?

- 2-3** Describe and draw the structure of the polyester obtained in each of the following polymerizations:



Will the structure of the polymer produced in each case depend on the relative amounts of the reactants? If so, describe the differences.

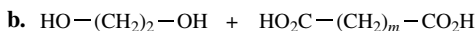
- 2-4** Describe and draw the structure of the polyester obtained in each of the following polymerizations:



Will the structure of the polymer produced in each of cases b, c, and d depend on the relative amounts of the reactants? If so, describe the differences.

- 2-5** Compare the molecular weight distributions that are expected for the polymerizations in Problems 2-3a, 2-4a, 2-4b, and 2-4c.

**2-6** Discuss the possibility of cyclization in the polymerization of



for the cases where  $m$  has values from 2 to 10? At what stage(s) in the reaction is cyclization possible? What factors determine whether cyclization or linear polymerization is the predominant reaction?

**2-7** Show that the time required to go from  $p = 0.98$  to  $p = 0.99$  is very close to the time to reach  $p = 0.98$  from the start of polymerization for the external acid-catalyzed polymerization of an equimolar mixture of a diol and diacid.

**2-8** The polymerization between equimolar amounts of a diol and diacid proceeds with an equilibrium constant of 200. What will be the expected degree of polymerization and extent of reaction if the reaction is carried out in a closed system without removal of the by-product water? To what level must  $[\text{H}_2\text{O}]$  be lowered in order to obtain a degree of polymerization of 200 if the initial concentration of carboxyl groups is  $2\text{ M}$ ?

**2-9** A heat-resistant polymer *Nomex* has a number-average molecular weight of 24,116. Hydrolysis of the polymer yields 39.31% by weight *m*-aminoaniline, 59.81% terephthalic acid, and 0.88% benzoic acid. Write the formula for this polymer. Calculate the degree of polymerization and the extent of reaction. Calculate the effect on the degree of polymerization if the polymerization had been carried out with twice the amount of benzoic acid.

**2-10** Calculate the number-average degree of polymerization of an equimolar mixture of adipic acid and hexamethylene diamine for extents of reaction 0.500, 0.800, 0.900, 0.950, 0.970, 0.990, 0.995.

**2-11** Calculate the feed ratio of adipic acid and hexamethylene diamine that should be employed to obtain a polyamide of approximately 15,000 molecular weight at 99.5% conversion. What is the identity of the end groups of this product? Do the same calculation for a 19,000-molecular-weight polymer.

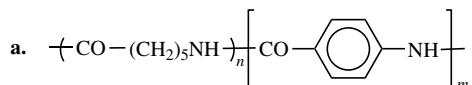
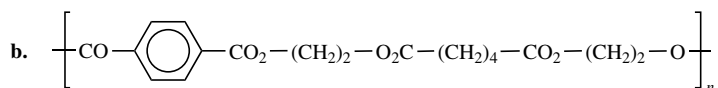
**2-12** What proportion of benzoic acid should be used with an equimolar mixture of adipic acid and hexamethylene diamine to produce a polymer of 10,000 molecular weight at 99.5% conversion? Do the same calculation for 19,000 and 28,000 molecular weight products.

**2-13** Calculate the extent of reaction at which gelation occurs for the following mixtures:

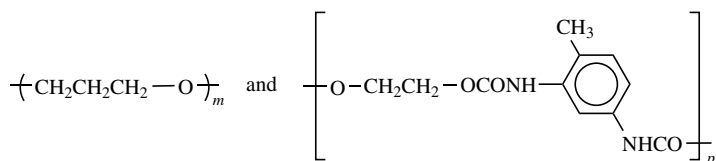
- a.** Phthalic anhydride and glycerol in stoichiometric amounts.
- b.** Phthalic anhydride and glycerol in the molar ratio 1.500 : 0.980
- c.** Phthalic anhydride, glycerol, and ethylene glycol in the molar ratio 1.500 : 0.990 : 0.002
- d.** Phthalic anhydride, glycerol, and ethylene glycol in the molar ratio 1.500 : 0.500 : 0.700

Compare the gel points calculated from the Carothers equation (and its modifications) with those using the statistical approach. Describe the effect of unequal functional groups reactivity (e.g., for the hydroxyl groups in glycerol) on the extent of reaction at the gel point.

- 2-14** Show by equations the polymerization of melamine and formaldehyde to form a crosslinked structure.
- 2-15** Describe by means of equations how random and block copolymers having the following compositions could be synthesized:



- 2-16** How would you synthesize a block copolymer having segments of the following structures?



- 2-17** Distinguish between spiro, ladder, and semiladder polymers. Give examples of each.
- 2-18** Describe the difference between the convergent and divergent approaches to synthesizing dendrimers.
- 2-19** For each of the following reactions system indicate whether the product is a linear, branched, crosslinked, or hyperbranched polymer.
- $\text{A}_2 + \text{B}_2$
  - $\text{AB}_2$
  - $\text{AB}_3$
  - $\text{A}_2 + \text{B}_3$
  - $\text{AB}_2 + \text{B}_3$
  - $\text{AB} + \text{B}_3$