2

Step-growth polymerization

2.1 Introduction

In Section 1.4 we discussed the classification of polymers into the categories of addition or condensation. At that time we noted that these classifications could be based on the following:

1. The stoichiometry of the polymerization reaction (small molecule eliminated?).
2. The composition of the backbone of the polymer (atoms other than carbon present?).
3. The mechanism of the polymerization (stepwise or chain reaction?).

It is the third of these criteria that offers the most powerful insight into the nature of the polymerization process for this important class of materials. We shall sometimes use the terms *step-growth* and *condensation polymers* as synonyms, although step-growth polymerization encompasses a wider range of reactions and products than either criteria (1) or (2) above would indicate.

The chapter is organized as follows. First, we examine how the degree of polymerization and its distribution vary with the progress of the polymerization reaction, with the latter defined both in terms of stoichiometry and time. In the first round, we consider these topics for simple reaction mixtures, those in which the proportions of reactants agree exactly with the stoichiometry of the reactions. After this we consider two important classes of condensation or step-growth polymers: polyesters and polyamides. Finally we consider nonstoichiometric proportions of reactants. The important case of multifunctional monomers, which can introduce branching and crosslinking into the products, is deferred until Chapter 10.

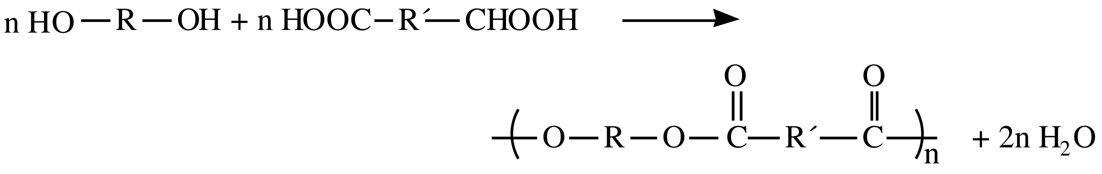
2.2 Condensation polymers: one step at a time

As the name implies, step-growth polymers are formed through a series of steps, and high molecular weight materials result from a large number of steps. Although our interest is in high molecular weight, long-chain molecules, a crucial premise of this chapter is that these molecules can be effectively discussed in terms of the individual steps that lead to the formation of the polymer. Thus polyesters and polyamides are substances which result from the occurrence of many steps in which ester or amide linkages are formed between reactants. Central to our discussion is the idea that these steps may be treated in essentially the same way, whether they occur between small molecules or polymeric species. We shall return to a discussion of the implications and justification of this *assumption of equal reactivity* throughout this chapter.

2.2A Classes of step-growth polymers

Here are examples of important classes of step-growth polymers,:

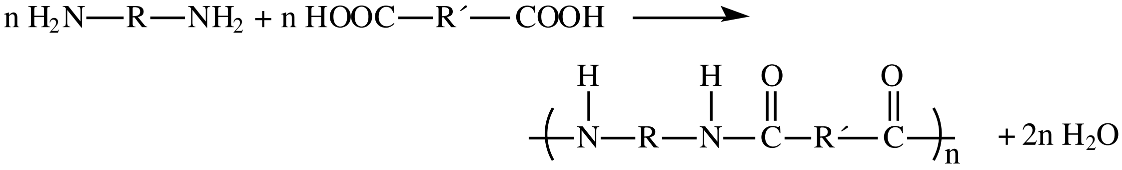
1. Polyesters. Successive reactions between diols and dicarboxylic acids:



$$n\,HO-R-OH + n\,HOOC-R'-CHOOH \longrightarrow \left(O-R-O-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C} \right)_n + 2n\,H_2O$$

(2.A)

2. Polyamides. Successive reactions between diamines and dicarboxylic acids:



$$n\,H_2N-R-NH_2 + n\,HOOC-R'-COOH \longrightarrow \left(\overset{\overset{H}{|}}{N}-R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C} \right)_n + 2n\,H_2O$$

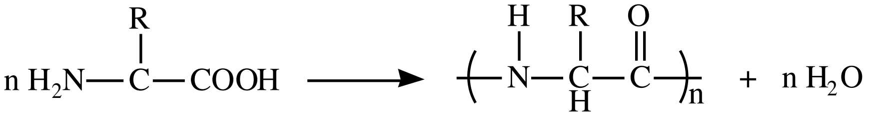
(2.B)

3. General. Successive reactions between difunctional monomer A–A and difunctional monomer B–B:

$$n\,\text{A—A} + n\,\text{B—B} \longrightarrow \text{—(A—A—B—B)}_n\text{—} + \cdots \qquad (2.C)$$

Since the two reacting functional groups can be located in the same reactant molecule, we add the following:

4. Poly(amino acid).



$$n\,\mathrm{H_2N{-}\overset{R}{\overset{|}{C}}{-}COOH} \longrightarrow \left(\mathrm{\overset{H}{\overset{|}{N}}{-}\underset{H}{\overset{R}{\overset{|}{C}}}{-}\overset{O}{\overset{\|}{C}}}\right)_n + n\,\mathrm{H_2O}$$

(2.D)

5. General.

$$n\,\text{A—B} \longrightarrow \text{—(A—B)}_n\text{—} + \cdots \qquad (2.E)$$

Of course, in reactions (2.A) and (2.B) the hydrocarbon sequences R and R′ can be the same or different, contain any number of carbon atoms, be linear or cyclic, and so on. Likewise, the general reactions (2.C) and (2.E) certainly involve hydrocarbon sequences between the reactive groups A and B. The notation involved in these latter reactions is particularly convenient, however, and we shall use it extensively in this chapter. It will become clear as we proceed that the stoichiometric proportions of reactive groups–A and B in the above notation–play an important role in determining the characteristics of the polymeric product. Accordingly, we shall confine our discussion for the present to reactions of the type given by (2.E), since equimolar proportions of A and B are assured by the structure of the monomer.

2.2B A first look at the distribution of products

Table 2.1 presents a hypothetical picture of how reaction (2.E) might appear if we examined the distribution of product molecules in detail. Row 1 of Table 2.1 shows the initial pool of monomers, 10 molecules in this example. Row 2 shows a possible composition after a certain amount of reaction has occurred. We shall see in Section 2.4 that the particular condensations which account for the differences between lines 1 and 2 are not highly probable. Our objective here is not to assess the probability of certain reactions, but rather to consider some possibilities. Stoichiometrically, we can still account for the initial set of 10 A groups and 10 B groups; we

Table 2.1 Hypothetical Step-Growth Polymerization of 10 AB Molecules*

Line	Molecular species present
1.	AB AB AB AB AB AB AB AB AB AB
2.	AbaB AbaB AbaB AbaB AB AB
3.	AbababaB AbaB AbabaB AB
4.	AbababaB AbababaB AB
5.	AbababaB AbabababaB
6.	AbababababababababaB

*A and B represent two different functional groups and ab is the product of their reaction with each other. Consult the text for a discussion of the line-by-line development of the reaction.

indicate those that have reacted with each other as ab groups. The same conservation of atom groupings would be obtained if line 2 showed one trimer, two dimers and three monomers instead of the four dimers and two monomers indicated. Other combinations could also be assembled. These possibilities indicate one of the questions that we shall answer in this chapter: How do the molecules distribute themselves among the different possible species as the reaction proceeds?

Line 3 of Table 2.1 shows the mixture after two more reaction steps have occurred. Again the components we have elected to show are an arbitrary possibility. For the monomer system we have chosen, the concentration of A and B groups in the initial monomer sample are equal to each other and equal to the concentration of monomer. In this case an assay of either A groups or B groups in the mixture could be used to monitor the progress of the reaction. Choosing the number of A groups for this purpose, we see that this quantity drops from 10 to 6 to 4, respectively, as we proceed through lines 1, 2, and 3 of Table 2.1. What we wish to point out here is the fact that the 10 initial monomers are now present in four molecules, so the number of average degree of polymerization is only 2.5, even though only 40% of the initial reactive groups remain. Another question is thus raised: In general, how does the average molecular weight vary with the extent of the reaction?

The reaction mixture in line 4 of Table 2.1 is characterized by a number average degree of polymerization $N_n = 10/3 = 3.3$, with only 30% of the functional groups remaining. This means that 70% of the possible reactions have already occurred, even though we are still dealing with a very low average degree of polymerization. Note that the average degree of polymerization would be the same if the 70% reaction of functional groups led to the mixture AbababababababaB and two AB's. This is because the initial 10 monomers are present in three molecules in both instances, and we are using number averages to talk about these possibilities. The weight average would be different in the two cases. This poses still another question: How does the molecular weight *distribution* vary with the extent of reaction?

By line 5, the reaction has reached 80% completion and the number average value of the degree of polymerization N_n is 5. Although we have considered this slowly evolving polymer in terms of the extent of reaction, another question starts to be worrisome: How long is this going to take?

Line 6 represents the end of the reaction as far as linear polymer is concerned. Of the 10 initial A groups, 1 is still unreacted, but this situation raises the possibility that the decamer shown in line 6 – or for that matter, some other i-mer, including monomer – might form a ring or cyclic compound, thereby eliminating functional groups without advancing the polymerization. Throughout this chapter we will assume that the extent of ring formation is negligible.

It is an easy matter to generalize the procedure we have been following and express the number of average degree of polymerization in terms of the extent of reaction, regardless of the initial sample size. We have been dividing the initial number of monomers present by the total number of molecules present after any extent reaction. Each molecular species–whether monomer or polymer of any length – contains just one A group. The total number of *monomers* is therefore equal to the initial (superscript o) number of A groups, $\nu_A{}^o$; the total number of *molecules* at any extent of reaction (no superscript) is equal to the number of A groups ν_A present at that point. The number average degree of polymerization is therefore given by

$$N_n = \frac{\nu_A{}^o}{\nu_A} \tag{2.2.1}$$

It is convenient to define the fraction of reacted functional groups in a reaction mixture by a parameter p, called the *extent of reaction.* Thus p is the fraction of A groups which have reacted at any stage of the process, and 1 - p is the fraction unreacted:

$$1 - p = \frac{\nu}{\nu_A^o} \tag{2.2.2}$$

or

$$p = 1 - \frac{\nu_A}{\nu_A^o} \tag{2.2.3}$$

Comparing eqs 2.2.1 and 2.2.2 enables us to write very simply

$$N_n = \frac{1}{1 - p} \tag{2.2.4}$$

This expression is consistent with the analysis of each of the lines in Table 2.1 as presented above and provides a general answer to one of the questions posed there. It is often a relatively easy matter to monitor the concentration of functional groups in a reaction mixture; eq 2.2.4 represents a quantitative summary of an end group method for determining N_n. We reiterate that eq 2.2.4 assumes equal numbers of A and B groups, with none of either lost in nonpolymer reactions.

From line 6 in Table 2.1, we see that $N_n = 10$ when $p = 0.9$. The fact that this is also the maximum value for N is an artifact of the example. In a larger sample of monomers higher average degrees of polymerization are attainable. Equation 2.2.4 enables us to calculate that N_n becomes 20, 100, and 200, respectively, for extents of reaction 0.950, 0.990, and 0.995. These results reveal why condensation polymers are often of relatively modest molecular weight: It may be very difficult to achieve the extents of reaction required for very high molecular weights. As p increases the concentration of H_2O (or other small molecule product) will increase, and the law of mass action will oppose further polymerization. Consequently, steps must be taken to remove the small molecule as it is formed, if high molecular weights are desired.

2.2C A first look at reactivity and reaction rates

Most of the questions raised in the past few paragraphs will be answered during the course of this chapter, some for systems considerably more involved than the one considered here. Before proceeding further, we should re-emphasize one premise which underlies the entire discussion of Table 2.1: How does the chemical reactivity of A and B groups depend on the degree of polymerization of the reaction mixture? In Table 2.1 successive entries were generated by simply linking together at random those species present in the preceding line. We have thus assumed that, as far as reactivity is concerned, an A reacts as an A and a B reacts as a B, regardless of the size of the molecule to which the group is attached. If this assumption of equal reactivity is valid, it results in a tremendous simplification; otherwise we shall have to characterize reactivity as a function of degree of polymerization, extent of reaction, and so on.

One of the most sensitive tests of the dependence of chemical reactivity on the size of the reacting molecules is the comparison of the rates of reaction for compounds which are members of a homologous series with different chain lengths. Studies by Flory and others on the rates of esterification and saponification of esters were the first investigations conducted to clarify the dependence of reactivity on molecular size [1]. The rate constants for these reactions are observed to converge quite rapidly to a constant value which is independent of molecular size, after an initial dependence on molecular size for small molecules. In the esterification of carboxylic acids, for example, the rate constants are different for acetic, propionic, and butyric acids, but constant for carboxylic acids with 4 – 18 carbon atoms. This observation on nonpolymeric compounds has been generalized to polymerization reactions as well. The latter are subject to several complications which are not involved in the study of simple model compounds, but when these complications are properly considered, the independence of reactivity on molecular size has been repeatedly verified.

The foregoing conclusion does not mean that a constant *rate* of reaction persists throughout Table 2.1. The rate of reaction depends on the concentrations of reactive groups, as well as on their reactivities. Accordingly, the rate of the reaction decreases as the extent of reaction progresses. When the rate law for the reaction is extracted from proper kinetic experiments, specific reactions are found to be characterized by fixed rate constants over a range of N_n values.

Among the further complications that can interfere with this conclusion is the possibility that the polymer becomes insoluble beyond a critical molecular weight or that the low molecular weight by-product molecules accumulate and thereby shift the equilibrium to favor reactants. It is also possible that the transport of reactants will be affected by the increasing viscosity of the polymerization medium, which is a very complicated issue.

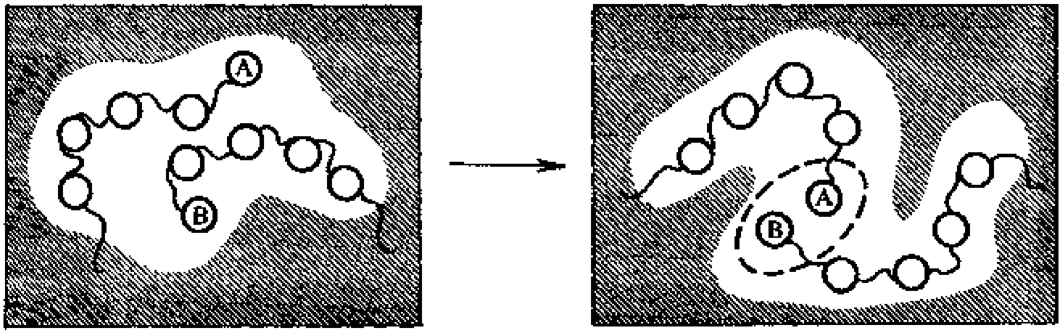


Figure 2.1
The reaction of A and B groups at the ends of two different chains. Note that rotations around only a few bonds will bring A and B into the same cage of neighboring groups, indicated by the dashed line enclosure.

Figure 2.1 suggests that reactive end-groups may be brought into contact by rotation around only a few bonds, an effect which is therefore independent of chain length. Once in close proximity, the A and B groups may be thought of as being in the same "cage" defined by near neighbors. It may take some time for the two reactive groups to diffuse together, but it will also take some time for them to diffuse apart; this provides the opportunity to react. The rate at which an A and a B group react to form an ab linkage therefore depends on the relative rates of three processes: the rate to diffuse together, the rate at which they diffuse apart, and the rate at which "trapped" A and B groups react. These considerations can be expressed more quantitatively by writing the process in terms of the following mechanism:

$$-A \quad + \quad -B \quad \underset{k_o}{\overset{k_i}{\leftrightarrow}} \quad (-A + B-)$$

$$(-A + B-) \quad \overset{k_r}{\rightarrow} \quad -ab- \tag{2.F}$$

where the parentheses represent the caged pair, as in Figure 2.1, and the k's are the rate constants for the individual steps: k_i and k_o for diffusion into and out of the cage, respectively, and k_r for the reaction itself.

Since this is the first occasion we have had to examine the rates at which chemical reactions occur, a few remarks about mechanistic steps and rate laws seem appropriate. The reader who feels the need for additional information on this topic should consult any introductory physical chemistry text.

As a brief review we recall the following:

1. The rate of a process is expressed by the derivative of a concentration (square brackets) with respect to time, d[A]/dt. If the concentration of reaction product is used, this quantity is positive; if a reactant is used, it is negative and a minus sign must be included. Also, each derivative d[A]/dt should be divided by the coefficient of that component in the chemical equation which describes the reaction, so that a single rate is described whichever component in the reaction is used to monitor it.
2. A *rate law* describes the rate of reaction as the product of a constant k, called the *rate constant*, and various concentrations, each raised to specific powers. The power of an

individual concentration term in a rate law is called the *order* with respect to that component, and the sum of the exponents of all concentration terms gives the *overall order* of the reaction. Thus in the rate law Rate = $k[X]^1[Y]^2$, the reaction is first order in X, second order in Y, and third order overall.

3. A rate law is determined experimentally and the rate constant evaluated empirically. *There is no necessary connection between the stoichiometry of a reaction and the form of the rate law.*
4. A mechanism is a series of simple reaction steps which, when added together, account for the overall reaction. The rate law for the individual steps of the mechanism may be written by inspection of the mechanistic steps. The coefficients of the reactants in the chemical equation describing the step become the exponents of these concentrations in the rate law for that step.
5. Frequently it is possible to write more than one mechanism that is compatible with an observed rate law. Thus the ability to account for an experimental rate law is a necessary but not a sufficient criterion for the correctness of the mechanism.

These ideas are readily applied to the mechanism described by reaction (2.F). To begin with, the rate at which ab links are formed is first order with respect to the concentration of entrapped pairs. In this sense the latter behaves as a reaction intermediate or transition state according to this mechanism. Therefore

$$\text{Rate of ab formation} \quad = \quad k_r\left[\left(-\text{A} + \text{B}-\right)\right] \qquad (2.2.5)$$

These entrapped pairs, in turn, form at a rate given by the rate at which the two groups diffuse together minus the rate at which they either diffuse apart or are lost by reaction:

$$\frac{d[(-A + B-)]}{dt} = k_i[A][B] - k_o[(-A + B-)] - k_r[(-A + B-)] \qquad (2.2.6)$$

The concentration of entrapped pairs is assumed to exist at some stationary-state (subscript s) level in which the rates of formation and loss are equal. In this stationary state $d[(-A + B-)]/dt = 0$ and eq 2.2.6 becomes

$$[(-A + B-)]_s = \frac{k_i}{k_o + k_r}[A][B] \qquad (2.2.7)$$

where the subscript s reminds us that this is the stationary-state value. Substituting eq 2.2.7 into eq 2.2.5 gives

$$\text{Rate of ab formation} = \frac{k_i k_r}{k_o + k_r}[A][B] \qquad (2.2.8)$$

We shall have considerably more to say about this type of kinetic analysis when we discuss chain-growth polymerization in Chapter 3.

According to the mechanism provided by reaction (2.F) and the analysis given by eq 2.2.8, the rate of polymerization is dependent upon the following:

1. The concentrations of both A and B, hence the reaction slows down as the conversion to polymer progresses, and

2 The three constants associated with the rates of the individual steps in reactions (2.F).

3. If the rate of chemical reaction is very slow compared to the rate of group diffusion ($k_r << k_i, k_o$), then eq 2.2.8 reduces to

$$\text{Rate of ab formation} = \frac{k_i}{k_o} k_r [A][B] \qquad (2.2.9)$$

4. The two constants k_i and k_o describe exactly the same kind of diffusional process, and differ only in direction. Hence they should have the same dependence on molecular size, whatever that might be, and that dependence therefore cancels out.

5. The reaction step in mechanism (2.F) is entirely comparable to the same reaction in low molecular weight systems. Such reactions involve considerably larger activation energies than physical processes like diffusion and, hence, do proceed slowly.

6. If $k_r >> k_i, k_o$, then eq 2.2.8 reduces to

$$\text{Rate of ab formation} = k_i [A][B] \qquad (2.2.10)$$

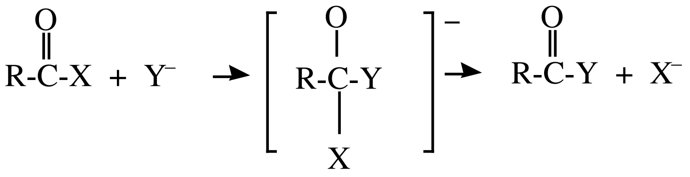
   Note that the rate law in this case depends only on k_i and any size dependence for this constant would not cancel out.

Both eqs 2.2.9 and 2.2.10 predict rate laws which are first order with respect to the concentration of each of the reactive groups; the proportionality constant has a different significance in the two cases, however. The observed rate laws which suggest a reactivity that is independent of molecular size and the *a priori* expectation cited in item (5) above regarding the magnitudes of different kinds of k values, lend credibility to the version presented in eq 2.2.9.

Our objective in the preceding argument has been to justify the attitude that each ab linkage forms according to the same rate law, regardless of the extent of the reaction. While our attention is focused on the rate laws, we might as well consider the question, raised above, about the actual rates of these reactions. This is the topic of the next section.

2.3 Kinetics of step-growth polymerization

In this section we turn to a consideration of the experimental side of condensation kinetics. The kind of ab links which have been most extensively studied are ester and amide groups, although numerous additional systems could also be cited. In many of these the carbonyl group is present and is believed to play an important role in stabilizing the actual chemical transition state involved in the reactions. The situation can be represented by the following schematic reaction:



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}X} + \mathrm{Y^-} \rightarrow \left[\mathrm{R{-}\underset{\underset{X}{|}}{\overset{\overset{O}{|}}{C}}{-}Y}\right]^- \rightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}Y} + \mathrm{X^-}$$

(2.G)

in which the intermediate is stabilized by coordination with protons, metal ions, or other Lewis acids. The point of this is to emphasize that the kinds of reactions we are considering are often conducted in the presence of an acid catalyst, frequently something like a sulfonic acid or a metal oxide. The purpose of a catalyst is to modify the rates of a reaction, so we must be attentive to the situation with respect to catalysts. For the present we assume a constant concentration of catalyst and attach a subscript c to the rate constant to remind us of the assumption. Accordingly, we write

$$-\frac{d[A]}{dt} = k_c[A][B] \tag{2.3.1}$$

which is consistent with both eqs 2.2.9 and 2.2.10. We expect the constant k_c to be dependent on the concentration of the catalyst in some way which means that eq 2.3.1 may be called a pseudo-second-order rate law. We shall presently consider these reactions in the absence of external catalysts. For now it is easier to proceed with the catalyzed case.

2.3A Catalyzed step-growth reactions

Equation 2.3.1 is the differential form of the rate law which describes the rate at which A groups are used up. To test a proposed rate law and to evaluate the rate constant it is preferable to work with the integrated form of the rate law. The integration of eq 2.3.1 yields different results, depending on whether the concentrations of A and B are the same or different:

1. We define [A] and [B] as the instantaneous concentrations of these groups at any time t during the reaction, and $[A]_o$ and $[B]_o$ as the concentrations of these groups at t = 0.
2. If $[A]_o = [B]_o$, the integration of eq 2.3.1 yields

$$\frac{1}{[A]} - \frac{1}{[A]_o} = k_c t \qquad (2.3.2)$$

3. If $[A]_o \neq [B]_o$, the integration yields

$$\frac{1}{[A]_o - [B]_o} \ln\left(\frac{[A][B]_o}{[A]_o [B]}\right) = k_c t \qquad (2.3.3)$$

Both of these results are readily obtained; we examine the less obvious relationship in eq 2.3.3 in the following example. The consequences of different A and B concentrations on the molecular weight of the polymer will be taken up in Section 2.7.

Example 2.1

By differentiation, verify that eq 2.3.3 is a solution to eq 2.3.1 for the conditions given.

Solution

Neither $[A]_o$ nor $[B]_o$ are functions of t, although both [A] and [B] are. We write the latter two as $[A] = [A]_o - x$ and $[B] = [B]_o - x$. Substitute these results into eq 2.3.3 and re-arrange:

$$\ln\frac{[A]_o - x}{[B]_o - x} + \ln\frac{[A]_o}{[B]_o} = \left([A]_o - [B]_o\right) k_c t$$

now differentiate with respect to t, noting that only x is a function of t:

$$\left(\frac{[B]_o - x}{[A]_o - x}\right)\left(\frac{-([B]_o - x) + ([A]_o - x)}{([B]_o - x)^2}\right)\frac{dx}{dt} = \left([A]_o - [B]_o\right) k_c$$

which after cancellation and re-arranging gives

$$\frac{dx}{dt} = k_c\left([A]_o - x\right)\left([B]_o - x\right) = k_c[A][B]$$

Since d[A]/dt = –dx/dt by the definition of x, this proves eq 2.3.3 to be a solution to eq 2.3.1. Equation 2.3.3 is undefined in the event $[A]_o = [B]_o$, but in this case the expression is inapplicable anyhow. Since A and B react in a 1:1 proportion, their concentrations are identical at all stages of reaction if they are equal initially. In this case, eq 2.3.1 would reduce to a simpler second-order rate law which integrates to eq 2.3.2.

We shall now proceed on the assumption that $[A]_o$ and $[B]_o$ are equal. As noted above, having both reactive groups on the same molecule is one way of enforcing this condition. Accordingly, we rearrange eq 2.3.2 to give the instantaneous concentrations of unreacted A groups as a function of time:

$$[A] = \frac{[A]_o}{1 + k_c [A]_o t} \tag{2.3.4}$$

At this point, it is convenient to recall the extent of reaction parameter, p, defined by eq 2.2.3. If we combine eqs 2.2.2 and 2.3.4, we obtain

$$1 - p = \frac{1}{1 + k_c [A]_o t} \tag{2.3.5}$$

or

$$\frac{1}{1 - p} = N_n = 1 + k_c [A]_o t \tag{2.3.6}$$

where we incorporated eq 2.2.4 into the present discussion. These last expressions provide two very useful views of the progress of a condensation polymerization reaction with time. Equation 2.3.4 describes how the concentration of A groups asymptotically approaches zero at long times; eq 2.3.6 describes how the number average degree of polymerization increases linearly with time.

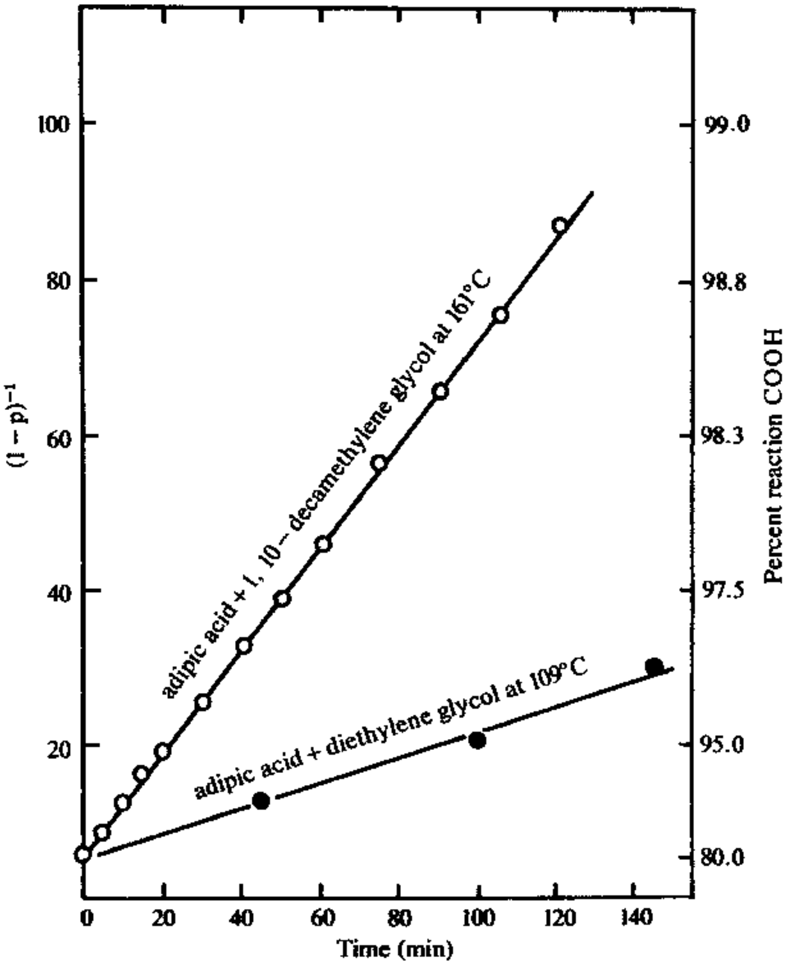


Figure 2.2

Plots of 1/(1–p))left ordinate) and p (right ordinate) versus time for the catalyzed esterifications shown, from Allcock, H. R., and Lampe, F. W., *Contemporary Polymer Chemistry*, 2nd Edition, Prentice Hall, Englewood Cliffs, NJ, 1990. Used with permission.

Equation 2.3.6 predicts a straight line when 1/(1 – p) is plotted against t. Figure 2.2 shows such a plot for adipic acid reacted with 1,10-decamethylene glycol and diethylene glycol.

In both cases the esterifications were catalyzed by *p*-toluene sulfonic acid. Interpreting the slopes of these lines in terms of eq 2.3.6 and in the light of actual initial concentrations gives values of k_c equal to 0.013 and 0.097 kg eq^{-1} min^{-1}, respectively, for diethylene glycol at 109 °C and decamethylene glycol at 161 °C. Note that the units of these constants imply group concentrations expressed as equivalents per kilogram; mass rather than volume units are often used for concentration, since substantial volume changes may occur during polymerization.

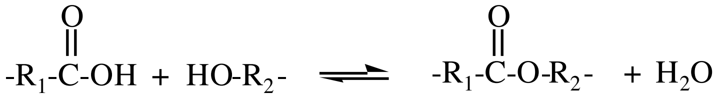
2.3B How should experimental data be compared with theoretical rate laws?

Although the results presented in Figure 2.2 appear to verify the predictions of eq 2.3.6, this verification is not free from controversy. This controversy arises because various workers in this field employ different criteria in evaluating the success of the relationships we have presented in fitting experimental polymerization data. One school of thought maintains that an adequate kinetic description of a process must apply to the data over a large part of the *time* of the experiment. A second point of view maintains that a rate law correctly describes a process when it applies over a wide portion of the *concentration change* which occurs during a reaction. Each of these criteria seeks to maximize the region of fit, but the former emphasizes maximizing the range of t while the latter maximizes the range of p. Both standards tolerate deviations from their respective ideals at the beginning and/or the end of the experiment. Deviations at the beginning of a process are rationalized in terms of experimental uncertainties at the point of mixing or modelistic difficulties upon attainment of stationary-state conditions.

The existence of these two different standards for success would be only of academic interest if the analysis we have discussed applied to experimental results over most of the time range *and* over most extents or reactions as well. Unfortunately, this is not the case in all of the systems which have been investigated. Reference [2], for example, shows one particular set of data – adipic acid and diethylene glycol at 166°C, the same reactants at a different temperature as the system in Figure 2.2 – analyzed according to two different rate laws. This system obeys one rate law between p = 0.50 and 0.85 that represents 15% of the duration of the experiment, and another rate law between p = 0.80 and 0.93 which spans 45% of the reaction time. These would be rated differently by the two different standards above. This sort of dilemma is not unique to the present problem, but arises in many situations where one variable undergoes a large percentage of its total change while the other variable undergoes only a small fraction of its change. In the present context one way out of the dilemma is to take the view that only the latter stages of the reaction are significant, since it is only beyond, say, p = 0.80 that it makes sense to consider the process as one of polymerization. Thus, it is only at large extents of reaction that polymeric products are formed and, hence, the kinetics of *polymerization* should be based on a description of this part of the process. This viewpoint intentionally focuses attention on a relatively modest but definite range of p values. Since the reaction is necessarily slow as the number of unreacted functional groups decreases, this position tends to maximize the time over which the rate law fits the data. Examination of the right-hand ordinate of Figure 2.2 shows that the data presented there represent only about the last 20% of the range of p values. The zero of the time scale has thus been shifted to pick up the analysis of the reaction at this point.

We commented above that deviations at the beginning or the end of kinetics experiments can be rationalized, although the different schools of thought would disagree as to what constitutes "beginning" and "end". Now that we have settled upon the polymer range, let us consider specifically why deviations occur from a simple second-order kinetic analysis in the case of catalyzed polymerizations. At the beginning of the experiment, say, up to $p \approx 0.5$, the concentrations of A and B groups change dramatically, even though the number average degree of polymerization has only changed from monomer to dimer. By ordinary polymeric standards, we are still dealing with a low molecular weight system which might be regarded as the solvent medium for the formation of polymer. During this transformation, however, 50% of the very polar A groups and 50% of the very polar B groups have been converted to the less polar ab groups. Thus a significant change in the polarity of the polymerization medium occurs during the first half of the change in p, even though an insignificant amount of true polymer has formed. In view of the role of ionic intermediates as suggested by reaction 2.G, the polarity of the reaction medium might very well influence the rate law during this stage of the reaction.

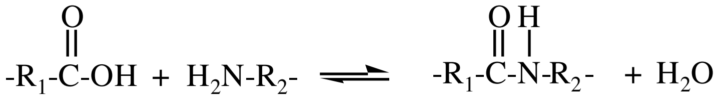
At the other end of the reaction, deviations from idealized rate laws are attributed to secondary reactions such as degradation of acids, alcohols, and amines through decarboxylation, dehydration, and deamination, respectively. The step-growth polymers which have been most widely studied are simple condensation products such as polyesters and polyamides. Although we shall take up these classes of polymers specifically in Sections 2.5 and 2.6, respectively, it is appropriate to mention here that these are typically equilibrium reactions



$$-R_1-\overset{O}{\overset{\|}{C}}-OH + HO-R_2- \rightleftharpoons -R_1-\overset{O}{\overset{\|}{C}}-O-R_2- + H_2O$$

(2.H)

and



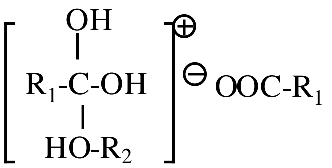
$$-R_1-\overset{O}{\overset{\|}{C}}-OH + H_2N-R_2- \rightleftharpoons -R_1-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R_2- + H_2O$$

(2.I)

In order to achieve large p's and high molecular weights, it is essential that these equilibria be shifted to the right by removing the by-product molecule, water in these reactions. This may be accomplished by heating, imposing a partial vacuum, or purging with an inert gas, or some combination of the three. These treatments also open up the possibility of reactant loss due to volatility, which may accumulate to a significant source of error for reactions which are carried out to large values of p.

2.3C Uncatalyzed step-growth reactions

Until now we have been discussing the kinetics of catalyzed reactions. Losses due to volatility and side reactions also raise questions as to the validity of assuming a constant concentration of catalyst. Of course, one way of avoiding this issue is to omit an outside catalyst; reactions involving carboxylic acids can be catalyzed by these compounds themselves. Experiments conducted under these conditions are informative in their own right and not merely as means of eliminating errors in the catalyzed case. As noted in connection with the discussion of reaction (2.G), the intermediate is stabilized by coordination with a proton from the catalyst. In the case of autoprotolysis by the carboxylic intermediate:



$$\left[\begin{array}{c} \text{OH} \\ | \\ \text{R}_1\text{-C-OH} \\ | \\ \text{HO-R}_2 \end{array}\right]^{\oplus} {}^{\ominus}\text{OOC-R}_1$$

Since this intermediate involves an additional equivalent of acid functional groups, the rate law for the disappearance of A groups becomes

$$-\frac{d[A]}{dt} = k_u [A]^2 [B] \qquad (2.3.7)$$

on the assumption that A represents carboxyl groups. In this case k_u is the rate constant for the uncatalyzed reaction. This differential rate law is the equivalent of eq 2.3.1 for the catalyzed reaction. Equation 2.3.7 is readily integrated when $[A]_o = [B]_o$, in which case it becomes

$$-\frac{1}{[A]^3} d[A] = k_u \, dt \qquad (2.3.8)$$

This integrates to

$$\frac{1}{[A]^2} - \frac{1}{[A]_o^2} = 2\,k_u t \qquad (2.3.9)$$

Thus for the uncatalyzed case we have the following:

1. The rate law is third order.

2. Since $[A]/[A]_o = 1 - p$, eq 2.3.9 may be rewritten as

   $$\frac{1}{(1-p)^2} = 1 + 2k_u\,[A]_o^2\,t \qquad (2.3.10)$$

   which shows that a plot of $(1 - p)^{-2}$ increases linearly with t.

3. Since $[A]/[A]_o = N_n$, eq 2.3.10 becomes

   $$N_n^2 = 1 + 2\,k_u\,[A]_o^2\,t \qquad (2.3.11)$$

   which shows that N_n increases more gradually with t than in the catalyzed case, all other things being equal.

Figure 2.3 shows data for the uncatalyzed polymerization of adipic acid and 1,10-decamethylene glycol at 161°C plotted according to eq 2.3.10. The various provisos of the catalyzed case apply here also, so it continues to be appropriate to consider only the final stages of the conversion to polymer. From these results, k_u is about 4.3×10^{-3} $\mathrm{kg}^2\,\mathrm{eq}^{-2}\,\mathrm{min}^{-1}$ at 161°C.

We conclude this section with a numerical example which serves to review and compare some of the important relationships we have considered.

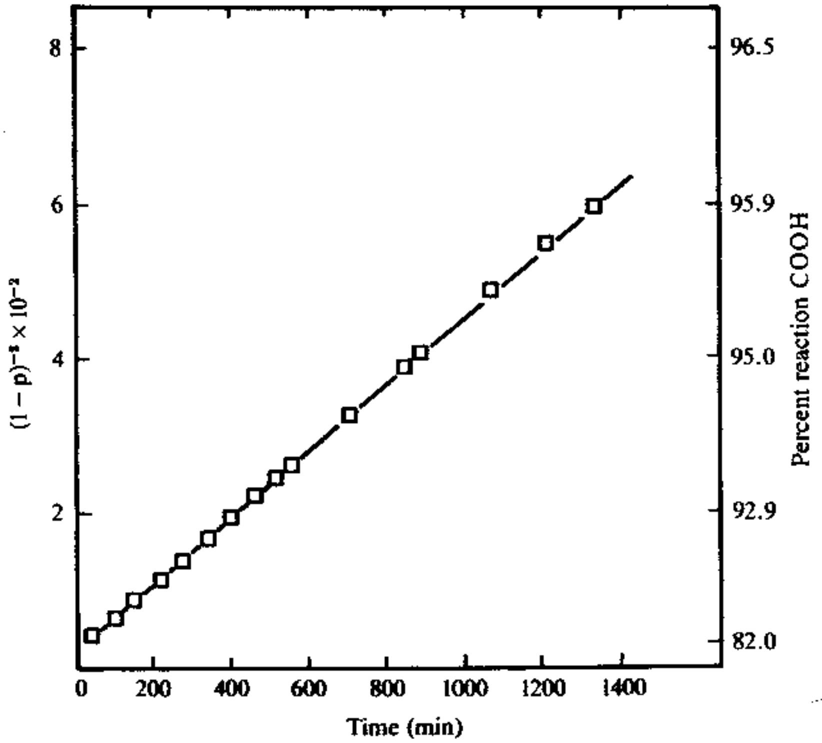


Figure 2.3

Plot of $1/(1-p)^2$ (left ordinate) and p (right ordinate) versus time for an uncatalyzed esterification. Data from S. D. Hamann, D. H. Solomon, and J. D. Swift, *J. Macromol. Sci. Chem.* A2, 153 (1968).

Example 2.2

Assuming that $k_c = 10^{-1}$ kg eq^{-1} min^{-1}, $k_u = 10^{-3}$ kg^2 eq^{-1} min^{-1}, and $[A]_o = 10$ eq kg^{-1}, calculate the times required for p to reach values 0.2, 0.4, 0.6 and so on, for both catalyzed and uncatalyzed polymerizations, assuming that eq 2.3.4 and 2.3.9, respectively, apply to the entire reaction. Compare the results obtained in terms of both the degree of polymerization and the fraction of unreacted A groups as a function of time.

Solution

Since we are asked to evaluate t, N_n, and $[A]/[A]_o$ for specific values of p, it is convenient to summarize the following relationships:

1. Eq 2.2.4: $N_n = 1/(1 - p)$.
2. Eq 2.2.2: $[A]/[A]_o = 1 - p$.
3. Eq 2.3.6: $t = (N_n - 1)/k_c[A]_o = N_n - 1$ if catalyzed, since $10^{-1}(10) = 1$.
4. Eq 2.3.11: $t = (N_n^2 - 1)/2\, k_u[A]_o^2 = (N_n^2 - 1)(5)$ if uncatalyzed, since $2(10^{-3})(10)^2 = 0.2$.

Using these relationships the accompanying table is developed.

p	**$[A]/[A]_o$**	**N_n**	**time (min) catalyzed**	**time (min) uncatalyzed**
0.2	0.8	1.25	0.25	2.8
0.4	0.6	1.67	0.67	8.9
0.6	0.4	2.50	1.5	26
0.8	0.2	5.00	4.0	120
0.9	0.1	10.0	9.0	500
0.95	0.05	20.0	19	2.0×10^3
0.99	0.01	100	99	5.0×10^4
0.992	0.008	120	119	7.2×10^4
0.998	0.002	500	499	1.3×10^6

A graphical comparison of the trends appearing here is presented in Figure 2.4. The importance of the catalyst is readily apparent in this hypothetical but not atypical system: To reach $N_n = 5$

requires 4 min in the catalyzed case and 120 min without any catalyst, assuming that the appropriate rate law describes the entire reaction in each case.

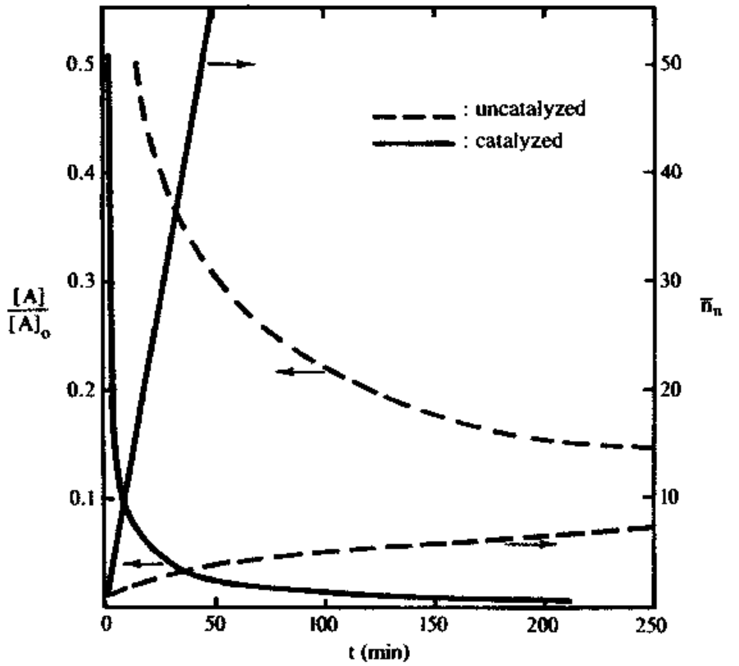


Figure 2.4
Comparison of catalyzed (solid lines) and un catalyzed (dashed lines) polymerizations using results calculated in Example 2.2. Here 1–p (left ordinate) and N_n (right ordinate) are plotted versus time.

The question posed in Section 2.2 – how long will it take to reach a certain extent of reaction or degree of polymerization? – is now answered. As is often the case, the answer begins, “It all depends….”

2.4 Distribution of molecular sizes

In this section we turn our attention to two other questions raised in Section 2.2, namely, how do the molecules distribute themselves among the different possible species, and how does this distribution vary with the extent of reaction? Since a range of species is present at each stage of polymerization, it is apparent that a statistical answer is required for these questions. This time, our answer begins, “On the average….”

We shall continue basing our discussion on the step-growth polymerization of the hypothetical monomer AB. In Section 2.7 we shall take a second look at this problem for the case of unequal concentrations of A and B groups. For now, however, we assure this equality by considering a monomer which contains one group of each type. In a previous discussion of the polymer formed from this monomer, we noted that remnants of the original functional groups are still recognizable, although modified, along the backbone of the polymer chain. This state of affairs is emphasized by the notation Ababa…abaB in which the a's and b's of the ab linkages are groups of atoms carried over the initial A and B reactive groups. In this type of polymer molecule, then, there are i–1 a's and 1 A if the degree of polymerization of the polymer is i. The a's differ from the A's precisely in that the former have undergone reaction whereas the latter have not. At any point during the polymerization reaction the fraction of the initial number of A groups which have reacted to become a's is given by p, and the fraction which remains as A's is given by 1 – p. In these expressions p is the same extent of reaction defined by eq 2.2.3.

2.4A Mole fractions of species

We now turn to the question of evaluating the fraction of i-mers in a mixture as a function of p. The fraction of molecules of a particular type in a population is just another way of describing the probability of such a molecule. Hence our restated objective is to find the probability of an i-mer in terms of p; we symbolize this quantity as the mole fraction $x_i(p)$. Since the i-mer consists of i–1 a's and 1 A, its probability is the same as the probability of finding i–1 a's and 1 A in the same molecule. Recalling from Chapter 1 how such probabilities are compounded, we write

$$x_i(p) = p_a^{i-1} p_A = p^{i-1}(1-p) \qquad (2.4.1)$$

where p_a and p_A are the probabilities of individual a and A groups, respectively, and $p_a = p$ and $p_A = 1 - p$. Equation 2.4.1 is known as the *Most Probable Distribution*, and it arises in several circumstances in polymer science, in particular free radical polymerization (Chapter 3). The probability of an i-mer can be converted to the number of i-mer molecules in the reaction mixture, n_i, by multiplying by the total number of molecules m in the mixture after the reaction has occurred to the extent p:

$$n_i = m p^{i-1} (1-p) \qquad (2.4.2)$$

Note that n_i/m gives the mole fraction of i-mers in a mixture at an extent of reaction p. As we have seen before, $m = (1 - p) A_o$, since each molecule in the mixture contains one unreacted A group. Incorporating this result into eq 2.4.2 yields

$$n_i = p^{i-1} (1-p)^2 m_o \qquad (2.4.3)$$

where m_o is the total number of monomers present initially; $m_o = A_o$ for AB monomers. This result may be used to evaluate the number of molecules of whatever degree of polymerization we elect to consider, in terms of p and m_o. As such, it provides the answer to one of the questions posed earlier.

Figure 2.5 is a plot of the ratio n_i/m versus i for several values of p. Several features are apparent from Figure 2.5 concerning the number distribution of molecules among the various species present:

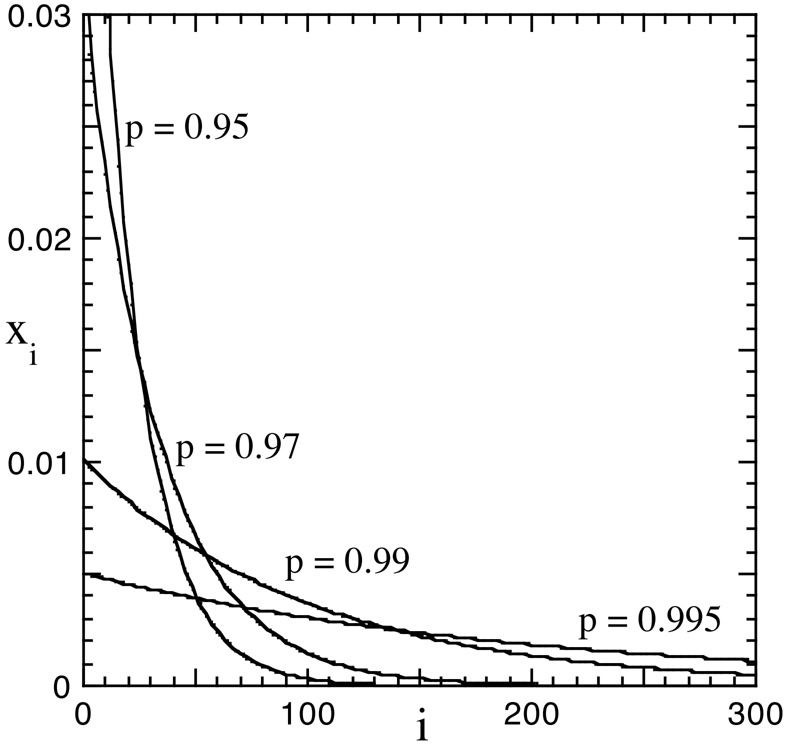


Figure 2.5
Mole fraction of i-mer as a function of i for several values of p.

1. On a number basis, the fraction of molecules always decreases with increasing i, regardless of the value of p. The distributions in Table 2.1 are unrealistic in this regard.
2. As p increases, the proportion of molecules with smaller i values decreases and the proportion with larger i values increases.
3. The combination of effects described in item (2) tends to flatten the curves as p increases, but not to the extent that the effect of item (1) disappears.

The number average degree of polymerization for these mixtures is easily obtained by recalling the definition of this average from Chapter 1.7. It is given by the sum of all possible i values, with each multiplied by its appropriate weighting factor provided by eq 2.4.1:

$$N_n = \sum_{i=1}^{m_o} i\, x_i(p) = \sum_{i=1}^{\infty} i\, p^{i-1}(1-p) \qquad (2.4.4)$$

Note that the upper limit of the second summation has been shifted from m_o to ∞ for mathematical reasons, namely that the answer is simple and known (see Appendix). The change is of little practical significance, since eq 2.4.1 drops off for very large values of i. In particular, the result derived in the Appendix is

$$\sum_{i=1}^{\infty} i\, p^{i-1} = \frac{1}{(1-p)^2}$$

Simplification of the summation in eq 2.4.4 thus yields

$$N_n = \frac{1}{1-p} \qquad (2.4.5)$$

Of course, this is the same result that was obtained more simply in eq 2.2.4. The earlier result, however, was based on purely stoichiometric considerations and not on the detailed distribution as is the present result.

2.4B Weight fractions of species

Next we turn our attention to the distribution of the molecules *by weight* among the various species. This will lead directly to the determination of the weight average molecular weight and the ratio M_w/M_n.

We begin by recognizing that the weight fraction w_i of i-mers in the polymer mixture at any value of p equals the ratio of the mass of i-mer in the mixture divided by the mass of the total mixture. The former is given by the product $i\,n_i\,M_o$, where M_o is the molecular weight of the repeat unit; the latter is given by m_oM_o. Therefore we write

$$w_i = \frac{i\,n_i}{m_o} \tag{2.4.6}$$

into which eq 2.4.3 may be substituted to give

$$w_i = i\,p^{i-1}(1-p)^2 \tag{2.4.7}$$

The weight fraction of i-mers is plotted as a function of i in Figure 2.6 for several large values of p. Inspection of Figure 2.6 and comparison with Figure 2.5 reveals the following:

1. At any p, very small and very large values of i contribute a lower weight fraction to the mixture than do intermediate values of i. This arises because of the product in_i in eq 2.4.6: n_i is large for monomers, in which case i is low, and then n_i decreases as i increases. At intermediate values of i, w_i goes through a maximum.
2. As p increases, the maximum in the curves shifts to larger i values and the tail of the curve extends to higher values of i.

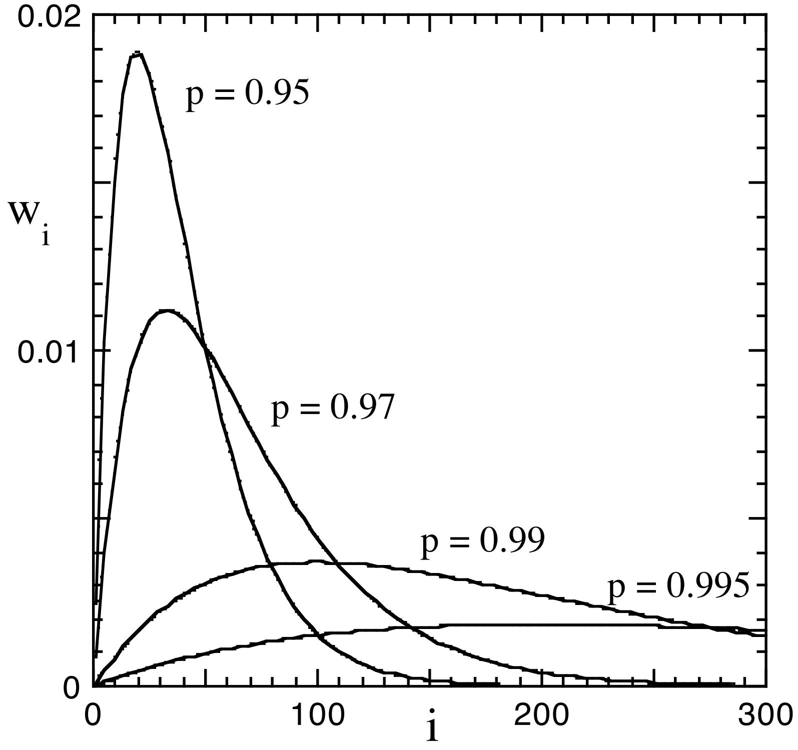


Figure 2.6
Weight fraction of i-mer as a function of i for several values of p.

3. The effect in item (2) is not merely a matter of shifting curves toward higher i values as p increases, but reflects a distinct broadening of the distribution of i values as p increases.

The weight average degree of polymerization is obtained by averaging the contributions of various i values using weight fractions as weighting factors in the averaging procedure:

$$N_w = \frac{\sum_{i=1}^{m_o} i\, w_i}{\sum_{i=1}^{m_o} w_i} = \frac{\sum_{i=1}^{\infty} i^2 p^{i-1}(1-p)^2}{\sum_{i=1}^{\infty} i\, p^{i-1}(1-p)^2} \tag{2.4.8}$$

where the upper limit on i has been extended to infinity as before. The new summation that we need is also evaluated in the Appendix:

$$\sum_{i=1}^{\infty} i^2 p^{i-1} = \frac{1+p}{(1-p)^3}$$

Using this in eq 2.4.8 gives

$$N_w = \frac{1+p}{1-p} \qquad (2.4.9)$$

which is the desired result.

We saw in Chapter 1 that the ratio M_w/M_n, or polydispersity index, is widely used in polymer chemistry as a measure of the width of a molecular weight distribution. If the effect of chain ends is disregarded, this ratio is the same as the corresponding ratio of i values:

$$\frac{M_w}{M_n} = \frac{N_w}{N_n} = 1 + p \qquad (2.4.10)$$

where the ratio of eq 2.4.9 to eq 2.2.4 has been used. Table 2.2 lists values of N_w, N_n, and N_w/N_n for a range of high p values. Note that $N_w/N_n \rightarrow 2$ as $p \rightarrow 1$; this is a characteristic result of the Most Probable Distribution. In light of eq 1.7.16, the standard deviation of the molecular distribution is equal to M_n for the polymer sample produced by this polymerization. In a manner of speaking, the molecular weight distribution is as wide as the average is high! The broadening of the distribution with increasing p is dramatically shown by comparing the values in Table 2.2 with the situation at a low p value, say p = 0.5. At p = 0.5, $N_n = 2$, $N_w = 3$, and $N_w/N_n = 1.5$.

Since eqs 2.3.5 and 2.3.11, respectively, give p as a function of time for the catalyzed and uncatalyzed polymerizations, the distributions discussed in the last few paragraphs can also be expressed with time as the independent variable instead of p.

The results we have obtained on the basis of the hypothetical monomer AB are also applicable to polymerizations between monomers of the AA and BB type, as long as the condition [A] = [B] is maintained. We shall extend the arguments of this section to conditions in which [A] ≠ [B] in Section 2.7 In the meanwhile we interrupt this line of reasoning by considering a few actual condensation polymers as examples of step-growth systems. The actual systems we discuss will serve both to verify and reveal the limitations of the concepts we have been discussing. In addition, they point out some of the topics which still need clarification. We anticipate some of the latter points by noting the following:

1. When [A] ≠ [B], both ends of the growing chain tend to be terminated by the group which is present in excess. Subsequent reaction of such a molecule involves reaction with the limiting group. The effect is a decrease in the maximum attainable degree of polymerization.
2. When a monofunctional reactant is present – one containing a single A or B group – the effect is also clearly a decrease in the average degree of polymerization. It is precisely because this type of reactant can only react once that it is sometimes introduced into polymer formulations, thereby eliminating the possibility of long-term combination of chain ends, and/or restricting the average molecular weight.

Table 2.2 Values of N_n, N_w, and N_w/N_n for various large values of p

p	N_n	N_w	N_w/N_n
0.90	10.0	19.0	1.90
0.92	12.5	24.0	1.92
0.94	16.7	32.3	1.94
0.96	25.0	49.0	1.96
0.98	50.0	99.0	1.98
0.990	100	199	1.990
0.992	125	249	1.992
0.994	167	332	1.994
0.996	250	499	1.996
0.998	500	999	1.998

Polyesters and polyamides are two of the most studied step-growth polymers, as well as being substances of great commercial importance. We shall consider polyesters in the next section, and polyamides in Section 2.6.

2.5 Polyesters

The preceding discussions of the kinetics and molecular weight distributions in the step-growth polymerizations of AB monomers are exemplified by esterification reactions between such monomers as glycolic acid and ω-hydroxydecanoic acid. Therefore one method of polyester synthesis is the following:

1. Esterification of a hydroxycarboxylic acid.

Several other chemical reactions are also widely used for the synthesis of these polymers. This list enumerates some of the possibilities, and Table 2.3 illustrates these reactions by schematic chemical equations.

2. Esterification of a diacid and a diol.
3. Ester interchange with alcohol.

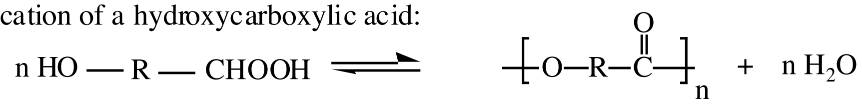
4. Ester interchange with ester.

5. Esterification of acid chlorides.

6. Lactone polymerization.

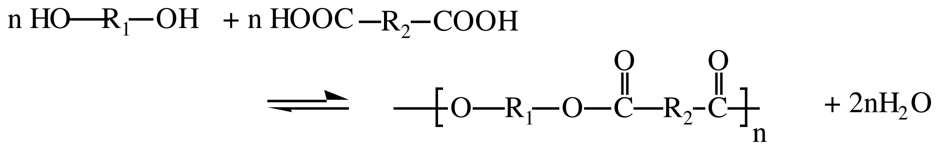
Table 2.3 Some schematic reactions for the formation of polyesters

1. Esterification of a hydroxycarboxylic acid:



$$n\,\mathrm{HO{-}R{-}CHOOH} \rightleftharpoons \left[\mathrm{O{-}R{-}\overset{\overset{\displaystyle O}{\|}}{C}}\right]_n + n\,\mathrm{H_2O}$$

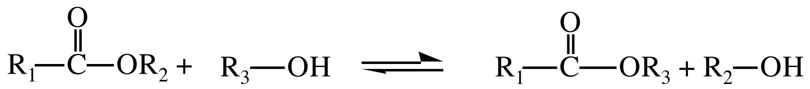
2. Esterification of diacid and diol:



$$n\,\mathrm{HO{-}R_1{-}OH} + n\,\mathrm{HOOC{-}R_2{-}COOH}$$

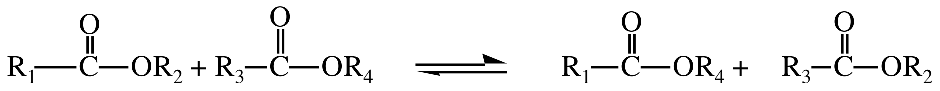
$$\rightleftharpoons \left[\mathrm{O{-}R_1{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R_2{-}\overset{\overset{\displaystyle O}{\|}}{C}}\right]_n + 2n\mathrm{H_2O}$$

3. Ester interchange with alcohol:



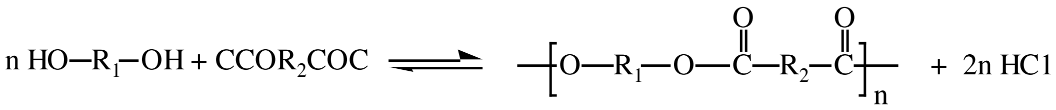
$$\mathrm{R_1{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR_2} + \mathrm{R_3{-}OH} \rightleftharpoons \mathrm{R_1{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR_3} + \mathrm{R_2{-}OH}$$

4. Ester interchange with ester ("transesterification"):



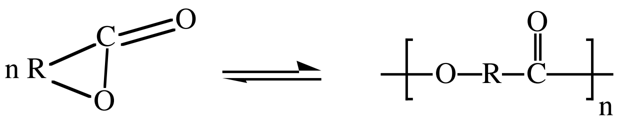
$$\mathrm{R_1{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR_2} + \mathrm{R_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR_4} \rightleftharpoons \mathrm{R_1{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR_4} + \mathrm{R_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR_2}$$

5. Esterification of acid chlorides (Schotten-Baumann reaction):

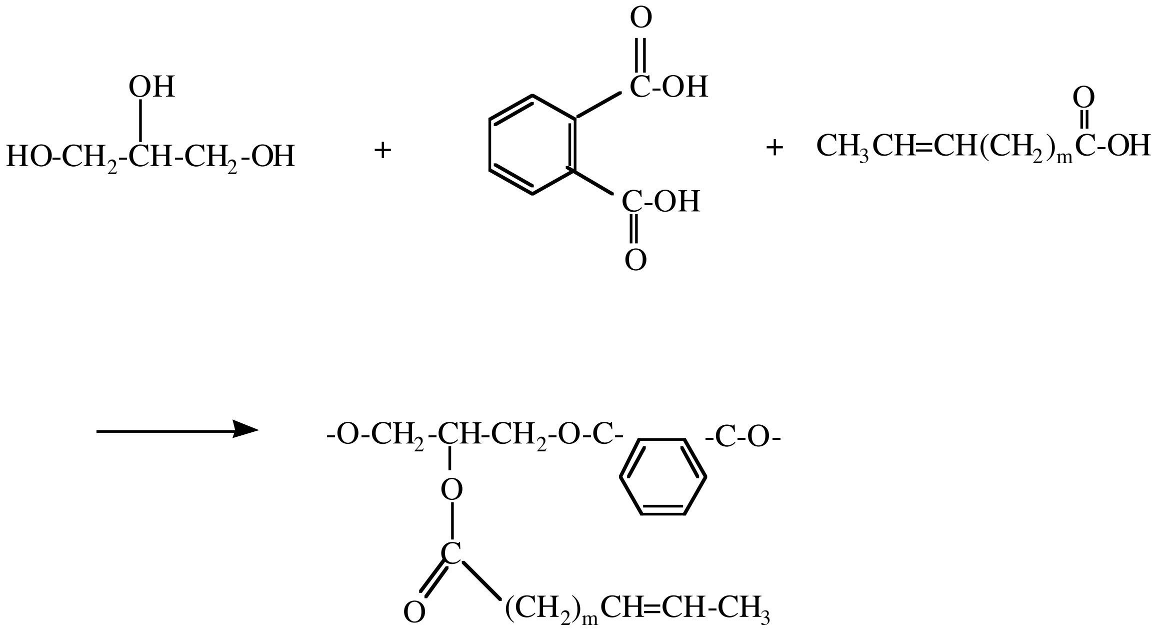


$$n\,\mathrm{HO{-}R_1{-}OH} + \mathrm{CCOR_2COC} \rightleftharpoons \left[\mathrm{O{-}R_1{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R_2{-}\overset{\overset{\displaystyle O}{\|}}{C}}\right]_n + 2n\,\mathrm{HCl}$$

6. Lactone polymerization:



We have not attempted to indicate the conditions of temperature, catalyst, solvent, and so on, for these various reactions. For this type of information, references that deal specifically with synthetic polymer chemistry should be consulted. In the next few paragraphs we shall comment on the various routes to polyester formation in the order summarized above and followed in Table 2.3. The studies summarized in Figures 2.2 and 2.3 are examples of reaction 2 in Table 2.3. While up to now we have emphasized bifunctional reactants, both monofunctional compounds and monomers with functionality greater than 2 are present in some polymerization processes, either intentionally or adventitiously. The effect of the monofunctional reactant is clearly to limit chain growth. As noted above, a functionality greater than 2 results in branching. A type of polyester that includes mono-, di-, and trifunctional monomers is the so-called alkyd resin. A typical example is based on the polymerization of phthalic acid (or anhydride), glycerol, and an unsaturated monocarboxylic acid. The following suggests the structure of a portion of such a polyester:

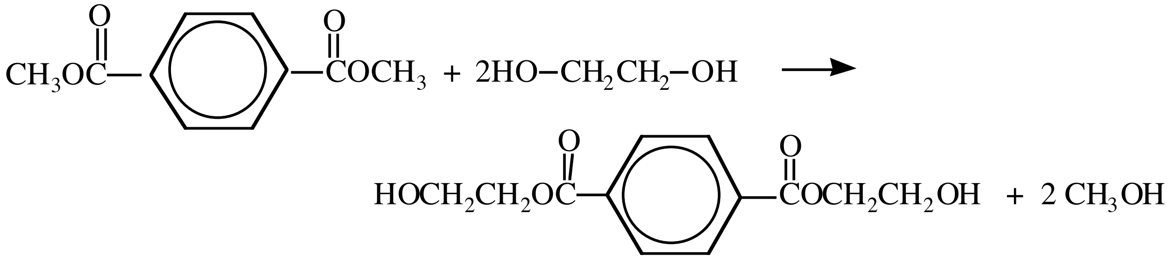


(2.J)

The presence of the unsaturated substituent along this polyester backbone gives this polymer crosslinking possibilities through a secondary reaction of the double bond. These polymers are used in paints, varnishes, and lacquers, where the ultimate cross-linked product results from the oxidation of the double bond as the coating cures. A cross-linked polyester could also result from reaction (2.J) without the unsaturated carboxylic acid, but the latter would produce a gel in which the entire reaction mass solidified, and is therefore not as well suited to coating applications as a polymer that crosslinks upon "drying".

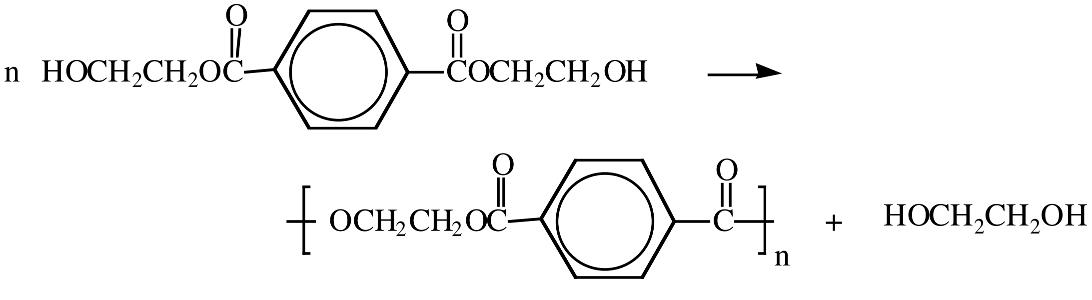
Many of the reactions listed at the beginning of this section are acid catalyzed, although a number of basic catalysts are also employed. Esterifications are equilibrium reactions, and are often carried out at elevated temperatures for favorable rate and equilibrium constants and to shift the equilibrium in favor of the polymer by volatilization of the by-product molecules. An undesired feature of higher polymerization temperatures is the increased possibility of side reactions, such as the dehydration of the diol or the pyrolysis of the ester. Basic catalysts tend to produce fewer undesirable side reactions.

Ester exchange reactions are valuable, since, say, methyl esters of dicarboxylic acids are often more soluble and easier to purify than the diacid itself. The methanol by-product is easily removed by evaporation. Poly(ethylene terephthalate) is an example of a polymer prepared by double application of reaction 4 in Table 2.3 The first stage of the reaction is conducted at temperatures below 200°C and involves the interchange of dimethyl terephthalate with ethylene glycol



(2.K)

The rate of this reaction is increased by using excess ethylene glycol, and removal of the methanol is assured by the elevated temperature. Polymer is produced in the second stage after the temperature is raised above the melting point of the polymer, about 260°C.



(2.L)

The ethylene glycol liberated by reaction (2.L) is removed by lowering the pressure or purging with an inert gas. Because the ethylene glycol produced by reaction (2.L) is removed, proper stoichiometry is assured by proceeding via the intermediate bis(2-hydroxyethyl) terephthalate; otherwise the excess glycol used initially would have a deleterious effect on the degree of polymerization. Poly(ethylene terephthalate) is more familiar by some of its trade names: Mylar as a film and Dacron, Kodel, or Terylene as fibers; it is also known by the acronym PET.

Ester interchange reactions like that shown in reaction 4 in Table 2.2 ("transesterification") can be carried out on polyesters themselves to produce a scrambling between the two polymers. Studies of this sort between high and low molecular weight prepolymers result in a single polymer with the same molecular weight distribution as would have been obtained from a similarly constituted diol-diacid mixture by direct polymerization. This is true when the time-catalyst conditions allow the randomization to reach equilibrium. If the two prepolymers are polyesters formed from different monomers, the product of the ester interchange reaction will be a copolymer of some sort. If the reaction conditions favor esterification, the two chains will merely link together and a block copolymer results. If the conditions favor the ester interchange reaction, then a scrambled copolymer molecule results. These possibilities underscore the idea that the derivations of the preceding sections are based on complete equilibrium among all molecular species present during the condensation reaction.

Example 2.3

It has been hypothesized that cross-linked polymers would have better mechanical properties if interchain bridges were located at the ends rather than the center of chains. To test this, low molecular weight polyesters were synthesized from a diol and two different diacids: one saturated, the other unsaturated. The synthetic procedure was such that the unsaturated acid units were located at either the center (centrene) or the ends (endene) of the chains. Some pertinent aspects of the overall experiment are listed below:

Data for Example 2.3

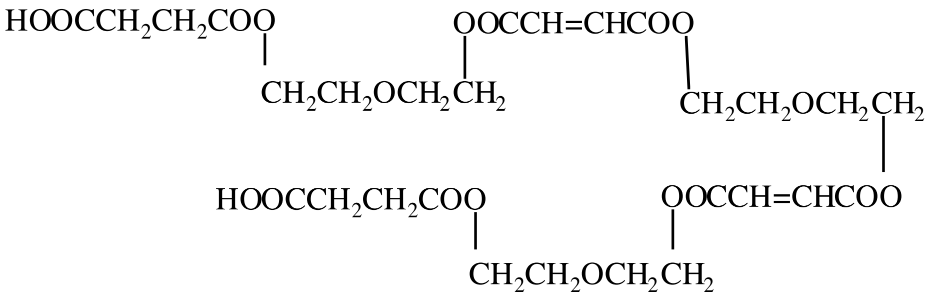
		Endene	Centrene
Step 1:	8 hr at about 150-200°C		
	Maleic anhydride (mol)	0	2.0
	Succinic anhydride (mol)	2.0	0
	Diethylene glycol (mol)	3.0	3.0
Step 2:	About 1/2 hr at about 120-130°C		
	Maleic anhydride (mol)	2.0	0
	Succinic anhydride (mol)	0	2.0
	Catalyst	0	0
Step 3:	30% styrene + catalyst		
	16 hr at 55°C + 1 hr at 110°C		
	Elastic modulus (Pa)	21,550	16,500

On the basis of these facts, do the following:

1. Comment on the likelihood that the comonomers are segregated as the names of these polymers suggest.
2. Sketch the structure of the average endene and centrene molecules.
3. Comment on the results in terms of the initial hypothesis.

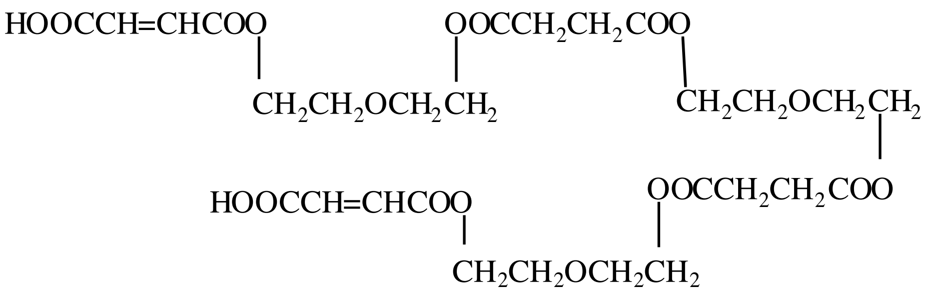
Solution

1. Since the reaction conditions are mild in step 2 (only 6% as much time allowed as in step 1 at a lower temperature) and no catalyst is present, it is unlikely that any significant amount of ester scrambling occurs. Isomerization of maleate to fumarate is also known to be insignificant under these conditions.
2. The idealized structures of these molecules are



$$\begin{gathered} HOOCCH_2CH_2COO \qquad OOCCH{=}CHCOO \\ CH_2CH_2OCH_2CH_2 \qquad CH_2CH_2OCH_2CH_2 \\ HOOCCH_2CH_2COO \qquad OOCCH{=}CHCOO \\ CH_2CH_2OCH_2CH_2 \end{gathered}$$

"centrene"



$$\begin{gathered} HOOCCH{=}CHCOO \qquad OOCCH_2CH_2COO \\ CH_2CH_2OCH_2CH_2 \qquad CH_2CH_2OCH_2CH_2 \\ HOOCCH{=}CHCOO \qquad OOCCH_2CH_2COO \\ CH_2CH_2OCH_2CH_2 \end{gathered}$$

"endene"

3. A cross-linked product with unsaturation at the chain ends does, indeed, have a higher modulus. This could be of commercial importance and indicates that industrial products might be formed by a nonequilibrium process precisely for this sort of reason. A fuller discussion of the factors that contribute to the modulus will be given in Chapter 10.

Acid chlorides are generally more reactive than the parent acids, so polyester formation via reaction 5 in Table 2.3 can be carried out in solution and at lower temperatures, in contrast with the bulk reactions of the melt as described above. Again, the by-product molecules must be eliminated either by distillation or precipitation. The method of interfacial condensation, described in the next section, can be applied to this type of reaction.

The formation of polyesters from the polymerization of lactones (reaction 6 in Table 2.3) is a ring-opening reaction that may follow either a step-growth or chain mechanism, depending on conditions. For now our only concern is to note that the equilibrium representing this reaction in Table 2.3 describes polymerization by the forward reaction and ring formation by the back reaction. Rings clearly compete with polymers for monomer in all polymerizations. Throughout the chapter we have assumed that all competing side reactions, including ring formation, could be neglected.

2.6 Polyamides

The discussion of polyamides parallels that of polyesters in many ways. To begin with, polyamides may be formed from an AB monomer, in this case amino acids:

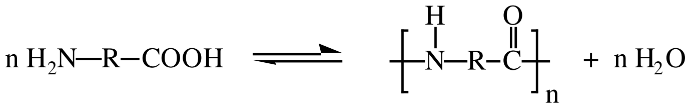
1. Amidation of amino acids.

Additional synthetic routes which closely resemble polyesters are also available. Several more of these are listed below and are illustrated by schematic reactions in Table 2.4:

2. Amidation of a diacid and a diamine.
3. Interchange reactions.
4. Amidation of acid chlorides.
5. Lactam polymerization.

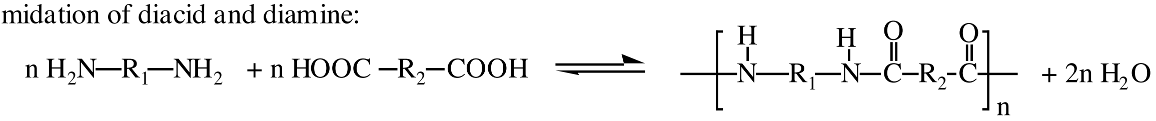
Table 2.4 Some schematic reactions for the formation of polyamides

1. Amidation of amino acids:



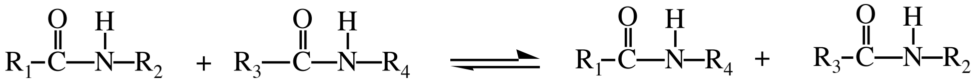
$$n\,H_2N{-}R{-}COOH \rightleftharpoons \left[\overset{H}{\overset{|}{N}}{-}R{-}\overset{O}{\overset{\|}{C}}\right]_n + n\,H_2O$$

2. Amidation of diacid and diamine:



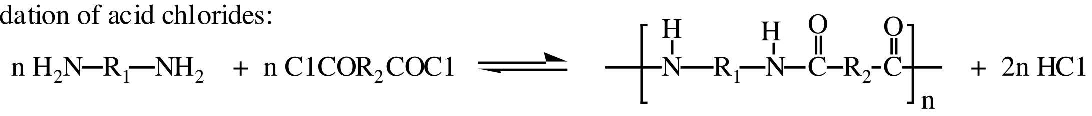
$$n\,H_2N{-}R_1{-}NH_2 + n\,HOOC{-}R_2{-}COOH \rightleftharpoons \left[\overset{H}{\overset{|}{N}}{-}R_1{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}R_2{-}\overset{O}{\overset{\|}{C}}\right]_n + 2n\,H_2O$$

3. Interchange reactions:



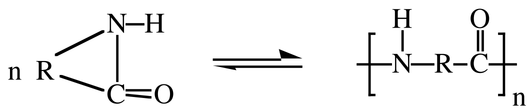
$$R_1{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R_2 + R_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R_4 \rightleftharpoons R_1{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R_4 + R_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R_2$$

4. Amidation of acid chlorides:



$$n\,H_2N{-}R_1{-}NH_2 + n\,C1COR_2COC1 \rightleftharpoons \left[\overset{H}{\overset{|}{N}}{-}R_1{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}R_2{-}\overset{O}{\overset{\|}{C}}\right]_n + 2n\,HC1$$

5. Lactam polymerization:



We only need to recall the trade name of synthetic polyamides, nylon, to recognize the importance of these polymers and the reactions employed to prepare them. Remember from Section 1.x the nylon system for naming these compounds: the first number after the name gives the number of carbon atoms in the diamine, and the second, the number of carbons in the diacid.

The diacid-diamine amidation described in reaction 2 in Table 2.4 has been widely studied in the melt, in solution, and in the solid state. When equal amounts of two functional groups are present, both the rate laws and the molecular weight distributions are given by the treatment of the preceding sections. The stoichiometric balance between reactive groups is readily obtained by precipitating the 1:1 ammonium salt from ethanol:

$$\mathrm{H_2N{-}R_1{-}NH_2} \;+\; \mathrm{HOOC{-}R_2{-}COOH} \;\longrightarrow\; \begin{array}{c}\mathrm{H_3N^{+}{-}R_1{-}{}^{+}NH_3}\\ \mathrm{{}^{-}OOC{-}R_2{-}COO^{-}}\end{array} \tag{2.M}$$

This compound is sometimes called a nylon salt. The salt ↔ polymer equilibrium is more favorable to the production of polymer than in the case of polyesters, so this reaction is often carried out in a sealed tube or autoclave at about 200 °C until a fairly high extent of reaction is reached; then the temperature is raised and the water driven off to attain high molecular weight polymer.

This process represented by reaction 2 in Table 2.4 actually entails a number of additional equilibrium reactions. Some of the equilibria that have been considered include the following:

$$\sim\mathrm{NH_3^{+}} \;+\; {}^{-}\mathrm{OOC}\sim \;\rightleftharpoons\; \sim\mathrm{CONH}\sim \;+\; \mathrm{H_2O} \tag{2.N}$$

$$\sim\mathrm{COOH} \;+\; \mathrm{H_2O} \;\rightleftharpoons\; \sim\mathrm{COO^{-}} \;+\; \mathrm{H_3O^{+}} \tag{2.O}$$

$$\sim\!\sim \mathrm{NH_2} + \mathrm{H_2O} \rightleftharpoons \sim\!\sim \mathrm{NH_3^+} + \mathrm{OH^-} \tag{2.P}$$

$$2\,\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-} \tag{2.Q}$$

$$\sim\!\sim \mathrm{COOH} + \mathrm{H^+} \rightleftharpoons \sim \mathrm{C(OH)_2^+} \tag{2.R}$$

$$\sim \mathrm{C(OH)_2^+} + \mathrm{H_2N}\sim\!\sim \rightleftharpoons \sim\!\sim \mathrm{CONH} \sim\!\sim + \mathrm{H_3O^+} \tag{2.S}$$

Reaction (2.N) describes the nylon salt ↔ nylon equilibrium. Reactions (2.O) and (2.P) show proton transfer with water between carboxyl and amine groups. Since proton transfer equilibria are involved, the self-ionization of water, reaction (2.Q), must also be included. Especially in the presence of acidic catalysts, reactions (2.R) and (2.S) are the equilibria of the acid-catalyzed intermediate described in general in reaction (2.G). The main point in including all of these equilibria is to indicate that the precise concentration of A and B groups in a diacid-diamine reaction mixture is a complicated function of the moisture content and the pH, as well as the initial amounts of reactants introduced. Because of the high affinity for water of the various functional groups present, the complete removal of water is impossible: the equilibrium moisture content of molten nylon-6,6 at 290 °C under steam at 1atm is 0.15%. Likewise, the various ionic possibilities mean that at both high and low pH values the concentration of un-ionized carboxyl or amine groups may be considerably different from the total concentration – without regard to state of ionization – of these groups. As usual, upsetting the stoichiometric balance of the reactive groups lowers the degree of polymerization attainable. The abundance of high-quality nylon products is evidence that these complications have been overcome in practice.

Amide interchange reactions of the type represented by reaction 3 in Table 2.4 are known to occur more slowly than direct amidation; nevertheless, reactions between high and low molecular weight polyamides result in a polymer of intermediate molecular weight. The polymer is initially a block copolymer of the two starting materials, but randomization is eventually attained.

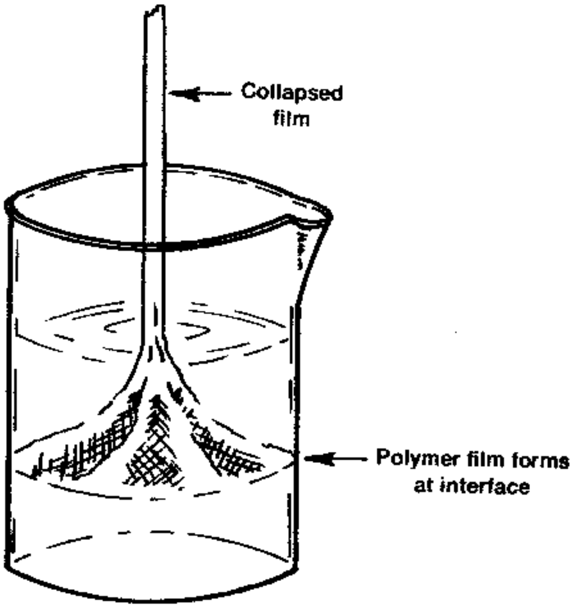


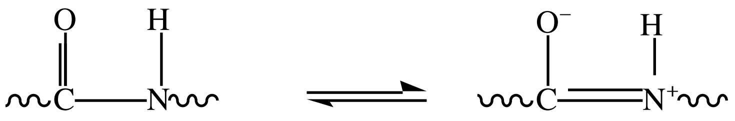
Figure 2.7
Sketch of an interfacial polymerization with the collapsed polymer film being withdrawn from the surface between the immiscible phases. Redrawn with permission from P. W. Morgan and S. L. Kwolek, *J. Chem. Educ.* 36, 182 (1959).

As with polyesters, the amidation reaction of acid chlorides may be carried out in solution because of the enhanced reactivity of acid chlorides compared with carboxylic acids. A technique known as interfacial polymerization has been employed for the formation of polyamides and other step-growth polymers, including polyesters, polyurethanes, and polycarbonates. In this method the polymerization is carried out at the interface between two immiscible solutions, one of which contains one of the dissolved reactants, while the second monomer is dissolved in the other. Figure 2.7 shows a polyamide film forming at the interface between layers of an aqueous diamine solution and a solution of diacid chloride in an organic solvent. In this form interfacial polymerization is part of the standard repertoire of chemical demonstrations. It is sometimes called the "nylon rope trick" because of the filament of nylon that can be produced by withdrawing the collapsed film.

The amidation of the reactive groups in interfacial polymerization is governed by the rates at which these groups can diffuse to the interface where the growing polymer is deposited. Accordingly, new reactants add to existing chains rather than interacting to form new chains. This is different than the bulk mechanism we have discussed elsewhere in this chapter, and it is evident that a higher molecular weight polymer should result from this difference. The HCl by-product of the amidation reaction is neutralized by also dissolving an inorganic base in the aqueous layer in interfacial polymerization. The choice of the organic solvent plays a role in determining the properties of the polymer produced, probably because of the differences in solvent quality for the resulting polymer. Since this reaction is carried out at low temperatures, the complications associated with side reactions can be kept to a minimum. Polymer yield may be increased by increasing the area of the interface between the two solutions by stirring.

Lactam polymerization represented by reaction 5 in Table 2.4 is another example of a ring-opening reaction, the reverse of which is a possible competitor with polymer for reactants.

The various mechanical properties of polyamides may be traced in many instances to the possibility of intermolecular hydrogen bonding between the polymer molecules, and to the relatively stiff chains these substances possess. The latter, in turn, may be understood by considering still another equilibrium, this one among resonance structures along the chain backbone:



(2.T)

The combination of strong intermolecular forces and high chain stiffness accounts for the high melting points of polyamides (see Chapter 13).

The remarks of this and the previous section represent only a small fraction of what could be said about these important materials. We have commented on aspects of the polymerization processes and of the polymers themselves that have a direct bearing on the concepts discussed throughout this volume. This material provides an excellent example of the symbiosis between theoretical and application-oriented points of view. Each stimulates and reinforces the other with new challenges, although it must be conceded that many industrial processes reach a fairly high degree of empirical refinement before the conceptual basis is quantitatively developed.

2.7 Stoichiometric imbalance

We now turn to one of the problems we have sidestepped until now. In this section we consider the polymerization of reactants in which a stoichiometric imbalance exists in the numbers of reactive groups A and B. In prior sections dealing with the quantitative aspects of step-growth polymerization, we focused attention on monomers of the AB type to assure equality of reactive groups. The results obtained above also apply to AA and BB polymerizations, provided that the numbers of reactive groups are equal. There are obvious practical difficulties associated with the requirement of stoichiometric balance. Rigorous purification of monomers is difficult and adds to the cost of the final product. The effective loss of functional groups to side reactions imposes restrictions on the range of experimental conditions at best and is unavoidable at worst. These latter considerations apply even in the case of the AB monomer. We have already stated that the effects of the imbalance of A and B groups is to lower the eventual degree of polymerization of the product. A quantitative assessment of this limitation is what we now seek.

We define the problem by assuming the polymerization involves AA and BB monomers and that the B groups are present in excess. We define ν_A and ν_B to be the numbers of A and B functional groups, respectively. The number of either of these quantities in the initial reaction mixture is indicated by a superscript o; the numbers at various stages of reaction have no superscript. The stoichiometric imbalance is defined by the ratio r, where

$$r \equiv \frac{\nu_A{}^o}{\nu_B{}^o} \tag{2.7.1}$$

This ratio cannot exceed unity by definition of the problem.

As with other problems with stoichiometry, it is the less abundant reactant that limits the product. Accordingly, we define the extent of reaction p to be the fraction of A groups that have reacted at any point. Since A and B groups react in a 1:1 proportion, the number of B groups that have reacted when the extent of reaction has reached p equals $p\nu_A{}^o$, which in turn equals $pr\nu_B{}^o$. The product pr gives the fraction of B groups that have reacted at any point. With these definitions in mind, the following relationships are readily obtained:

1. The number of unreacted functional groups after the reaction reaches extent p is

$$\nu_A = (1-p)\nu_A{}^o \tag{2.7.2}$$

and

$$\nu_B = (1-p\,r)\nu_B{}^o = (1-p\,r)\frac{\nu_A{}^o}{r} \tag{2.7.3}$$

2. The total number of chain ends is given by the sum of eqs. 2.7.2 and 2.7.3:

$$\nu_{ends} = \left(1-p+\frac{1-p\,r}{r}\right)\nu_A{}^o \tag{2.7.4}$$

3. The total number of chains is half the number of chain ends:

$$\nu_{\text{chains}} = \frac{1}{2}\left(1 + \frac{1}{r} - 2p\right)\nu_A{}^o \tag{2.7.5}$$

4. The total number of repeat units distributed among these chains is the number of monomer molecules present initially:

$$\nu_{\text{repeat units}} = \frac{1}{2}\nu_A{}^o + \frac{1}{2}\nu_B{}^o = \frac{1}{2}\left(1 + \frac{1}{r}\right)\nu_A{}^o \tag{2.7.6}$$

The number average degree of polymerization is given by dividing the number of repeat units by the number of chains, or

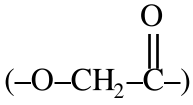
$$N_n = \frac{1 + 1/r}{1 + 1/r - 2p} = \frac{1 + r}{1 + r - 2pr} \tag{2.7.7}$$

As a check that we have done this correctly, note that eq 2.7.7 reduces to the previously established eq 2.4.5 when $r = 1$.

One distinction that should be pointed out involves the comparison of eqs 2.2.1 and 2.7.7. In the former we considered explicitly the AB monomer, whereas the latter is based on the polymerization of AA and BB monomers. In both instances N_n is obtained by dividing the total number of monomer molecules initially present by the total number of chains after the reaction has occurred to extent p. Following the same procedure for different reaction mixtures results in a different definition of the repeat unit. In the case of the AB monomer, the repeat unit is the ab entity, which differs from AB by the elimination of the by-product molecule. In the case of the AA and BB monomers, the repeat unit in the polymer is the aabb unit, which differs from AA + BB by two by-product molecules. Equation 2.2.1 counts the number of ab units in the polymer directly. Equation 2.7.7 counts the number of aa plus bb units. The number of aa plus bb units is twice the number of aabb units. Rather than attempting to formalize this distinction by introducing more complex notation, we simply point out that application of the formulas of this chapter to specific systems must be accompanied by a reflection on the precise meaning of the calculated quantity for the system under consideration.

The distinction pointed out in the last paragraph carries over to the evaluation of M_n from N_n. We assume that the chain length of the polymer is great enough to render unnecessary any correction for the uniqueness of chain ends. In such a case the molecular weight of the polymer is obtained from the degree of polymerization by multiplying the latter by the molecular weight of the repeat unit. The following examples illustrate the distinction under consideration:

1. Polymerization of an AB monomer is illustrated by the polyester formed from glycolic acid. The repeat unit in this polymer has the structure

   $$(\text{–O–CH}_2\text{–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–})$$

   and $M_o = 58$. Neglecting end groups, we have $M_n = 58\ N_n$ with N_n given by eq 2.2.1.

2. Polymerization of AA and BB monomers is illustrated by butane-1,4-diol and adipic acid. The aabb repeat unit in the polymer has an M_o value of 200. If eq 2.2.4 is used to evaluate N_n, it gives the number of aa plus bb units; therefore $M_n = 200\ N_n/2$.

3. An equivalent way of looking at the conclusion of item (2) is to recall that eq. 2.7.7 gives the (number average) number of monomers of both kinds in the polymer; we should multiply this quantity by the average molecular weight of the two kinds of units in the structure: (88 + 112)/2 = 100.

Equation 2.7.7 also applies to the case when some of the excess B groups present are in the form of monofunctional reagents. In this latter situation the definition of r is modified somewhat (and labeled with a prime) to allow for the fact that some of the B groups are in BB-type monomers (unprimed) and some are in monofunctional (primed) molecules:

$$r' = \frac{\nu_A}{\nu_B + 2\nu_{B'}} \qquad (2.7.8)$$

The parameter r′ continues to measure the ratio of the number of A and B groups; the factor 2 enters since the monofunctional reagent has the same effect on the degree of polymerization as a difunctional molecule with two B groups, hence, is doubly effective compared to the latter. With this modification taken into account, eq 2.7.7 enables us to evaluate quantitatively the effect of stoichiometric imbalance or monofunctional reagents, whether these are intentionally introduced to regulate N_n or whether they arise from impurities or side reactions.

Table 2.5 Some values of N_n calculated by eq 2.7.7 for values of r and p close to unity

r	p = 0.95	p = 0.97	p = 0.99	p = 1.00
0.95	13.5	18.2	28.3	39.0
0.97	15.5	22.3	39.9	65.7
0.99	18.3	28.7	66.8	199
1.00	20.0	33.3	100	∞

The parameter r varies between 0 and 1; as such it has the same range as p. Although the quantitative effect of r and p on N_n is different, the qualitative effect is similar for each: higher degrees of polymerization are obtained the closer each of these fractions is to unity. Table 2.5 shows some values of N_n calculated from eq 2.7.7 for several combinations of (larger values of) r and p. Inspection of Table 2.5 reveals the following:

1. For any value of r, N_n is greater for larger values of p; this conclusion is the same whether the proportions of A and B are balanced or not.

2. The final 0.05 increase in p has a bigger effect on N_n at r values that are closer to unity than for less-balanced mixtures.
3. For any value of p, N_n is greater for larger values of r; stoichiometric imbalance lowers the average chain length for the preparation.
4. An 0.05 increase in r produces a much bigger increase in N_n at $p = 1$ than in mixtures that have reacted to a lesser extent.

An interesting special case occurs when $p = 1$; eq 2.7.7 becomes

$$N_n = \frac{1 + r}{1 - r} \tag{2.7.9}$$

The following example illustrates some of the concepts developed in this section.

Example 2.4

It is desired to prepare a polyester with $M_n = 5000$ by reacting 1 mol of butane-1, 4-diol with 1 mol of adipic acid.

1. Calculate the value of p at which the reaction should be stopped to obtain this polymer, assuming perfect stoichiometric balance and neglecting end group effects on M_n.
2. Assuming that 0.5 mol % of the diol is lost to polymerization by dehydration to olefin, what would be the value of M_n if the reaction were carried out to the same extent as in (1)?
3. How could the loss in (2) be offset so that the desired polymer is still obtained?

4. Suppose the total number of carboxyl groups in the original mixture is 2 mol, of which 1.0% is present as acetic acid to render the resulting polymer inert to subsequent esterification. What value of p would be required to produce the desired polymer in this case, assuming no other stoichiometric imbalance?

Solution

The various expressions we have developed in this section relating p to the size of the polymer are all based on N_n. Accordingly, we note that the average reactant molecule in this mixture has a molecular weight of 100 as calculated above. Therefore the desired polymer has a value of $N_n = 50$.

1. We use eq 2.4.5 for the case of equal numbers of A and B groups and find that $p = 1 - 1/N_n = 0.980$. Even though eq 2.4.5 was derived for an AB monomer, it applies to this case with the "average monomer" as the repeat unit.

2. Component AA is the diol in this case and $\nu_A = 0.995$ mol; therefore $r = 0.995/1.00 = 0.995$. We use eq 2.7.7 and solve for N_n with $p = 0.980$ and $r = 0.995$:

$$N_n = \frac{1.995}{1.995 - 2(0.995)(0.980)} = 44.5$$

and therefore $M_n = 44.5(100) = 4450 \text{ g mol}^{-1}$

3. The effect of the lost hydroxyl groups can be offset by carrying out the polymerization to a higher extent of reaction. We use eq 2.7.7 and solve for p with $N_n = 50$ and $r = 0.995$:

$$p = \left(1 - \frac{1}{N_n}\right)\left(\frac{1+r}{2r}\right) = \left(1 - \frac{1}{50}\right)\frac{1.995}{1.990} = 0.9825$$

4. The monofunctional reagent B′ is the acetic acid in this case and the number of monofunctional carboxyl groups is 2(0.010) = 0.020 = $\nu_B{}'$. The number of B groups in BB monomers is 1.980 = ν_B. We use eq 2.7.8 to define r′ for this situation, assuming the number of hydroxyl groups equals 2.00 mol:

$$r' = \frac{2.00}{1.980 + 2(0.020)} = 0.990$$

Equation 2.7.7 is now solved for p using $N_n = 50$ and $r' = 0.990$:

$$p = \left(1 - \frac{1}{N_n}\right)\left(\frac{1 + r'}{2r'}\right) = \left(1 - \frac{1}{50}\right)\frac{1.990}{1.980} = 0.9849$$

Remember from Section 2.3 that a progressively longer period of time is required to shift the reaction to larger values of p. In practice, therefore, the effects of side reactions and monofunctional reactants are often not compensated by longer polymerization times, but are accepted in the form of lower molecular weight polymers.

CHAPTER SUMMARY

In this chapter we have considered step-growth or condensation polymerization, one of the two main routes to synthetic polymers. Our emphasis has been on the description of the distribution of polymer sizes as a function of the extent of reaction and the concentration of reactants, and on the associated kinetics. In addition, we have given an introduction to the two major classes of commercial condensation polymers, polyesters and polyamides, and the different ways they may be produced. The principal results are as follows:

1. In the simplest case of stoichiometric balance, i.e., equal numbers of A and B reactive groups, the number average degree of polymerization N_n is given by $1/(1 - p)$, where p is the extent of reaction, equal to the fraction of A (or B) groups reacted. In general, therefore, the reaction must be driven far toward products ($p \rightarrow 1$) before appreciable molecular weights can be attained.
2. The resulting distribution of molecular sizes is called the Most Probable Distribution, and the associated polydispersity index approaches 2 as $p \rightarrow 1$. Two important features of this distribution are that there are always more i-mers present than (i+1)-mers, for any value of i, but there is an intermediate value of i for which the weight fraction w_n is maximum.
3. If the reaction is run in the presence of a catalyst (the usual situation), then N_n should grow linearly in time, whereas for the uncatalyzed case, N_n will grow with the square root of time.
4. In reality N will almost always be lower than the theoretical value for a given p, due to a combination of side reactions, including ring formation, contamination by monofunctional reagents, and stoichiometric imbalance.
5. The analysis of these reactions builds on the Principle of Equal Reactivity, the assumption that the reactivity of a given functional group is independent of the molecular

weight of the polymer to which it is attached. This assumption is quite reliable in most cases of interest.

References

[1]. see, for example, P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.

[2]. D. H. Solomon, Ed., *Step Growth Polymerization*, Marcel Dekker, New York (1972).

Further information on step-growth polymerization may be found in the following books:

Allcock, H. R., and Lampe, F. W., *Contemporary Polymer Chemistry*, 2nd Edition, Prentice Hall, Englewood Cliffs, NJ, 1990.

Odian, G., *Principles of Polymerization*, 2nd Ed., Wiley, New York, 1981.

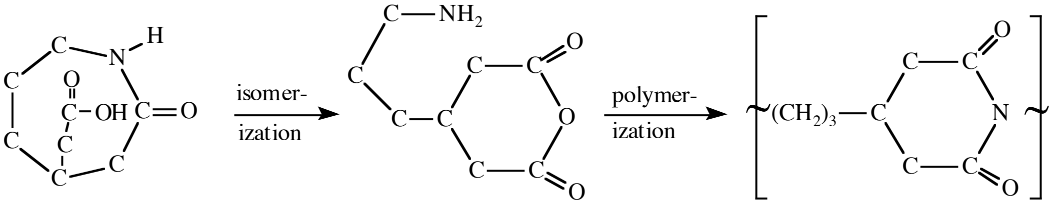
Rempp, P., and Merrill, E. W., *Polymer Synthesis*, 2nd Ed., Hüthig & Wepf, Basel. 1991.

Problems

1. Howard describes a model system used to test the molecular weight distribution of a condensation polymer (G. J. Howard, *J. Polym. Sci.* 37, 310 (1959)): "The polymer sample was an acetic acid-stabilized equilibrium nylon-6,6. Analysis showed it to have the following end group composition (in equivalents per 10^6 g): acetyl = 28.9, amine = 35.3 and carboxyl = 96.5. The number average degree of polymerization is, therefore, 110 and the conversion degree (= extent of reaction) = 0.9909." Verify the self-consistency of those numbers.

2. Haward et al. have reported some research in which a copolymer of styrene and hydroxyethylmethacrylate was cross-linked by hexamethylene di-isocyanate (R. N. Haward, B. M. Parker, and E. F. T. White, *Adv. Chem.* 91, 498 (1969)). Draw the structural formula for a portion of this cross-linked polymer and indicate what part of the molecule is the result of a condensation reaction and what part results from addition polymerization. These authors indicate that the crosslinking reaction is carried out in sufficiently dilute solutions of copolymer that the crosslinking is primarily intramolecular rather than intermolecular. Explain the distinction between these two terms and why concentration affects the relative amounts of each.

3. The polymerization of β-carbonxymethyl caprolactam has been observed to consist of initial isomerization via a second-order kinetic process followed by condensation of the isomer to polymer:

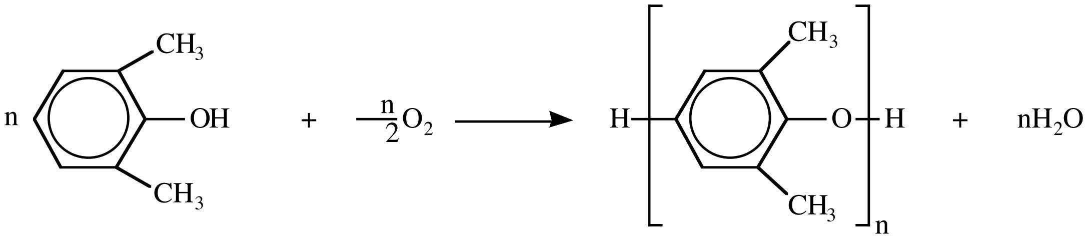


The rate of polymerization is thus first order in ν_{NH_2} and first order in $\nu_{(CO)_2O}$ or second order overall. Since $\nu_{NH_2} = \nu_{(CO)_2O}$, rate = kc^2, if catalyzed; third order is expected under uncatalyzed conditions. The indirect evaluation of c was accomplished by measuring the amount of monomer reacted, and the average degree of polymerization of the mixture was determined by viscosity at different time. The following data were obtained at 270 °C ; the early part of the experiment gives nonlinear results (H. K. Reimschuessel, *Adv. Chem.* 91, 717 (1969)). Graphically test whether these data indicate catalyzed or uncatalyzed conditions, and evaluate the rate of constant for polymerization at 270° C. Propose a name for the polymer.

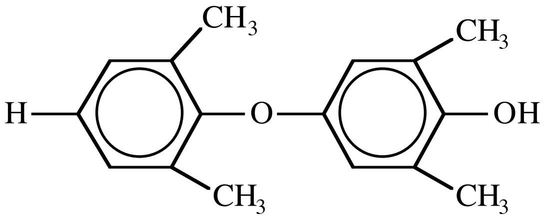
t (min)	c (mole fraction)	t (min)	c (mole fraction)
20	0.042	90	0.105
30	0.039	110	0.013
40	0.028	120	0.012
50	0.024	150	0.0096
60	0.021	180	0.0082
80	0.018		

4. Examination of Figure 2.5 shows that N_i/N is greater for i = 40 at p = 0.97 than at either p = 0.95 or p = 0.99. This is generally true: various i-mers go through a maximum in numerical abundance as p increases. Show that the extent of reaction at which this maximum occurs varies with i as follows: $p_{max} = (i-1)/(i+1)$. For a catalyzed AB reaction, extend this expression to give a function for the time required for an i-mer to reach its maximum numerical abundance. If $k_c = 2.47 \times 10^{-4}$ liter mol^{-1} sec^{-1} at 160.5 °C for the polymerization of 12-hydroxystearic acid (C. E. H. Bawn and M. B. Huglin, *Polymer* 3, 257 (1962)), calculate the time at which 15-mers show their maximum abundance if the initial concentration of monomer is 3.0 M.

5. In the presence of pyridine-cuprous chloride catalyst, the following polymerization occurs:



In an investigation to examine the mechanism of this reaction, the dimer (i=2)



was used as a starting material. The composition of the mixture was studied as the reaction progressed and the accompanying results were obtained (G. D. Cooper and A. Katchman, *Adv. Chem.* 91, 660 (1969)):

Percent of theoretical O_2 absorbed	Weight percent composition in reaction mixture			
	Monomer	Dimer	Trimer	Tetramer
9	1	69	15	9
12	1.5	68	24	9
20	3	38. 5	23	9
35	6	26	21	11
60	11	4	4	1
80	1	0	0	0

Plot a family of curves, each of different i, with composition as the y axis and O_2 absorbed as the x axis. Evaluate w_i by eq 2.4.7 for i = 1, 2, 3, and 4 and $0.1 \leq p \leq 0.9$ in increments of 0.1. Plot these results (w_i on y axis) on a separate graph drawn to the same scale as the experimental results. Compare your calculated curves with the experimental curves with respect to each of the following points: (1) coordinates used, (2) general shape of curves, and (3) labeling curves.

6. The polymer described in the last problem is commercially called poly(phenylene oxide), which is not a "proper" name for a molecule with this structure. Propose a more correct name. Use the results of the last problem to criticize or defend the following proposition: The experimental data for dimer polymerization can be understood if it is assumed that one molecule of water *and* one molecule of monomer may split out in the condensation step. Steps involving incorporation of the monomer itself (with only water split out) also occur.

7. Taylor carefully fractionated a sample of nylon-6.6 and determined the weight fraction of different i-mers in the resulting mixture (G. B. Taylor, *J. Am. Chem. Soc.* 69, 638 (1947)). The results obtained are given below. Evaluate N_w from these data, then use eq 2.4.9 to calculate the corresponding value of p. Calculate the theoretical weight fraction of i-mers using this value of p and a suitable array of i values. Plot your theoretical curve and the above data points on the same graph. Criticize or defend the following proposition: although the fit of the data points is acceptable with this value of p, it appears that a slightly smaller value of p would give an even better fit.

i	$w_i \times 10^{-4}$	i	$w_i \times 10^{-4}$
12	6.5	311	15.2
35	19.6	334	14.1
58	29.4	357	13.0
81	33.0	380	11.5
104	35.4	403	11.0
127	36.5	426	9.1
150	33.0	449	7.2
173	27.6	472	6.5
196	25.2	495	4.9
219	22.9	518	4.3
242	19.4	541	3.9
265	18.5	564	3.3
288	16.8		

8. Paper chromatograms were developed for 50:50 blends of nylon-6,6 and nylon-6,10 after the mixture had been heated to 290 °C for various periods of time (C. W. Ayers, *J. Appl. Chem.* 4, 444 (1954)). The following observations describe the chromatograms after the indicated times of heating:

    0 hr – two spots with R_f values of individual polymers.

    1/4 hr – two distinct spots, but closer together than those of 0 hr.

    1/2 hr – spots are linked together.

    3/4 hr – one long, diffuse spot.

    1 1/2 hr – one compact spot, intermediate R_f value.

    On the basis of these observations, criticize or defend the following proposition: the fact that the separate spots fuse into a single spot of intermediate R_f value proves that block copolymers form between the two species within the blend upon heating.

9. Reimschuessel and Dege‡ polymerized caprolactam in sealed tubes containing about 0.0205 mol H_2O per mole caprolactam (H. K. Reimschuessel and G. J. Dege, *J. Polym. Sci.* A-1, 2343 (1971)). In addition, acetic acid (V), sebacic acid (S), hexamethylene

diamine (H) and trimesic acid (T) were introduced as additives into separate runs. The following table lists (all data per mole caprolactam) the amounts of additive present and the analysis for end groups in various runs. Neglecting end group effects, calculate M_n for each of these polymers from the end group data. Are the trends in molecular weight qualitatively what would be expected in terms of the role of the additive in the reaction mixture? Explain briefly.

Additives	Moles additive	—COOH (mEq)	—NH_2 (mEq)
None	—	5.40	4.99
V	0.0205	19.8	2.3
S	0.0102	21.1	2.3
H	0.0102	1.4	19.7
T	0.0067	22.0	2.5

10. In the study described in the last problem, caprolactam was polymerized for 24 hr at 225 °C in sealed tubes containing various amounts of water. M_n and M_w were measured for the resulting mixture by osmometry (see Chapter 7) and light scattering (see Chapter 8), respectively, and the following results were obtained§:

Moles H_2O ($\times 10^3$)/mole caprolactam	$M_n \times 10^{-3}$	$M_n \times 10^{-3}$
49.3	13.4	20.0
34.0	16.4	25.6
25.6	17.9	29.8
20.5	19.4	36.6

Use the molecular weight ratio to calculate the apparent extent of reaction of the caprolactam in the systems. Is the variation in p qualitatively consistent with your expectations of the effect of increased water content in the system? Plot p versus moisture content and estimate by extrapolation equilibrium moisture content of nylon-6 at 255 °C. Does the apparent equilibrium moisture content of this polymer seem consistent with the value given in Section 2.6 for nylon-6,6 at 290 °C?

11. At 270 °C adipic acid decomposes to the extent of 0.31 mol % after 1.5 hr (V. V. Korshak and S. V. Vinogradova, *Polyesters*, Pergamon, Oxford, 1965). Suppose an initially equimolar mixture of adipic acid and diol achieves a value of p = 0.990 after 1.5 hr. Compare the expected and observed values of N_n in this experiment. Criticize or defend the following proposition: the difference between the observed and expected values would be even greater than calculated above if, instead of the extent of reaction being measured analytically, the value of p expected (neglecting decomposition) after 1.5 hr were calculated by an appropriate kinetic equation.