Chapter 6

Condensation (Step-Reaction) Polymerization

I. INTRODUCTION

Condensation polymerization is chemically the same as a condensation reaction that produces a small organic molecule. However, as we saw in Chapter 2, in condensation polymerization (i.e., production of a macromolecule) the functionality of reactants must be at least 2. Recall that functionality was defined as the average number of reacting groups per reacting molecule. To derive expressions that describe the physical phenomena occurring during condensation polymerization (polycondensation) — a tool vital to process design and product control — three approaches have been traditionally adopted: kinetic, stoichiometric, and statistical. Various degrees of success have been achieved by each approach. We treat each approach in the succeeding sections. Before then, we briefly discuss the overall mechanism of polycondensation reactions.

II. MECHANISM OF CONDENSATION POLYMERIZATION

The mechanism of polycondensation reactions is thought to parallel that of the low-molecular-weight analogs. As a result of their macromolecular nature, polymers would be expected to have retarded mobility. It was therefore predicted, purely on theoretical arguments, that the chemical reactivity of polymers should be low.

- The collision rate of polymer molecules should be small due to their low kinetic velocity. This should be accentuated by the high viscosity of the liquid medium consisting of polymer molecules.
- Shielding of the reactive group within the coiling chain of its molecule should impose steric restrictions on the functional group. This would lead to a reduction in the reactivity of the reactants.

Flory[1] has shown from empirical data that for a homologous series the velocity constant measured under comparable conditions approaches an asymptotic limit as the chain length increases. He therefore proposed the equal reactivity principle, which states in essence that “the intrinsic reactivity of all functional groups is constant, independent of the molecular size.” This principle is in apparent contradiction to the theoretical prediction of low chemical reactivity for macromolecules discussed above. Flory used the following arguments to explain the equality of reactivity between macromolecules and their low-molecular-weight analogs.

1. Low diffusivity of macromolecules — Undoubtedly, large molecules diffuse slowly. But the gross mobility of functional groups must not be confused with the overall diffusion rate of the molecule as a whole. The terminal group, though attached to a sluggish moving polymer molecule, can diffuse through a considerable region due to the constant conformational changes of polymer segments in its vicinity. The mobility of the functional group is much greater than would be indicated by the macroscopic viscosity. Thus it was concluded that the actual collision frequency had little relation to the molecular mobility or macroscopic viscosity.

   A pair of neighboring functional groups may collide repeatedly before they either diffuse apart or react. The lower the diffusion rate, the longer these groups remain in the same vicinity. Consequently, the number of collisions will be greater and hence the probability of fruitful collisions will be greater. However, by the same token, once reactants diffuse apart, it will take a proportionately longer time before two reactants meet to engage in another series of collisions. Flory therefore concluded that for a sufficiently long time span, the decreased mobility resulting from larger molecular size and/or high viscosity will alter the time distribution of collisions experienced by a given functional group but not the average number of collisions.
2. Steric factor — Flory expected steric-factor-related reduction in chemical reactivity due to shielding of functional groups by coiling of their chain to occur only in dilute solution where sufficient space is

available for molecules to coil independently. In concentrated systems, however, polymer chains intertwine extensively. Functional groups show no preference for their own chains. The chains act as diluents whose effects can be accounted for by writing rate expressions in terms of concentration of functional groups and not in terms of molecules or mole fractions of molecules.

Example 6.1: The esterification of a monobasic acid by alcohol proceeds according to the following reaction.

$$H(CH_2)_{10}COOH + C_2H_5OH \xrightarrow{HCl} H(CH_2)_{10}COOC_2H_5 + H_2O \qquad \text{(Str. 1)}$$

The rate of ester formation is given by the equation:

$$\frac{d[\text{ester group}]}{dt} = k\,[\text{COOH}]\,[H^+]$$

For carboxyl group and HCl concentrations of 10^3 and 10^{-2} g-eq/l, respectively, the rate of esterification was found to be 7.6×10^{-3} g-eq/l/s. For the esterification of the dibasic acid $(CH_2)_{1000}(COOH)_2$, how much ester is formed in a 8-h day shift using a 100-l reactor if the carboxyl group concentration is 10^2 g-eq/l and the acid (HCl) concentration is 10^{-3} g-eq/l?

Solution: Notes:

1. The reactivity of one carboxyl group in the dibasic acid is unaffected by esterification of the other. Consequently, the same rate equation holds for the esterification of both monobasic and dibasic acids.
2. The rate equation is applicable to the esterifications of all polymethylene dibasic acids for which n is unity or greater.

From the above two observations, it follows that esterification rate constant for homologous series of dibasic acid is the same as those for monobasic acids.

$$\text{Rate} = k\left(10^3\,\frac{g\cdot eq}{\text{liter}}\right)\left(10^{-2}\,\frac{g\cdot eq}{\text{liter}}\right) = 7.6\times10^{-3}\left(\frac{g\cdot eq}{l\cdot s}\right)$$

$$k = 7.6\times10^{-4}\left(\frac{g\cdot eq}{l}\right)^{-1}\cdot\left(\frac{1}{s}\right)$$

$$\text{Rate (dibasic acid)} = \left(7.6\times10^{-4}\,\frac{l}{g\cdot eq}\,\frac{1}{s}\right)\left(10^2\,\frac{g\cdot eq}{l}\right)\left(10^{-3}\,\frac{g\cdot eq}{l}\right)$$

$$\left(7.6\times10^{-5}\,\frac{g\cdot eq}{l\cdot s}\right)(100\ l)\,(8\times3600\ s)$$

$$= 7.6\times10^{-5}\times100\times28800\ g\cdot eq$$

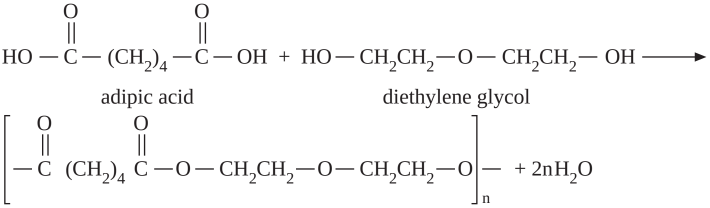
$$= 7.6\times28.8\ g\cdot eq$$

Concentrations are written as equivalents of functional groups. $(CH_2)_{1000}(COOC_2H_5)_2$: gram equivalent of functional group = 73. Ester produced in 8 h = $\frac{7.6\times28.8\times146}{10^3}$ = 32 kg.

III. KINETICS OF CONDENSATION POLYMERIZATION

Flory's equal reactivity principle, which has been validated on mechanistic and experimental grounds, has greatly simplified an otherwise complicated kinetic analysis of condensation polymerization. This principle in effect amounts kinetically to the proposition that all steps in a condensation polymerization have equal rate constants. We now consider two cases.

Case 1: Polymerization without Added Strong Acid: Consider esterification — the formation of a polyester from a glycol and a dibasic acid. The progress of reaction is easily followed by titrating the unreacted carboxyl groups in samples removed from the reaction mixture. This polyesterification and other simple esterifications are acid-catalyzed. In the absence of an added strong acid, a second molecule of the acid being esterified acts as the



$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH + HO-CH_2CH_2-O-CH_2CH_2-OH \longrightarrow$$

$$\left[-\overset{\overset{O}{\|}}{C}\ (CH_2)_4\ \overset{\overset{O}{\|}}{C}-O-CH_2CH_2-O-CH_2CH_2-O\right]_n- \ +2nH_2O$$

(Str. 2)

catalyst. The rate of polyesterification process can therefore be written:

$$\frac{-d[COOH]}{dt} = k[OH][COOH]^2 \tag{6.1}$$

where concentrations (written in square brackets) are expressed as equivalents of the functional groups. As written here Equation 6.1 assumes that the rate constant k is independent of molecular size of reacting species and is the same for all functional groups.

If the concentration, C, of the unreacted carboxyl and hydroxyl groups at time t are equal, Equation 6.1 may be rewritten as:

$$\frac{-dc}{dt} = kc^3 \tag{6.2}$$

On integration, this yields the third-order reaction expression

$$2\,kt = \frac{1}{c^2} - \text{constant} \tag{6.3}$$

Now, let us introduce the *extent of reaction*, p, defined as the fraction of the functional group that has reacted at time t. That is,

$$p = \frac{C_o - C}{C_o} \tag{6.4}$$

where C_o = initial concentration of one of the reactants. From Equation 6.4,

$$C = C_o(1-p) \tag{6.5}$$

Hence, on substitution, Equation 6.3 becomes

$$2C_o^2kt = \frac{1}{(1-p)^2} - 1 \tag{6.6}$$

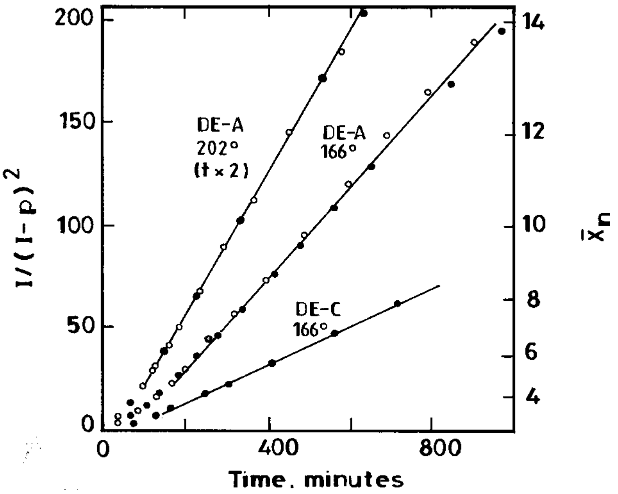


Figure 6.1 *Reaction of diethylene glycol with adipic acid (DE-A) and of diethylene glycol with caproic acid (DE-C). Time values at 202°C have been multiplied by two. (From Flory, P.J., J. Am. Chem. Soc., 61, 3334, 1939; 62, 2261, 1940. Copyright 1940 American Chemical Society. With permission.)*

A plot of $\frac{1}{(1-p)^2}$ against time should be linear. Figure 6.1 verifies this third-order kinetic expression. Note from Figure 6.1 that when $\frac{1}{(1-p)^2} = 25$ (i.e., when $\frac{1}{1-p} = \bar{x}_n = 5$) the plot is not linear. However, this behavior is not unique to polyesterification. A similar behavior is exhibited by the nonpolymer esterification of diethylene glycol and caproic acid. The similarity in behavior of both mono- and polyesterification provides a direct verification of the nondependence of reactivity on molecular size. The quantity $\frac{1}{1-p}$ is called the degree of polymerization, DP, which as we saw earlier corresponds to the average number of monomer molecules in the chain.

Case II: Polymerization with Added Strong Acid: The kinetic expression can be greatly simplified if the polyesterification is carried out in the presence of a small amount of strong acid, e.g., *p*-toluene sulfonic acid. With the catalyst concentration kept constant throughout the process, the rate expression becomes

$$\frac{-dc}{dt} = k'c^2 \tag{6.7}$$

where k′ = k [catalyst] and where the alcohol and carboxylic acid concentrations are kept constant. Integrating this second-order rate equation and inserting the extent of reaction, p, we have:

$$C_o k't = \frac{1}{1-p} - 1 \tag{6.8}$$

Figure 6.2 shows the linear relation between $\frac{1}{1-p}$ and time.

IV. STOICHIOMETRY IN LINEAR SYSTEMS

As noted earlier, linear polymers are obtained from condensation polymerization when the functionality of the reactants is 2. Two cases may be considered. Some commercial examples of step-growth polymerization are illustrated in Figure 6.3. Reactions A and B are two routes (esterification and ester interchange) for preparing the same compound [poly(ethylene terephthalate), PETP]. Reaction C is

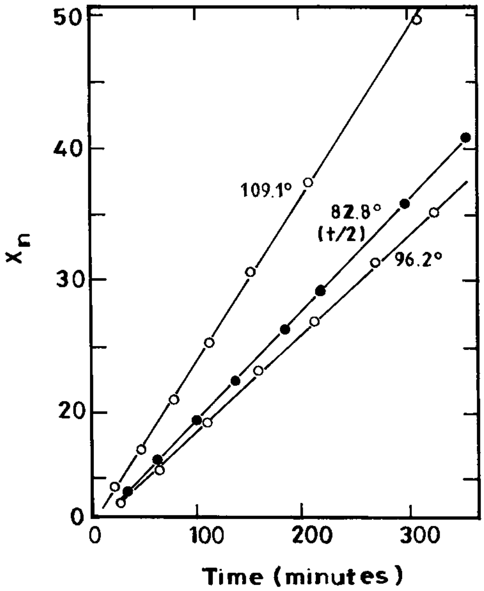


Figure 6.2 *Reaction of decamethylene glycol with adipic acid at the temperature indicated, catalyzed by 0.10 eq% of p-toluenesulfonic acid. The time scale for the results at 82.8°C is to be multiplied by two. (From Flory, P.J., J. Am. Chem. Soc., 61, 3334, 1939; 62, 2261, 1940. Copyright 1940 American Chemical Society. With permission.)*

preparation of nylon 6,6 from adipic acid and hexamethylenediamine. Note that in each of these three reactions, each of the two monomers is bifunctional and contains the same functionality at each end, that is, A–A or B–B. Alternatively, a polymer can also be formed by intramolecular reaction. An example is the formation of an aliphatic polyester by the self-condensation of ω-hydroxycarboxylic acid (reaction D, Figure 6.3). Since the end functional groups of the acid are different, this polyesterification reaction is an example of an A-B step-growth condensation polymerization.

We now proceed to discuss the stoichiometry of these two types of linear system represented by:

$$\begin{aligned} &\text{I:}\ \ \text{A–B} \rightarrow (\text{A–B–A–B–A–B}) + \text{small molecule} \\ &\text{II:}\ \ \text{A–A} + \text{B–B} \rightarrow \text{A}(\text{B–A–B–A–B–A})\text{–B} + \text{simple molecule} \end{aligned} \tag{Str. 3}$$

Suppose we start with the bifunctional monomers exclusively such that the number of A groups is precisely equivalent to that of B groups. Obviously, the requirement that A and B groups be present in equivalent amounts is automatically satisfied by A–B type polycondensation provided the monomers are pure and no side reactions occur. For type A–A/B–B polymerization we require, in addition, that the reactants must be present in equivalent proportions. At any stage of the polymerization process, each molecule will be terminated on either side by an unreacted functional group. Therefore, the number of molecules present can be determined by measuring the number of structural units per molecule, i.e., the number-average degree of polymerization, $\bar{X}_n$, is given by the ratio of the initial number of molecules to the final number of molecules, i.e.,

$$\begin{aligned} \bar{X}_n &= \frac{\text{original number of molecules}}{\text{final number of molecules}} \\ &= \frac{C_o}{C_o(1-p)} = \frac{1}{1-p} \end{aligned} \tag{6.9}$$

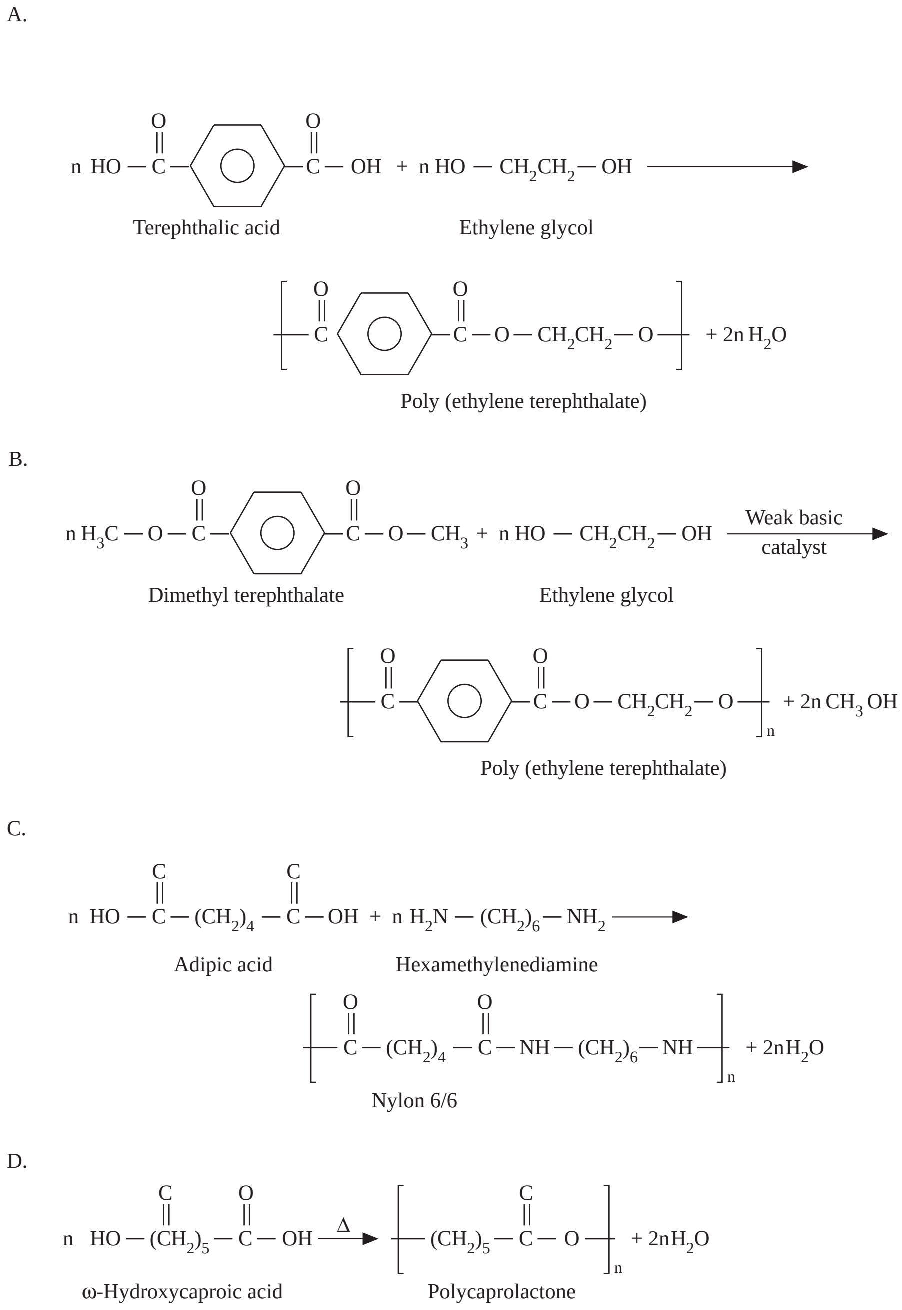


Figure 6.3 *Classical condensation reactions; are (A) esterification, (B) ester interchange, (C) amidization, and (D) intramolecular reaction. Two routes, A and B, can be taken to prepare PET. (From Fried, J.R., Plast. Eng., 38(10), 27, 1982. With permission.)*

From the definition of $\overline{X}_n$, it follows that the number-average molecular weight will be given by the expression:

$$\overline{M}_n = \overline{X}_n M_o = \frac{M_o}{1 - p} \tag{6.10}$$

where M_o = average molecular weight of the structural unit.

To avoid confusion, it is necessary to reemphasize the definition of structural unit — the residue from a glycol or from a dibasic acid. This means that the number of structural units equals the total number of bifunctional monomers initially present. Thus the repeating unit of a chain derived from A–A/B–B type monomers consists of two structural units, while the repeat unit in the case of type A–B monomers is the same as the structural unit.

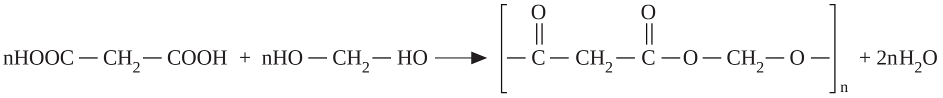
Table 6.1 *High Molecular Weight Achieved Only by High Conversion*

P	0	0.5	0.8	0.9	0.95	0.99	0.999	0.9999	1.0
$\overline{M}_n$	1	2	5	10	20	100	1,000	10,000	∞

A closer look at Equation 6.9 reveals that in condensation polymerization, a high molecular weight product is obtained only when the extent of reaction is almost 100% as shown in Table 6.1. Polymers, by definition, derive their unique properties from their high molecular weights. Thus, commercially useful condensation polymers are obtained only under the rather stringent condition of almost quantitative reaction. This means that in addition to high conversion, a step-growth polymerization requires high yield and high monomer(s) purity.

Example 6.2: For condensation polymerization between a dibasic acid and a glycol, show that M_o is the average molecular weight of the structural units where the structural unit is the residue from each monomer.

Solution: Consider the polycondensation reaction



$$nHOOC-CH_2-COOH + nHO-CH_2-HO \longrightarrow \left[-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-O- \right]_n + 2nH_2O$$

(Str. 4)

Assume that we start with 10 moles of each monomer and suppose that the extent of reaction at a time t equals p = 0.5. By definition

$$p = \frac{N_i - N}{N_i}$$

N_i = initial number of moles
N = number of moles at time t

At time t,

$$\begin{aligned} N &= N_i (1 - p) \\ &= 20 (1 - 0.5) \\ &= 10 \end{aligned}$$

Now

$$\overline{X}_n = \frac{1}{1-P} = \frac{1}{1-0.5} = 2$$

$$\overline{M}_n = \overline{X}_n M_o = \frac{M_o}{1-P} = 2M_o$$

M_o = molecular weight of structural unit

Three cases have to be considered.

Case 1:

M_o = molecular weight of repeating unit
= 116 kg/kg mol
$\overline{M}_n = 2M_o$ = 232 kg/kg mol
Mass of polymer = 232 × 10 = 2320 kg

Case 2:

M_o = average molecular weight of starting monomers
$= \frac{104 + 48}{2} = 76$
$M_n = 2M_o = 152$
Mass of polymer produced at t = 152 × 10 = 1520 kg

Case 3:

M_o = average molecular weight of structural units where structural unit equals residue from each monomer
$= \frac{116}{2} = 58$
$\overline{M}_n = 2 \times 58 = 116$
Mass of polymer produced = $M_n \times 10$ = 1160 kg

To establish which of the above definitions of M_o is correct, we need to carry out a simple mass balance:

Initial mass = sum of masses of reactants = 104 × 10 + 48 × 10 = 1520 kg
Mass of product = mass of polymer + mass of H_2O split off
Mass of water split off = $2nH_2O = 2 \times 10 \times 18 = 360$

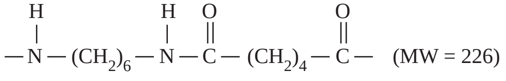
Case 1: mass of product = 2320 + 360 = 2680 kg
Case 2: mass of product = 1520 + 360 = 1880 kg
Case 3: mass of product = 1160 + 360 = 1520 kg

From mass balance, it is obvious that only Case 3 gives a correct mass balance.

Example 6.3: A 21.3 g sample of poly(hexamethylene adipamide) is found to contain 2.50×10^{-3} mol of carboxyl groups by both titration with base and infrared spectroscopy. From these data calculate

a. The number-average molecular weight
b. The extent of reaction

What assumption is made in your calculations?



$$-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}- \quad (MW = 226)$$

(Str. 5)

$$\overline{M}_n = \frac{\sum W_i}{\sum N_i} = \frac{W}{N} = \frac{21.3}{2.5 \times 10^{-3}} = 8520 \text{ g/g mol}$$

$$\overline{X}_n = \frac{1}{1-p} = \frac{\overline{M}_n}{M_o}$$

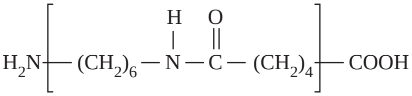
where M_o = average molecular weight of residue $= \frac{226}{2} = 113$.

$$\frac{1}{1-p} = \frac{8520}{113} = 75.40$$

$$1 - p = 0.013$$

$$p = 98.7\%$$

Assumption is that each polymer molecule contains one –COOH group, i.e.,



$$H_2N\left[(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4\right]COOH$$

(Str. 6)

V. MOLECULAR WEIGHT CONTROL

From the above discussion, it is obvious that in addition to high conversion, a step-growth polymerization requires high yield and high monomer purity to obtain a polymer of high molecular weight. High yield means the absence of any side reactions that could deactivate the polymerization process. For example, any side reactions that would lead to monofunctional units that are incapable of further reaction would limit the formation of high molecular weight of A–A/B–B or A–B type polymers. In general, depression of molecular weight can be brought about by:

- Nonequivalence of reactants
- Monofunctional ingredients introduced as impurities formed by side reaction
- Unbalance in stoichiometric proportions

Suppose an excess of a functional group is obtained by the addition of reactant designated B+B. In this case the two types of polymerizations discussed above become:

Case I: A–B + little B+B
Case II: A–A + B– + little B+B

Then let

N_A = total number of A groups initially present
N_B = total number of B groups initially present

$$r = \frac{N_A}{N_B} < 1 \quad \text{i.e., } N_A < N_B \tag{6.11}$$

P_A = fraction of A groups that have reacted at a given stage of the reaction

Total number of units = $\frac{N_A + N_B}{2}$

$$= \frac{N_A}{2}\left[1 + \frac{1}{r}\right] \tag{6.12}$$

At any stage of the reaction, possible types of chains are

A–BA–BA–BA–B	(type IA)
B–AB–AB–AB–AB–B	(type IB)

Number of molecules of type IA = $N_A\,(1 - P_A)$, and number of molecules of type IB = $\frac{N_B - N_A}{2}$ (i.e., number of molecules due to excess reactant):

Total number of molecules at any stage of the reaction:

$$N_A\left(1-p_A\right)+\frac{N_A}{2}\left[\frac{1}{r}-1\right]$$

$$=\frac{N_A}{2}r\left[2r\left(1-P_A\right)+\left(r-r\right)\right]$$

Now

$$\overline{X}_n=\frac{\text{original no. of molecules}}{\text{final no. of molecules}} \tag{6.13}$$

$$\overline{X}_n=\frac{1+r}{2r\left(1-P_A\right)+1-r} \tag{6.14}$$

For r = 1 (for stoichiometric amounts of A and B)

$$\overline{X}_n=\frac{1}{1-p} \tag{6.15}$$

For p = 1, i.e., degree of polymerization is maximum.

$$\overline{X}_n=\frac{1+r}{1-r} \tag{6.16}$$

By playing around with Equation 6.14 we see how the degree of polymerization and hence the molecular weight of the product is influenced by a proper control of the purity of reactants and prevention of extraneous reactions. In practice the molecular weight of nylons can be stabilized by the deliberate addition of a predetermined amount of a monofunctional monomer like acetic acid.

Note that Equation 6.14 can be used to evaluate the degree of polymerization in a system containing bifunctional reactants and a small amount of monofunctional species provided r is defined as

$$r=\frac{N_A}{N_A+2N_{B+}} \tag{6.17}$$

VI. MOLECULAR WEIGHT DISTRIBUTION IN LINEAR CONDENSATION SYSTEMS

From Flory's equal reactivity principle, it follows that each functional group during condensation polymerization has an equal chance of reacting irrespective of the molecular size of the group to which it is attached. Therefore, the probability that a given functional group has reacted should simply be equal to the extent of reaction of that functional group. For type A–B polycondensations or for stoichiometric quantities in type A–A/B–B polymerization, this probability is equal to $P_A = P_B$. Obviously, since the reaction of functional groups is a random event, various molecular sizes of product will be present in the reaction mixture at any particular stage of the reaction. The question therefore is the probability of finding a molecule of size, say, X. Consider the following molecule of A–B type polycondensation:

$$ARB_1-ARB_2-ARB_3\ldots\ldots\ldots\ldots ARB-ARB_{x-1}-ARB_x \tag{Str. 7}$$

The probability that the first functional group B has undergone condensation with A is p, the extent of reaction. By similar reasoning, the probability that the second B has also reacted is also p and so on. A molecule containing X units must have undergone X – 1 reactions. The probability that this number of reactions has occurred is simply the product of individual reaction probabilities, i.e., p^{x-1}. The probability of finding an unreacted end group is 1 – p. Therefore the total probability, P_x, that a given polymer molecule contains X units is

$$P_x = p^{x-1}(1-p). \tag{6.18}$$

Evidently this P_x must be equal to the mole fraction, n_x, of X-mers in the reaction system of the extent of reaction p.

$$P_x = n_x = \frac{N_x}{N} \tag{6.19}$$

where N is the total number of molecules of all sizes in the system and N_x is the number of X-mers. But N is related to the initial number of monomers, N_o, by the relation:

$$N = N_o(1-p) \tag{6.20}$$

On substitution the number of X-mers in terms of the initial amount of monomers and the extent of reaction, Equation 6.19 becomes:

$$N_x = N_o\,p^{x-1}(1-p)^2 \tag{6.21}$$

The weight fraction, W_x, of X-mers is obtained by dividing the weight of X-mers by the weight of all the molecules, i.e.,

$$W_x = \frac{xN_x}{N_o} \tag{6.22}$$

or substitution, in Equation 6.21, we obtain

$$W_x = xp^{x-1}(1-p)^2. \tag{6.23}$$

The distributions given in Equations 6.21 and 6.23 are known as the *most probable distributions* and are shown graphically in Figures 6.4 and 6.5.

From Equation 6.21 it is observed that on a mole fraction basis, low-molecular-weight chains are most abundant even at high extents of reaction. However, on a weight fraction basis (Equation 6.23), W_x passes through a maximum near the number average value of x. Also, low-molecular-weight chains are less significant.

VII. MOLECULAR WEIGHT AVERAGES

The most probable distributions derived above lead to expressions for molecular weight averages $\overline{M}_n$ and $\overline{M}_w$. From Chapter 3, $\overline{M}_n$ is defined by the relation:

$$\overline{M}_n = \frac{\sum_{x-1}^{\infty} M_x N_x}{\sum_{x=1}^{\infty} N_x} = \frac{\sum_{x=1}^{\infty} (M_o X) N_x}{\sum_{x=1}^{\infty} N_x} \tag{6.24}$$

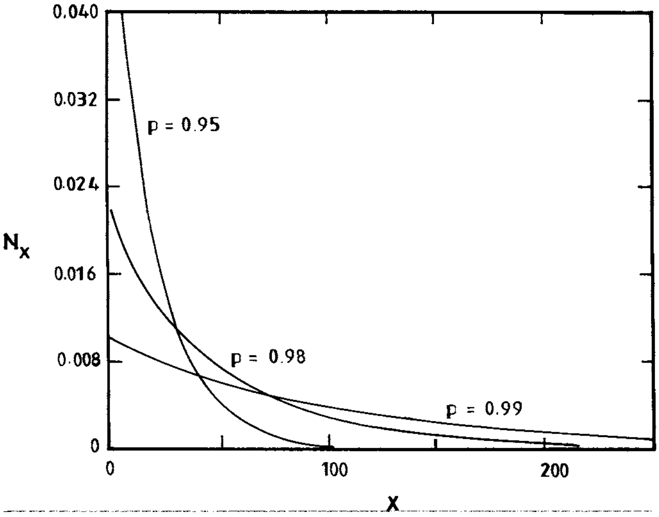


Figure 6.4 *Mole fraction distribution of chain molecules in a linear condensation polymer for several extents of reaction. (From Flory, P.J., Chem. Rev., 39, 137, 1946. With permission.)*

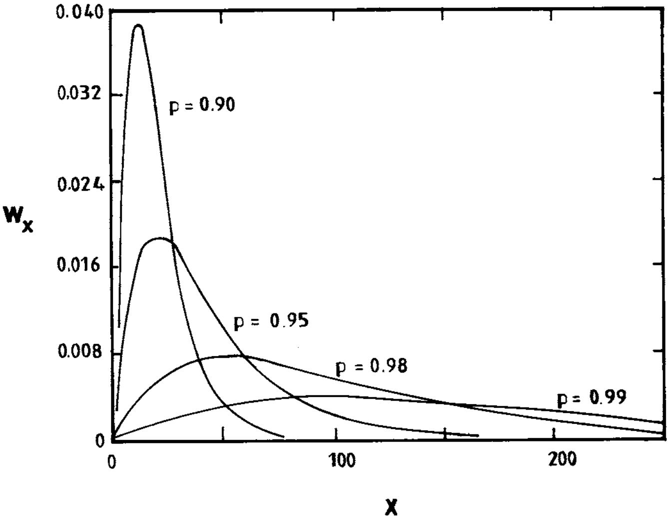


Figure 6.5 *Weight fraction distribution of chain molecules in linear condensation polymers for several extents of reaction. (From Flory, P.J., Chem. Rev., 39, 137, 1946. With permission.)*

Here M_n = molecular weight of an X-mer. Thus,

$$\overline{M}_n = M_o \Sigma x(1-p)p^{x-1} \tag{6.25}$$

It can be shown that

$$\overline{X}_n = \Sigma x(1-p)p^{x-1} \tag{6.26}$$

$$\overline{X}_n = \frac{1}{1-p} \tag{6.27}$$

and

$$\overline{M}_n = \frac{M_o}{1-p} \tag{6.28}$$

The weight-average molecular weight is defined by:

$$\overline{M}_w = \frac{\sum_{x-1}^{\infty} M_x w_x}{\sum_{x=1}^{\infty} w_x} = \frac{\sum_{x=1}^{\infty} M_o (X)^2 N_x}{\sum_{x=1}^{\infty} M_o (X) N_x} \tag{6.29}$$

where w_x = weight fraction of X-mers

$= \dfrac{w_x}{w}\ \dfrac{\text{weight of X-mers}}{\text{weight of all molecules}}$

From where

$$\overline{X}_w = \frac{1+p}{1-p} \tag{6.30}$$

and

$$\overline{M}_w = M_o \overline{X}_w \tag{6.31}$$

The ratio

$$\frac{\overline{X}_n}{\overline{X}_n} = 1 + p \tag{6.32}$$

is a quantitative measure of polydispersity or the spread of the molecular weight curve as

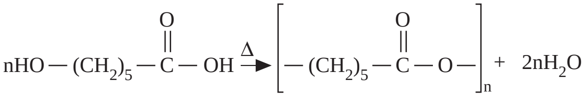
$$p \rightarrow 1, \frac{\overline{X}_w}{\overline{X}_n} \rightarrow 2 \tag{6.33}$$

Example 6.4: a. Polyester fibers for "lace" material can, in principle, be produced from ω = hydroxycaproic acid. If the initial 100 moles of the hydroxyacid are reduced to 2 moles after 10 h reaction time, calculate:

1. The number average molecular weight $\overline{M}_n$
2. The weight average molecular weight $\overline{M}_w$
3. The probability that the reaction mixture contains tetramers
4. The weight fraction of these tetramers.

b. As a result of extraneous reactions of the hydroxyl groups, a 5% excess of the carboxylic acid is present in the reaction mixture. Calculate the number-average molecular weight for the same extent of reaction in a.

Solutions: a. The polymerization of ω-hydroxycaproic acid proceeds according to the following equation:



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

(Str. 8)

$$\text{Extent of reaction } p = \frac{C_o - C}{C_o} = \frac{100-2}{100} = 0.98$$

1. $$\bar{M}_n = \bar{X}_n M_o + \frac{M_o}{1-p} = \frac{114}{0.02} = 5700$$

2. $$\bar{M}_w = X_w M_o = M_o\left[\frac{1+p}{1-p}\right] = 114\left[\frac{1.98}{0.02}\right] = 11{,}286$$

3. $$P_x = p^{x-1}(1-p)$$
$$= (0.98)^{4-1}(1-0.98) = 0.019$$

4. $$W_x = X\left(p^{x-1}\right)(1-p)$$
$$= 4(0.98)^3(0.02)^2 = 1.51 \times 10^{-3}$$

b. $$\bar{X}_n = \frac{1+r}{2r(1-p)+1-r}$$

$$r = \frac{100}{105} = 0.95$$

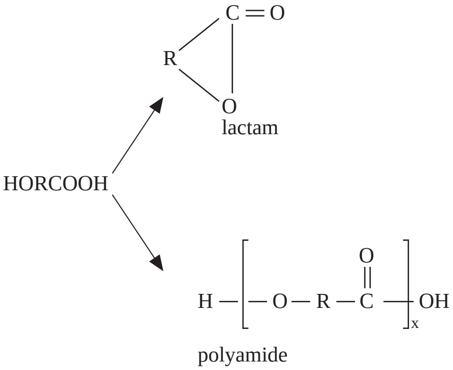
$$\bar{X}_n = \frac{1+0.95}{2(0.95)(1-0.98)+1-0.95} = 22.16$$

$$\bar{M}_n = \bar{X}_n M_o = 2526$$

Notice the depression in $\bar{M}_n$ as a result of stoichiometric imbalance.

VIII. RING FORMATION VS. CHAIN POLYMERIZATION

We observed earlier that polymer formation requires that the reacting monomer(s) must be at least bifunctional. It is pertinent to point out at this stage that polyfunctionality of reactants is a necessary but not sufficient condition for the formation of a polymer. Bifunctional monomers whether of the A–A/B–B or A–B types may react intramolecularly to produce cyclic products. For example, hydroxy acids when heated may yield lactams or linear polyamides.



(Str. 9)

The prime factor that determines the type of product is the size of the ring that is obtained by cyclization. If the ring size is less than five atoms or more than seven, polymer formation is almost entirely favored. If a five-membered ring can be formed, this occurs exclusively. If a ring of six or seven atoms can form, either the ring or linear polymer or both will be the product. Larger rings can be formed under special conditions.

The difficulty of forming rings with less than five members is due to the strain imposed by the valence angles of the ring atom. Five-membered rings are strain-free while all larger rings can be strainless if nonplanar forms are possible.

IX. THREE-DIMENSIONAL NETWORK STEP-REACTION POLYMERS

As recalled from our earlier discussion, we stated that if one of the reactants in step-growth polymerization has a functionality greater than 2, then the formation of a branched or a three-dimensional or cross-linked polymer is potentially possible. An example is the reaction between a dibasic acid and glycerol, which has two primary and one secondary hydroxyl groups (functionality of 3). A monomer that possesses such a functionality is referred to as a *branch unit.* Every reaction of such a molecule introduces a *branch point* for the development of the three-dimensional network. The portion of a polymer molecule lying between two branch points or a branch point and a chain end is called a *chain section* or *segment.*

As polymerization proceeds many branch points are formed. Reaction between large molecules considerably increases the number of reaction groups per polymer chain. The size of the polymer molecules increases rapidly, culminating in the formation of a three-dimensional network polymer of infinite molecular weight. During this process, the viscosity of the reaction medium increases gradually at first and experiences a sudden and enormous increase just before the formation of the three-dimensional network (Figure 6.6). The reaction medium loses fluidity, and bubbles cease to rise through it. *Gelation* is said to have occurred at this point, which is referred to as the *gel point.*

The sudden onset of gelation does not indicate that all the reactants have become bound together in the resulting three-dimensional network. Gelation marks the division of the reaction medium into an insoluble material called the *gel* and a portion still soluble in an appropriate solvent referred to as the *sol.* If polymerization is continued beyond the gel point, the gel fraction increases at the expense of the sol. As would be expected, at gelation there is a considerable depletion of individual molecules, and consequently the number-average molecular weight becomes very low. On the other hand, the weight-average molecular weight becomes infinite.

X. PREDICTION OF THE GEL POINT

We want to be able to define under which conditions a three-dimensional network will be formed, that is, the point at which gelation takes place during a reaction. To do this, let us introduce the term branching coefficient, α, which is defined as the probability that a given functional group of a branch unit is connected via a chain of bifunctional units to another branch unit. Let us illustrate this through the following example.

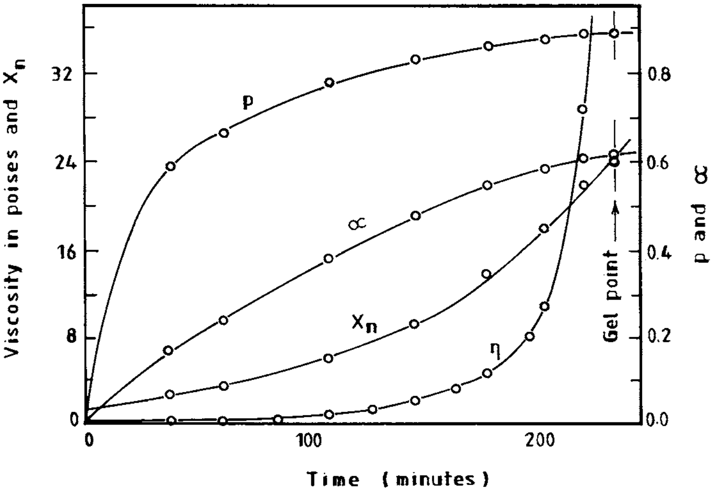
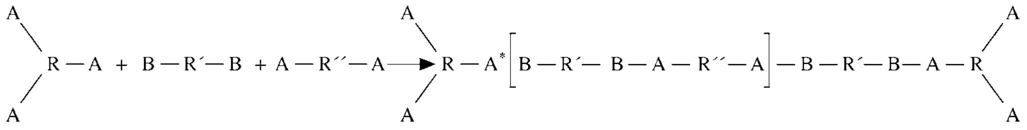


Figure 6.6 *The course of typical three-dimensional polyesterification. (From Flory, P.J., J. Am. Chem. Soc., 63, 3083, 1941. Copyright 1941 American Chemical Society.)*



(Str. 10)

where i varies from 0 to ∞.

In considering this reaction, assumptions are made:

- The principle of equal reactivity of functional groups holds through the condensation. This means that the reactivity of a given A or B group is independent of the size or structure to which the group is attached. In practice this is not strictly true, for it is known, for example, that in glycerol the secondary hydroxyl is less reactive than either of the two primary groups.
- Intramolecular reactions between A and B are forbidden. This, again, is not entirely correct.

We will, however, neglect for the moment errors that will be introduced into our calculations as a result of these assumptions. With these assumptions in mind, we note that the probability that A* has reacted is P_A, the fraction (or extent of reaction) of A groups that have reacted. Similarly, the probability that B** has reacted is P_B.

Now let us define another fractional parameter ρ, as the ratio of A groups both reacted and unreacted on the branch units to all or the total A groups in the mixture. In this case, the probability that a B group has reacted with an A on a branch unit is $P^B\rho$ while the probability that a B group has reacted with an A group on a bifunctional unit (A–A) is $P_B(1 - \rho)$. It follows that the probability that the chain segment shown is formed is given by $P_A{*}P_B(1 - \rho)\ P_A{*}^i\ P_B\ \rho$. Summing overall values of i yields

$$\alpha = \frac{P_A P_B \rho}{1 - P_A P_B (1 - \rho)} \tag{6.34}$$

If we define $r = \frac{N_A}{N_B} = \frac{\text{A groups initially present}}{\text{B groups initially present}}$,

then $P_A = rP_A$.

To eliminate either P_A or P_B, we substitute this relation in Equation 6.34 to obtain:

$$\alpha = \frac{rP_A^2\rho}{1 - rP_A^2(1-\rho)} \tag{6.35}$$

or

$$\alpha = \frac{P_B^2\rho}{r - P_B^2(1-\rho)} \tag{6.36}$$

Consider special cases of interest.

1. When A and B groups are present in equivalent quantities: $r = 1$, $P_A = P_B = P$, and

$$\alpha = \frac{P^2\rho}{1 - P^2(1-\rho)} \tag{6.37}$$

2. If there are no bifunctional A–R–A units, $\rho = 1$ and

$$\alpha = rP_A^2 = P_B^2/r \tag{6.38}$$

3. If the above two conditions apply, $r = \rho = 1$ and

$$\alpha = p^2 \tag{6.39}$$

4. If there are only branch units, then the probability that a functional group on a branch units leads to another branch unit is simply the extent of reaction

$$\alpha = p \tag{6.40}$$

Note that the above equations are completely general and independent of the functionality of the branch unit.

The outstanding problem is to deduce the critical value of α at which the formation of an infinite network becomes possible. To tackle this problem, we consider a branch unit which is trifunctional. In this case, each chain that terminates in a branch unit is succeeded by two more chains. These two chains will, in turn, generate four additional chains and the propagation of chains will continue in like manner. In general therefore for trifunctional branch units, chain sections emanating from n chains will generate 2n chains under the conditions described. Recall, however, that the probability that chain segments originating from branch units will terminate in other branch units is α. Therefore the expected number of branch units from n branch units is $2n\alpha$. Now, it is easy to visualize that the condition for continued expansion of the network is that the number of chains emanating from n chains must be greater than n. That is, the succeeding generation of chains must outnumber the preceding generation. For a trifunctional unit, therefore, if $\alpha < 1/2$ (i.e., $2n\alpha < n$), an infinite network cannot be generated since there is less than an even chance that each chain will terminate in a branch unit. On the hand, if $\alpha > 1/2$ (i.e., $2n\alpha > n$), generation of an infinite network is possible. It is obvious that for a trifunctional branch unit, the critical value of α is $\alpha = 1/2$. This argument can be extended to systems containing polyfunctional branch units with the general result that

$$\alpha_c = \frac{1}{f-1} \tag{6.41}$$

where f is the functionality of the branch unit. If there is more than one type of branch unit present, $(f - 1)$ must be replaced by an appropriate average weighted according to the number of functional groups attached to the various branched units and the molar amount of each present.

XI. MORPHOLOGY OF CROSS-LINKED POLYMERS

As we saw in Section 3, the properties of polymeric materials are dictated by their morphologies. Considerable knowledge has been accumulated about the morphology of semicrystalline polymers over the last four to five decades. Unfortunately, the same cannot be said for cross-linked polymers or thermosets. From the discussion in Section IX for example, in the absence of intramolecular reactions, polyfunctional condensation reactions where different functional groups are chemically equivalent result in a giant molecule with an infinite cross-linked network. For a long time, this concept of an infinitely large molecule with a homogeneous cross-linked network was used to describe the morphology of cross-linked polymers. However, the presence of inhomogeneities in the cross-link density of polymer networks has been established empirically through electron microscopy, thermomechanical studies, and swelling experiments. Today, it is generally recognized that the model that most adequately describes the morphology of thermosets is that of an inhomogeneously cross-linked network consisting of regions of higher cross-linked density (referred to as nodules) immersed in a less cross-linked matrix.[5,6]

XII. PROBLEMS

6.1. United Nigeria Textile (Ltd) UNTL Kaduna is making nylon 6,6 from hexamethylenediamine and adipic acid. One batch is made on every 8-h shift. In each batch equimolar reactants are used and conversion is usually 98.0%. At the end of the run the bulk product is extruded and chopped into pellets.

a. Calculate the number-average molecular weight.
b. The afternoon shift operator dumped in too much adipic acid. From his records you calculate that the mole ratio was 2% excess adipic acid. If the batch went to the usual conversion, what was its number-average molecular weight?
c. The night shift operator weighed things correctly but fell asleep and let the reaction run too long — 99% conversion. What will be the M_n of this batch?
d. How should the UNTL engineer mix these batches to obtain the $\overline{M}_n$ of the usual product. What will be $\overline{M}_w$?

6.2. A polyester system has a number-average molecular weight $\overline{M}_n$ of 6000 and a polydispersity of 2. The system is fractionated into two samples of the $\overline{M}_n$ (2000 and 10,000, respectively). Equimolar proportions of these are mixed.

a. What are the $\overline{M}_n$ and $\overline{M}_w$ for the new (mixed) system?
b. How will the melt viscosity of the new system (fractionated and mixed) change in relation to the unfractionated (original) polymer?

6.3. A polymer chemist prepared nylon from the following amino acid (ω-amino caproic acid): $[NH_2 - (CH_2)_5 - COOH]$. Due to improper purification of the reactant, side reactions occurred leading to a 5% stoichiometric imbalance (i.e., 5% excess of one of the functional groups). Calculate:

a. The number-average molecular weight if conversion was 98%.
b. The number-average molecular weight for the maximum degree of polymerization.

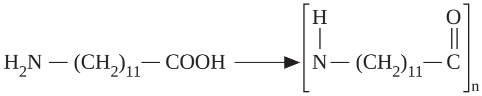
6.4. Consider a polyesterification reaction.

a. Suppose 1 mol each of dicarboxylic acid and glycol is used. What is the degree of polymerization when the extent of reaction is 0.5, 0.99, and 1.0?
b. Suppose 101 mol glycol is reached with 100 mol of the dicarboxylic acid. What is the maximum degree of polymerization?
c. Suppose the dicarboxylic acid contains 2 mol% monoacid impurity. What is the maximum degree of polymerization?

6.5. The preparation of poly(ethylene terephthalate) from terephthalic acid and ethylene glycol is stopped at 99% conversion. Calculate:

a. The number-average degree of polymerization.
b. The weight-average degree of polymerization.
c. The probability that the reaction mixture contains trimers.
d. The weight-fraction of the trimers.

6.6. The preparation of nylon 12 is shown by the following equation.



$$H_2N-(CH_2)_{11}-COOH \longrightarrow \left[\overset{H}{\overset{|}{N}}-(CH_2)_{11}-\overset{O}{\overset{||}{C}}\right]_n$$

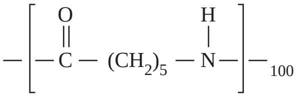
(Str. 11)

Calculate the weight fraction of n-mers in the reaction mixture if the conversion is

a. 10%
b. 90%

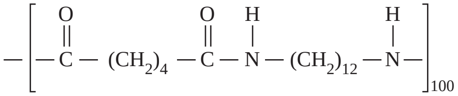
for n = 1 and 100. Comment on your answer.

6.7. What are the number-average molecular weights for the following nylons if 95% of the functional groups have reacted?



$$-\left[-\overset{O}{\overset{||}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}}-\right]_{100}-$$

nylon 6 (Str. 12)



$$-\left[-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_{12}-\overset{H}{\overset{|}{N}}-\right]_{100}$$

nylon 6,12 (Str. 13)

What is the weight fraction of monomers in the mixture?

6.8. Calculate (1) the mole fraction and (2) the weight fraction of the following polymer in the reaction medium if 98% of the functional groups has undergone conversion.

$$\left[-CO-(CH_2)_5-CO-NH-(CH_2)_9-NH-\right]_{100}$$

(Str. 14)

What is the weight fraction of the monomers in the mixture?

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