

Polymer Chemistry

Second Edition



Paul C. Hiemenz
Timothy P. Lodge

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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. Stoichiometry of the polymerization reaction (small molecule eliminated?)
2. Composition of the backbone of the polymer (atoms other than carbon present?)
3. 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 (Section 2.2 through Section 2.4). Initially we consider these topics for simple reaction mixtures, that is, 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 (Section 2.5 and Section 2.6). Finally we consider nonstoichiometric proportions of reactants (Section 2.7). The important case of multifunctional monomers, which can introduce branching and cross-linking into the products, is deferred until Chapter 10.

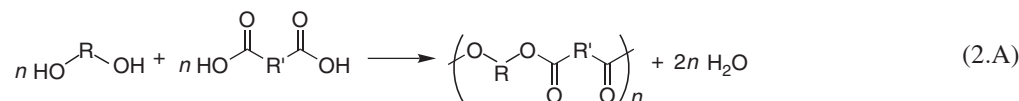
2.2 Condensation Polymers: One Step at a Time

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 lies 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 that result from the occurrence of many steps in which ester or amide linkages are formed between the 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.

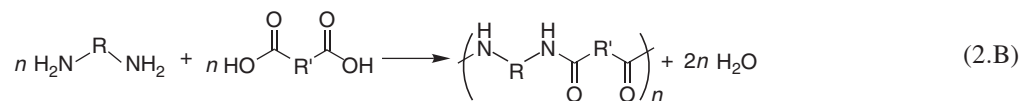
2.2.1 Classes of Step-Growth Polymers

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

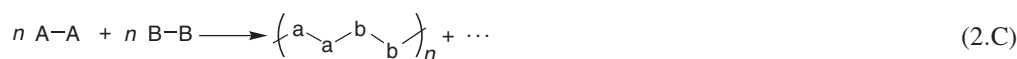
1. Polyesters—successive reactions between diols and dicarboxylic acids:



2. Polyamides—successive reactions between diamines and dicarboxylic acids:

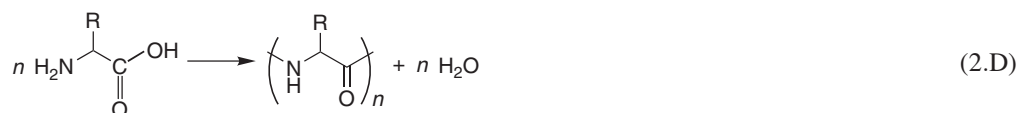


3. General—successive reactions between difunctional monomer A–A and difunctional monomer B–B:



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

4. Poly(amino acid)



5. General



Of course, in Reaction (2.A) and Reaction (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, Reaction (2.C) and Reaction (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 Reaction (2.E), since equimolar proportions of A and B are assured by the structure of the monomer.

2.2.2 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,

Table 2.1 Hypothetical Step-Growth Polymerization of 10 AB Molecules^a

Row	Molecular species present
1.	AB AB AB AB AB AB AB AB AB AB
2.	AbaB AbaB AbaB AbaB AB AB
3.	AbababB AbaB AbababB AB
4.	AbababB AbabababB AB
5.	AbababB AbababababB
6.	AbabababababababB

^aA 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.

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 that account for the differences between the first and second rows 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 indicate those that have reacted with each other as ab groups. The same conservation of atom groupings would be obtained if row 2 showed one trimer, two dimers, and three monomers instead of the four dimers and two monomers indicated in Table 2.1. 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?

Row 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 rows 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 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 the fourth row 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 AbababababababB 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 the fifth row, 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?

The sixth row 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 row 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 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 of 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, ν_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

$$N_n = \frac{\nu_A^o}{\nu_A} \quad (2.2.1)$$

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 that have reacted at any stage of the process, and $1-p$ is the unreacted fraction:

$$1-p = \frac{\nu_A}{\nu_A^0} \quad (2.2.2)$$

or

$$p = 1 - \frac{\nu_A}{\nu_A^0} \quad (2.2.3)$$

Comparison of Equation 2.2.1 and Equation 2.2.2 enables us to write very simply:

$$N_n = \frac{1}{1-p} \quad (2.2.4)$$

This expression is consistent with the analysis of each of the rows 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; Equation 2.2.4 represents a quantitative summary of an end group method for determining N_n . We reiterate that Equation 2.2.4 assumes equal numbers of A and B groups, with none of either lost in nonpolymer reactions.

From row 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 for extents of reaction 0.950, 0.990, and 0.995, respectively. 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.

2.2.3 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 reemphasize one premise that underlies the entire discussion of Table 2.1: How do the chemical reactivities 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 row. 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 that 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 that 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

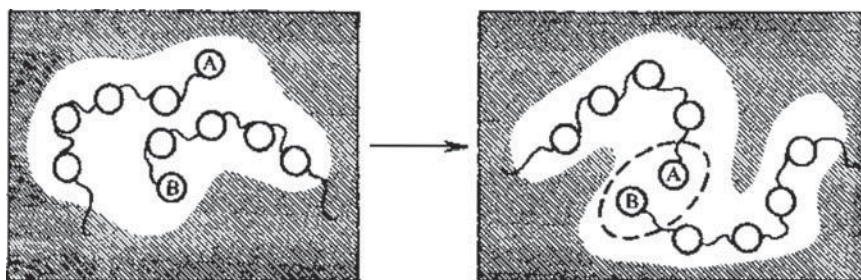


Figure 2.1 The reaction of A and B groups at the ends of two different chains. Note that rotations around only a few bonds will bring A and B into the same cage of neighboring groups, indicated by the dashed-line enclosure.

generalized to polymerization reactions as well. The latter are subject to several complications that 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 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:



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 that 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 $\text{Rate} = k[X]^1[Y]^2$, 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 that, 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

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

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:

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

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 Equation 2.2.6 becomes

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

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

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

We shall return to this type of kinetic analysis in Chapter 3 where we discuss chain-growth polymerization.

According to the mechanism provided by Reaction (2.F) and the analysis given by Equation 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.
2. The three constants associated with the rates of the individual steps in Reaction (2.F).

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

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

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 mechanism in Reaction (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 $k_r \gg k_i, k_o$, then Equation 2.2.8 reduces to

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

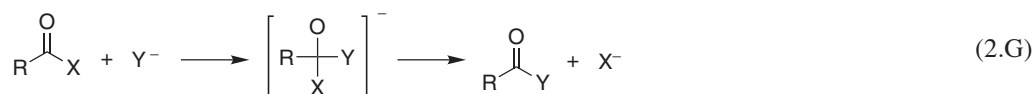
Note that the rate law in this case depends only on k_i and any size dependence for this constant would not cancel out.

Both Equation 2.2.9 and Equation 2.2.10 predict rate laws that 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 Equation 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 consider the experimental side of condensation kinetics. The kinds of ab links that have been most extensively studied are ester and amide groups, although numerous additional systems could also be cited. In many of these systems the carbonyl group is present and 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:



in which the intermediate is stabilized by coordination with protons, metal ions, or other Lewis acids. The importance 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 rate of a reaction, so we must be attentive to the situation with respect to catalysts. At 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

$$-\frac{d[A]}{dt} = k_c [A][B] \quad (2.3.1)$$

which is consistent with both Equation 2.2.9 and Equation 2.2.10. We expect the constant k_c to be dependent on the concentration of the catalyst in some way which means that Equation 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.

2.3.1 Catalyzed Step-Growth Reactions

Equation 2.3.1 is the differential form of the rate law that describes the rate at which A groups are used up. To test a proposed rate law and evaluate the rate constant it is preferable to work with the integrated form of the rate law. The integration of Equation 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 $[A]_0$ and $[B]_0$ as the concentrations of these groups at $t=0$.
2. If $[A]_0 = [B]_0$, the integration of Equation 2.3.1 yields

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_c t \quad (2.3.2)$$

3. If $[A]_0 \neq [B]_0$, the integration yields

$$\frac{1}{[A]_0 - [B]_0} \ln \left(\frac{[A][B]_0}{[A]_0[B]} \right) = k_c t \quad (2.3.3)$$

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

Example 2.1

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

Solution

Neither $[A]_0$ nor $[B]_0$ are functions of t , although both $[A]$ and $[B]$ are. We write the latter two as $[A] = [A]_0 - x$ and $[B] = [B]_0 - x$. Substitute these results into Equation 2.3.3 and rearrange:

$$\ln \frac{[A]_0 - x}{[B]_0 - x} + \ln \frac{[B]_0}{[A]_0} = ([A]_0 - [B]_0) k_c t$$

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

$$\left(\frac{[B]_0 - x}{[A]_0 - x} \right) \left(\frac{-([B]_0 - x) + ([A]_0 - x)}{([B]_0 - x)^2} \right) \frac{dx}{dt} = ([A]_0 - [B]_0) k_c$$

that after cancellation and rearrangement gives

$$\frac{dx}{dt} = k_c ([A]_0 - x)([B]_0 - x) = k_c [A][B]$$

Since $d[A]/dt = -dx/dt$ by the definition of x , this proves Equation 2.3.3 to be a solution to Equation 2.3.1. Equation 2.3.3 is undefined in the event $[A]_0 = [B]_0$, but in this case the expression is anyhow inapplicable. 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, Equation 2.3.1 would reduce to a simpler second-order rate law, which integrates to Equation 2.3.2.

We shall now proceed on the assumption that $[A]_0$ and $[B]_0$ are equal. As noted above, having both reactive groups on the same molecule is one way of enforcing this condition. Accordingly, we

rearrange Equation 2.3.2 to give the instantaneous concentrations of unreacted A groups as a function of time:

$$[A] = \frac{[A]_0}{1 + k_c[A]_0 t} \quad (2.3.4)$$

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

$$1 - p = \frac{1}{1 + k_c[A]_0 t} \quad (2.3.5)$$

or

$$\frac{1}{1 - p} = N_n = 1 + k_c[A]_0 t \quad (2.3.6)$$

where we incorporated Equation 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; Equation 2.3.6 describes how the number average degree of polymerization increases linearly with time.

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, catalyzed by *p*-toluene sulfonic acid. The reaction had already been run to consume 82% of the reactive groups before this experiment was conducted. Interpreting the slope of the line in terms of Equation 2.3.6 and in the light of actual initial concentrations gives a value of $k_c = 0.097 \text{ kg eq}^{-1} \text{ min}^{-1}$. Note that

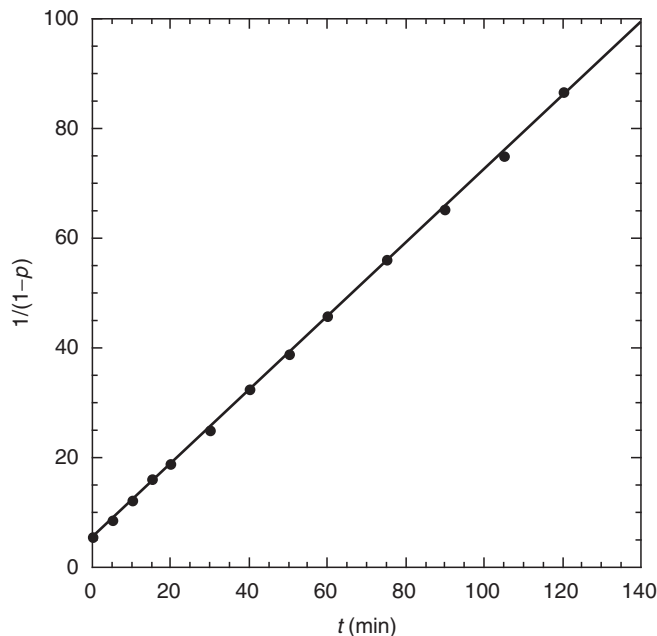


Figure 2.2 Plot of $1/(1-p)$ versus time for the late stages of esterification of adipic acid with 1,10-decamethylene glycol at 161°C , catalyzed by *p*-toluene sulfonic acid. The reaction time $t = 0$ corresponds to a previous extent of reaction in which 82% of the COOH groups had been consumed. (Data from Hamann, S.D., Solomon, D.H., and Swift, J.D., *J. Macromol. Sci. Chem.*, A2, 153, 1968.)

these units imply group concentrations expressed as equivalents per kilogram. Mass rather than volume units are often used for concentration, as substantial volume changes may occur during polymerization.

2.3.2 How Should Experimental Data Be Compared with Theoretical Rate Laws?

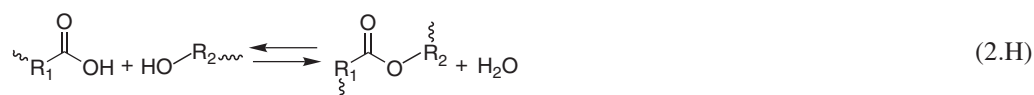
Although the results presented in Figure 2.2 appear to verify the predictions of Equation 2.3.6, this verification is not free from controversy. This controversy arises because various workers in this field employ different criteria in evaluating the success of the relationships we have presented in 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* that 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 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 on 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 of reactions as well. Unfortunately, this is not the case in all of the systems that have been investigated. Ref. [2], for example, shows one particular set of data—adipic acid and diethylene glycol at 166°C, similar reactants 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 interpreted differently by the two 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, as 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. Calculation from the 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 timescale has thus been shifted to pick up the analysis of the reaction at this point.

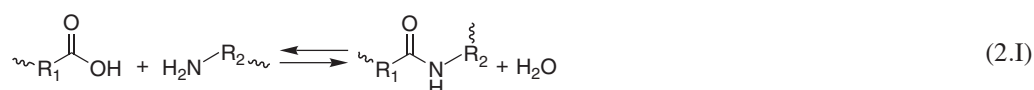
We commented above that the deviations at the beginning or the end of kinetic experiments can be rationalized, although the different schools of thought would disagree as to what constitutes “beginning” and “end.” Now that we have settled upon the polymer range, let us consider specifically why deviations 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 that 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 that have been most widely studied are simple condensation products such as polyesters and polyamides. Although we shall take up these classes of polymers—polyesters and polyamides—specifically in Section 2.5 and Section 2.6, respectively, it is appropriate to mention here that these are typically equilibrium reactions.



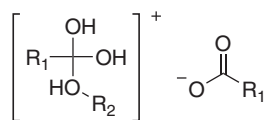
and



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 that are carried out to large values of p .

2.3.3 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 a 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,



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

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

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 Equation 2.3.1 for the catalyzed reaction. Equation 2.3.7 is readily integrated when $[A]_0 = [B]_0$, in which case it becomes

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

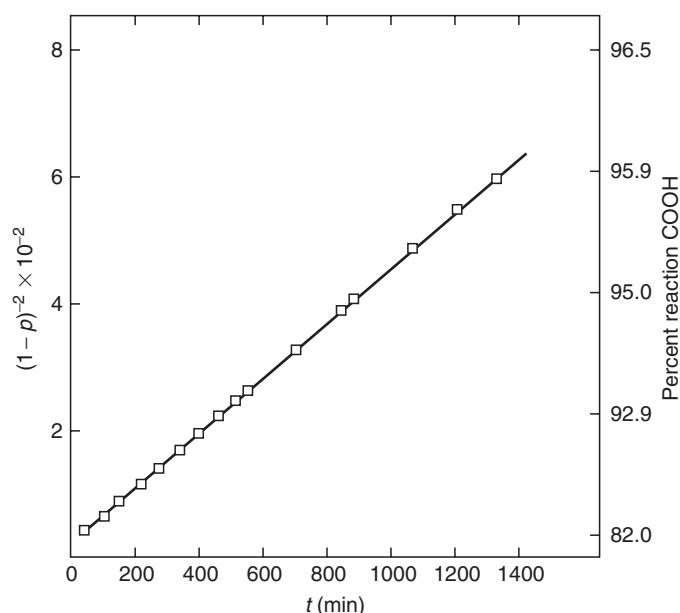


Figure 2.3 Plot of $1/(1-p)^2$ (left ordinate) and p (right ordinate) versus time for an uncatalyzed esterification. (Data from Hamann, S.D., Solomon, D.H., and Swift, J.D., *J. Macromol. Sci. Chem.*, A2, 153, 1968.)

This integrates to

$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2k_u t \quad (2.3.9)$$

Thus for the uncatalyzed reaction, we have the following:

1. The rate law is third order.
2. Since $[A]/[A]_0 = 1-p$, Equation 2.3.9 may be rewritten as

$$\frac{1}{(1-p)^2} = 1 + 2k_u [A]_0^2 t \quad (2.3.10)$$

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

3. Since $[A]/[A]_0 = 1/N_n$, Equation 2.3.10 becomes

$$N_n^2 = 1 + 2k_u [A]_0^2 t \quad (2.3.11)$$

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 Equation 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 $4.3 \times 10^{-3} \text{ kg}^2 \text{ eq}^{-2} \text{ min}^{-1}$ at 161°C.

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

Example 2.2

Assuming that $k_c = 10^{-1} \text{ kg eq}^{-1} \text{ min}^{-1}$, $k_u = 10^{-3} \text{ kg}^2 \text{ eq}^{-2} \text{ min}^{-1}$, and $[A]_0 = 10 \text{ eq kg}^{-1}$, calculate the time required for p to reach values 0.2, 0.4, 0.6, and so on, for both catalyzed and

uncatalyzed polymerizations, assuming that Equation 2.3.2 and Equation 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 $[A]/[A]_0$ for specific values of p , it is convenient to summarize the following relationships:

1. Equation 2.2.4: $N_n = 1/(1-p)$.
2. Equation 2.2.2: $[A]/[A]_0 = 1-p$.
3. Equation 2.3.6: $t = (N_n - 1)/k_c[A]_0 = N_n - 1$ if catalyzed, since $10^{-1}(10) = 1$.
4. Equation 2.3.11: $t = (N_n^2 - 1)/2 k_u[A]_0^2 = (N_n^2 - 1)(5)$ if uncatalyzed, since $2(10^{-3})(10)^2 = 0.2$.

Using these relationships, the accompanying table is developed.

p	$[A]/[A]_0$	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.

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 that 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 $Ababa \dots abaB$ 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

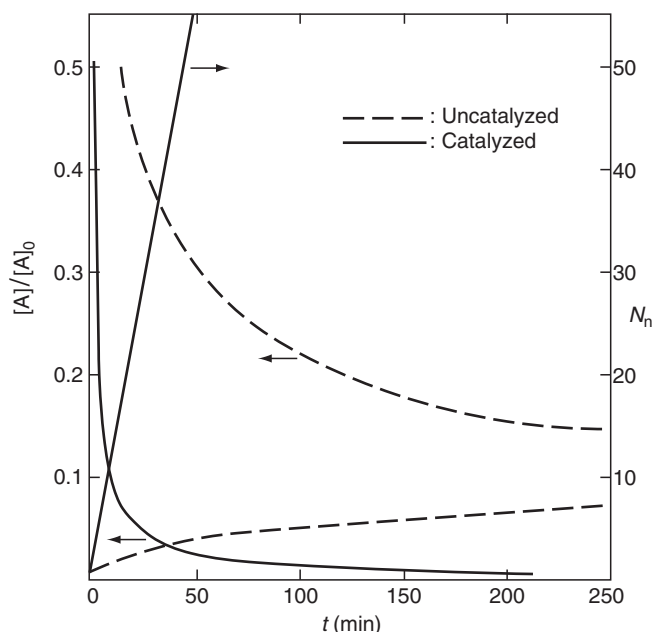


Figure 2.4 Comparison of catalyzed (solid lines) and uncatalyzed (dashed lines) polymerizations using results calculated in Example 2.2. Here $1-p$ (left ordinate) and N_n (right ordinate) are plotted versus time.

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 that have reacted to become a's is given by p , and the fraction that remains as A's is given by $1-p$. In these expressions p is the same extent of reaction defined by Equation 2.2.3.

2.4.1 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

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

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 (see 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 :

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

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, $m = (1-p) [A]_0$, since each molecule in the mixture contains one unreacted A group. Incorporating this result into Equation 2.4.2 yields

$$n_i = p^{i-1}(1-p)^2 m_0 \quad (2.4.3)$$

where m_0 is the total number of monomers present initially; $m_0 = [A]_0$ 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_0 . 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:

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 Section 1.7. It is given by the sum of all possible i values, with each multiplied by its appropriate weighting factor provided by Equation 2.4.1:

$$N_n = \sum_{i=1}^{m_0} i x_i(p) = \sum_{i=1}^{\infty} i p^{i-1} (1-p) \quad (2.4.4)$$

Note that the upper limit of the second summation has been shifted from m_0 to ∞ for mathematical reasons, namely that the answer is simple and known (see Appendix). The change is of little practical significance, since Equation 2.4.1 drops off for very large values of i . In particular, the result derived in the Appendix is

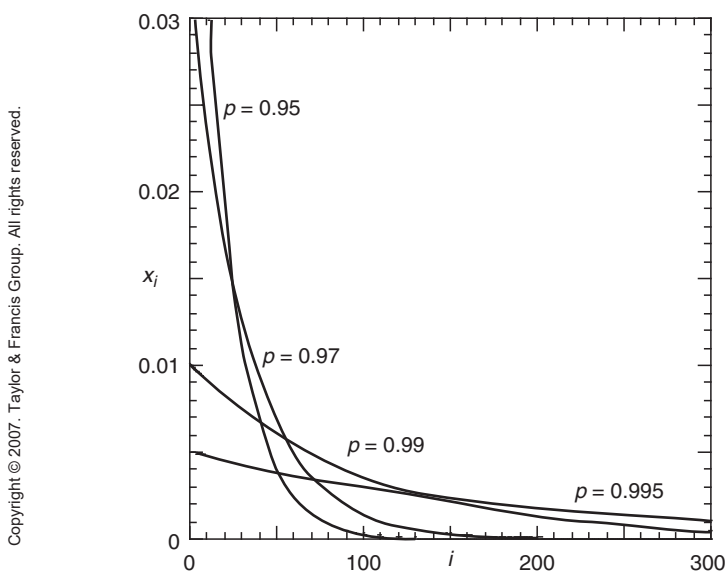


Figure 2.5 Mole fraction of i -mer as a function of i for several values of p .

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

Simplification of the summation in Equation 2.4.4 thus yields

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

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

2.4.2 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 $i n_i M_0$, where M_0 is the molecular weight of the repeat unit; the latter is given by $m_0 M_0$. Therefore we write

$$w_i = \frac{i n_i}{m_0} \quad (2.4.6)$$

into which Equation 2.4.3 may be substituted to give

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

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:

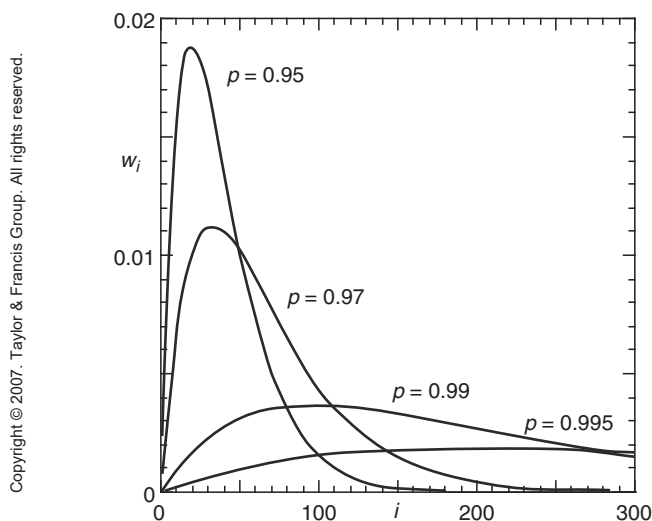


Figure 2.6 Weight fraction of i -mer as a function of i for several values of p .

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 Equation 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 .
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:

$$N_w = \frac{\sum_{i=1}^{m_0} i w_i}{\sum_{i=1}^{m_0} w_i} = \frac{\sum_{i=1}^{\infty} i^2 p^{i-1} (1-p)^2}{\sum_{i=1}^{\infty} i p^{i-1} (1-p)^2} \quad (2.4.8)$$

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 Equation 2.4.8 gives

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

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:

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

where the ratio of Equation 2.4.9 to Equation 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

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

of the most probable distribution. In light of Equation 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 Equation 2.3.5 and Equation 2.3.11 give p as a function of time for the catalyzed and uncatalyzed polymerizations, respectively, 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. In Section 2.7, we shall extend the arguments of this section to conditions in which $[A] \neq [B]$. In the meanwhile, we interrupt this line of reasoning by considering a few particular 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 that still need clarification. We anticipate some of the latter points by noting the following:

1. When $[A] \neq [B]$, both ends of the growing chain tend to be terminated by the group that 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.

Polyesters and polyamides are two of the most-studied step-growth polymers, as well as substances of great commercial importance. We shall consider polyesters in Section 2.5 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

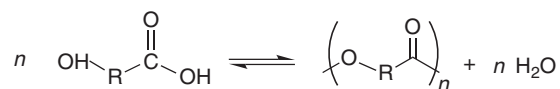
Several other chemical reactions are also widely used for the synthesis of these polymers. This list enumerates some of the possibilities, and Table 2.3 illustrates these reactions by schematic chemical equations.

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

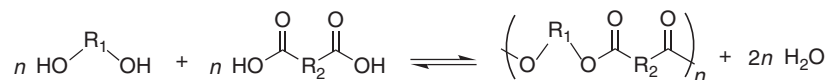
We have not attempted to indicate the conditions of temperature, catalyst, solvent, and so on, for these various reactions. For this type of information, references that deal specifically with synthetic polymer chemistry should be consulted. In the next few paragraphs we shall comment on the various routes to polyester formation in the order summarized above and followed in Table 2.3. The studies summarized in Figure 2.2 and Figure 2.3 are examples of Reaction 2 in Table 2.3.

Table 2.3 Some Schematic Reactions for the Formation of Polyesters

1. Esterification of a hydroxycarboxylic acid:



2. Esterification of diacid and diol:



3. Ester interchange with alcohol:



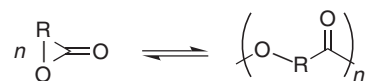
4. Ester interchange with ester ("transesterification"):



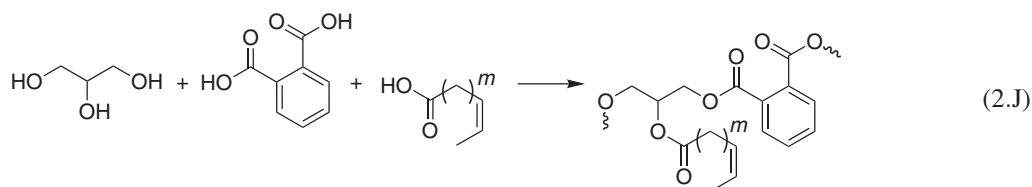
5. Esterification of acid chlorides (Schotten–Baumann reaction):



6. Lactone polymerization:



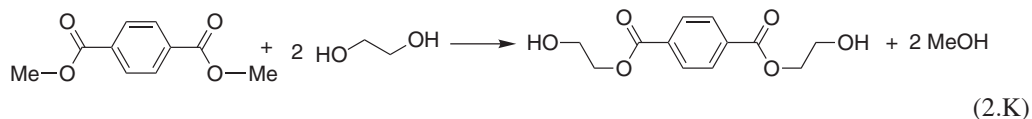
While up to now we have emphasized bifunctional reactants, both monofunctional compounds and monomers with functionality greater than 2 are present in some polymerization processes, either intentionally or adventitiously. The effect of the monofunctional reactant is clearly to limit chain growth. As 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:



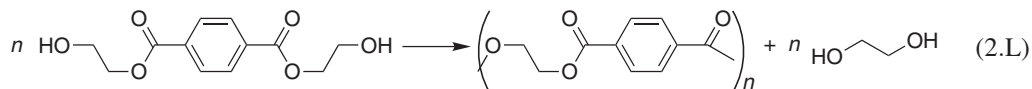
The presence of the unsaturated substituent along this polyester backbone gives this polymer cross-linking possibilities through a secondary reaction of the double bond. These polymers are used in paints, varnishes, and lacquers, where the ultimate cross-linked product results from the oxidation of the 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 cross-links 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 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.



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.



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 2.3 (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 and 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:

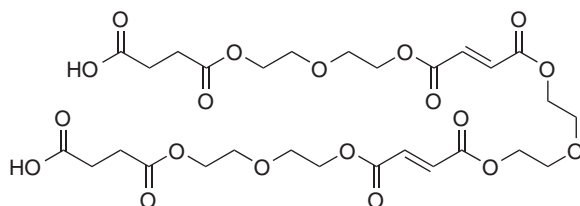
		Endene	Centrene
Step 1:	8 h at about 150°C–200°C		
	Maleic anhydride (mol)	0	2.0
	Succinic anhydride (mol)	2.0	0
	Diethylene glycol (mol)	3.0	3.0
Step 2:	About 1/2 h at about 120°C–130°C		
	Maleic anhydride (mol)	2.0	0
	Succinic anhydride (mol)	0	2.0
	Catalyst	0	0
Step 3:	30% Styrene + catalyst		
	16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

On the basis of these facts, do the following:

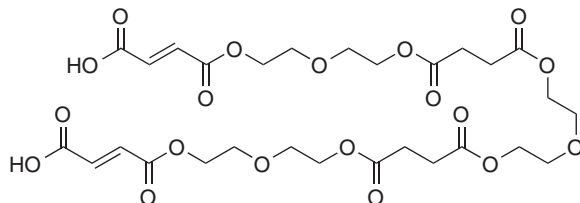
1. Comment on the likelihood that the comonomers are segregated as the names of these polymers suggest.
2. Sketch the structure of the average endene and centrene molecules.
3. Comment on the results in terms of the initial hypothesis.

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



Centrene



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 and Chapter 12.

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 Section 2.6, 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

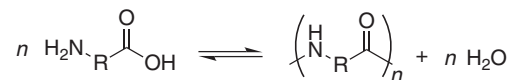
The discussion of polyamides parallels that of polyesters in many ways. To begin with, polyamides may be formed from an AB monomer, in this case amino acids:

1. Amidation of amino acids

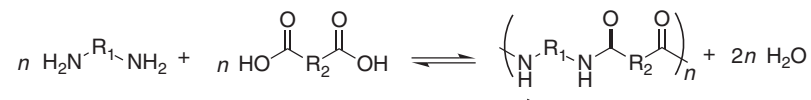
Additional synthetic routes that closely resemble polyesters are also available. Several more of these are listed below and are illustrated by schematic reactions in Table 2.4:

Table 2.4 Some Schematic Reactions for the Formation of Polyamides

1. Amidation of amino acids:



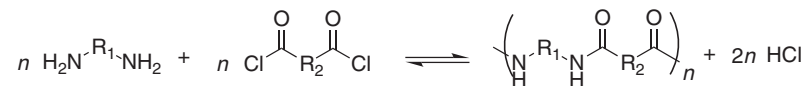
2. Amidation of diamine and diacid:



3. Interchange reactions:



4. Amidation of acid chlorides:



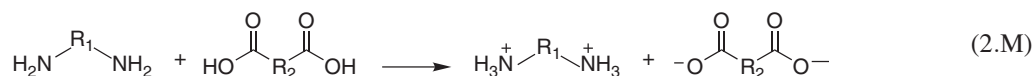
5. Lactam polymerization:



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

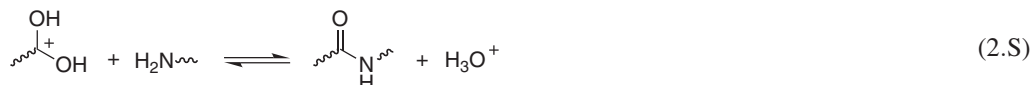
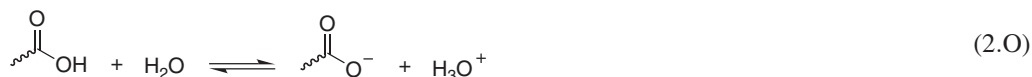
We only need to recall the trade name of synthetic polyamides, nylon, to recognize the importance of these polymers and the reactions employed to prepare them. Recall the system for naming these compounds (see Section 1.5): the first number after the name gives the number of carbon atoms in the diamine, 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, solution, and 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:



This compound is sometimes called a nylon salt. The salt $\rightleftharpoons$ 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. Also in contrast to polyesters, Reaction 1 and Reaction 2 in Table 2.4 can be conducted rapidly without an acid catalyst.

The 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:



Reaction (2.N) describes the nylon salt $\rightleftharpoons$ nylon equilibrium. Reaction (2.O) and Reaction (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, Reaction (2.R) and Reaction (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 1 atm is 0.15%. Likewise, the various ionic possibilities mean that at both high and low pH values the concentration of unionized 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.

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

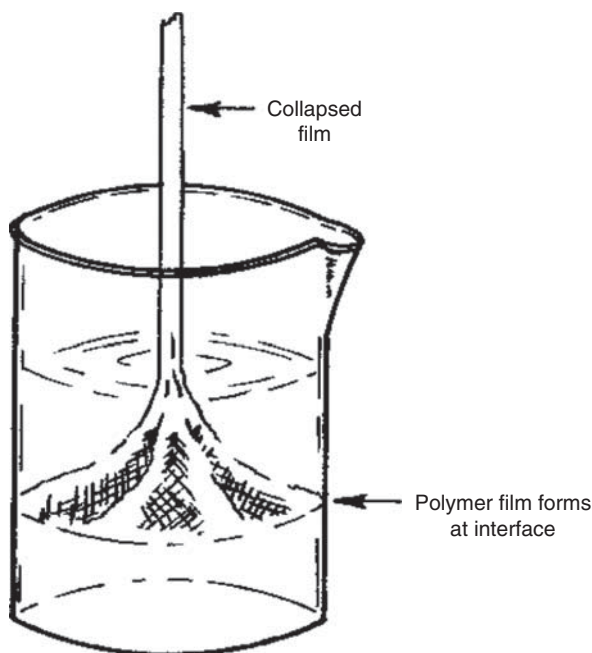


Figure 2.7 Sketch of an interfacial polymerization with the collapsed polymer film being withdrawn from the surface between the immiscible phases. (From Morgan, P.W. and Kwolek, S.L. *J. Chem. Educ.*, 36, 182, 1959. With permission.)

different than the bulk mechanism that 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:



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 section and Section 2.5 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 viewpoints. 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—the polymerization of reactants in which a stoichiometric imbalance exists in the numbers of reactive groups A and B. In earlier 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 effect 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 that 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

$$r \equiv \frac{\nu_A^o}{\nu_B^o} \quad (2.7.1)$$

By definition of the problem, this ratio cannot exceed unity.

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 $p\nu_A^0$, which in turn equals $pr\nu_B^0$. 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

$$\nu_A = (1 - p)\nu_A^0 \quad (2.7.2)$$

and

$$\nu_B = (1 - pr)\nu_B^0 = (1 - pr)\frac{\nu_A^0}{r} \quad (2.7.3)$$

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

$$\nu_{\text{ends}} = \left(1 - p + \frac{1 - pr}{r}\right)\nu_A^0 \quad (2.7.4)$$

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

$$\nu_{\text{chains}} = \frac{1}{2} \left(1 + \frac{1}{r} - 2p\right)\nu_A^0 \quad (2.7.5)$$

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

$$\nu_{\text{repeat units}} = \frac{1}{2}\nu_A^0 + \frac{1}{2}\nu_B^0 = \frac{1}{2} \left(1 + \frac{1}{r}\right)\nu_A^0 \quad (2.7.6)$$

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

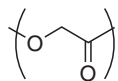
$$N_n = \frac{1 + 1/r}{1 + 1/r - 2p} = \frac{1 + r}{1 + r - 2pr} \quad (2.7.7)$$

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

One distinction that should be pointed out involves the comparison of Equation 2.2.1 and Equation 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 + bb units. *The number of aa + 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



- and $M_0 = 58$. Neglecting end groups, we have $M_n = 58 N_n$ with N_n given by Equation 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_0 value of 200. If Equation 2.2.4 is used to evaluate N_n , it gives the number of aa + 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 Equation 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:

$$r' = \frac{\nu_A^0}{\nu_B^0 + 2\nu_{B'}^0}, \quad (2.7.8)$$

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, Equation 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.

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: the closer each of these fractions is to unity, higher degrees of polymerization are obtained. Table 2.5 shows some values of N_n calculated from Equation 2.7.7 for several combinations of (larger values of) r and p . Inspection of Table 2.5 reveals the following:

Table 2.5 Some Values of N_n Calculated by Equation 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	∞

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 $p = 1$; Equation 2.7.7 then becomes

$$N_n = \frac{1+r}{1-r} \quad (2.7.9)$$

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 Equation 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 Equation 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 $\nu_A^0 = 0.995$ mol; therefore $r = 0.995/1.00 = 0.995$. We use Equation 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 $M_n = 44.5 \times 100 = 4450 \text{ g mol}^{-1}$.

3. The effect of the lost hydroxyl groups can be offset by carrying out the polymerization to a higher extent of reaction. We use Equation 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

$1.980 = \nu_B$. We use Equation 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.

2.8 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, that is, 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_i 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.

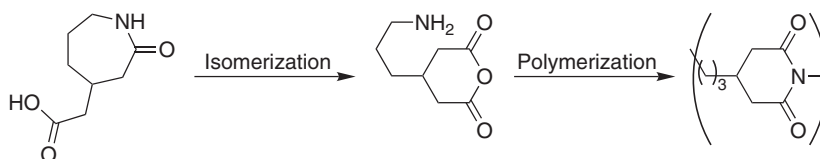
Problems

1. Howard describes a model system used to test the molecular weight distribution of a condensation polymer.[†] "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

[†] G.J. Howard, *J. Polym. Sci.*, 37, 310 (1959).

polymerization is, therefore, 110 and the conversion degree (= extent of reaction) = 0.9909.” Verify the self-consistency of those numbers.

- Haward et al. have reported some research in which a copolymer of styrene and hydroxyethylmethacrylate was cross-linked by hexamethylene di-isocyanate.[†] 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 cross-linking reaction is carried out in sufficiently dilute solutions of copolymer that the cross-linking is primarily intramolecular rather than intermolecular. Explain the distinction between these two terms and why concentration affects the relative amounts of each.
- The polymerization of β -carboxymethyl caprolactam has been observed to consist of initial isomerization via a second-order kinetic process followed by condensation of the isomer to polymer:



The rates of polymerization are thus of first order in ν_{NH_2} and in $\nu_{(\text{CO})_2\text{O}}$ or second order overall. Since $\nu_{\text{NH}_2} = \nu_{(\text{CO})_2\text{O}}$, the 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 times. The following data were obtained at 270°C; the early part of the experiment gives nonlinear results.[‡] 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	0.015
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		

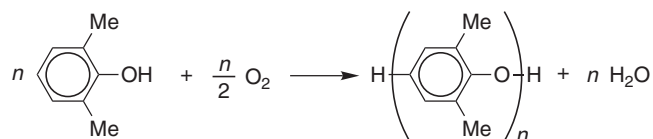
- Examination of Figure 2.5 shows that N_i/N is greater for $i=40$ at $p=0.97$ than at either $p=0.95$ or $p=0.99$. This is generally true: various i -mers go through a maximum in numerical abundance as p increases. Show that the extent of reaction at which this maximum occurs varies with i as follows: $p_{\text{max}} = (i-1)/i$. 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 $k_c = 2.47 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ at 160.5°C for the polymerization of 12-hydroxystearic acid,[§] calculate the time at which 15-mers show their maximum abundance if the initial concentration of monomer is 3.0 M.

[†]R.N. Haward, B.M. Parker, and E.F.T. White, *Adv. Chem.*, 91, 498 (1969).

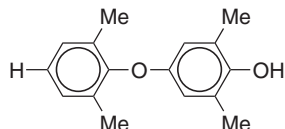
[‡]H.K. Reimschuessel, *Adv. Chem.*, 91, 717 (1969).

[§]C.E.H. Bawn and M.B. Huglin, *Polymer*, 3, 257 (1962).

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:[†]

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 O₂ absorbed as the x -axis. Evaluate w_i by Equation 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 the 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 of 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.[‡] The results obtained are given below. Evaluate N_w from these data, then use Equation 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

[†] G.D. Cooper and A. Katchman, *Adv. Chem.*, 91, 660 (1969).

[‡] G.B. Taylor, *J. Am. Chem. Soc.*, 69, 638 (1947).

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.[†] The following observations describe the chromatograms after the indicated times of heating:

0 h—two spots with R_f values of individual polymers.

1/4 h—two distinct spots, but closer together than those of 0 h.

1/2 h—spots are linked together.

3/4 h—one long, diffuse spot.

1 1/2 h—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 H₂O per mole caprolactam.[‡] 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 h at 225°C in sealed tubes containing various amounts of water. M_n and M_w were measured for the

[†] C.W. Ayers, *J. Appl. Chem.*, 4, 444 (1954).

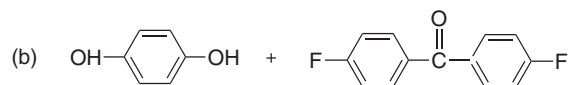
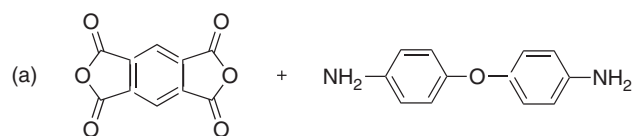
[‡] H.L. Reimschuessel and G.J. Dege, *J. Polym. Sci.*, A-1, 2343 (1971).

resulting mixture by osmometry (see Chapter 7) and light scattering (see Chapter 8), respectively, and the following results were obtained:

Moles H ₂ O ($\times 10^3$)/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 these 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 the 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 h.[†] Suppose an initially equimolar mixture of adipic acid and diol achieves a value of $p = 0.990$ after 1.5 h, 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 h was calculated by an appropriate kinetic equation.
12. Show the reaction sequence and the structure of the resulting polymer from the polycondensation of these two monomers; note that the reaction (a) has two distinct steps, and that (b) it is base-catalyzed.



13. A polyester is prepared under conditions of stoichiometric balance, but no attempt is made to remove water. Eventually, the reaction comes to equilibrium with equilibrium constant K . If $[\text{COOH}]_0$ is the initial concentration of carboxylic acid groups, show that the equilibrium water concentration is

$$[\text{H}_2\text{O}] = K \frac{[\text{COOH}]_0}{N_n(N_n - 1)}$$

14. For the most probable distribution, it is clear that there is always more i -mer present than $(i+1)$ -mer, at any $0 < p < 1$. However, the absolute amount of an i -mer should go through a maximum with time, as the reaction progresses; there is zero to start, but at late enough stages i -mer will have mostly reacted to contribute to all the larger species. Use the chain rule and any

[†] V.V. Korshak and S.V. Vinogradova, *Polyesters*, Pergamon, Oxford, 1965.

suitable simplifications ($k[A]_0 t \gg 1$) to find the degrees of conversion at which the mole fraction and the absolute concentration of i -mer have their maximum in time. Compare this to the number average degree of polymerization at the same conversion; does the answer make sense?

15. For the polymerization of succinic acid and 1,4-butanediol under stoichiometric balance in xylene:
 - (a) Draw the chemical structures of the reactants, products, and important intermediates for both the strong acid-catalyzed and self-catalyzed case.
 - (b) Generate a quantitative plot of N_n versus time for the self-catalyzed case up to 28,000 s, given $k = 6 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-2}$ and 3 mol L^{-1} starting concentration of each monomer. How many hours would it take to make a polymer with $N_n = 300$?
 - (c) Do the same for the catalyzed case, with $k = 6 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$ and the same starting concentration. How many hours would it take to make a polymer with $N_n = 300$?
 - (d) Qualitatively explain the origin of the different shapes of the curves in the two plots.
16. Hydrolysis of an aromatic polyamide with $M_n = 24,116$ gives 39.31% by weight m -aminoaniline, 59.81% terephthalic acid, and 0.88% benzoic acid. Draw the repeat unit structure of the polymer. Calculate the degree of polymerization and the extent of reaction. Calculate what the degree of polymerization would have been if the amount of benzoic acid were doubled.
17. Calculate the feed ratio of adipic acid and hexamethylene diamine necessary to achieve a molecular weight of approximately 10,000 at 99.5% conversion. What would the identity of the end groups be in the resulting polymer?

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

Further Readings

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10

Networks, Gels, and Rubber Elasticity

10.1 Formation of Networks by Random Cross-Linking

In this chapter we consider one of the three general classes of polymers in the solid state: infinite networks. The other two categories, glassy polymers and semicrystalline polymers, will be taken up in Chapter 12 and Chapter 13, respectively. We will shortly define the term network more precisely, but we have in mind a material in which covalent bonds (or other strong associations) link different chain molecules together to produce a single molecule of effectively infinite molecular weight. These linkages prevent flow and thus the material is a solid. There are two important subclasses of network materials: elastomers and thermosets. An *elastomer* is a cross-linked polymer that undergoes the glass transition well below room temperature; consequently, the solid is quite soft and deformable. The quintessential everyday example is a rubber band. Such materials are usually made by cross-linking after polymerization. A *thermoset* is a polymer in which multifunctional monomers are polymerized or copolymerized to form a relatively rigid solid; an epoxy adhesive is a common example. In this chapter we will consider both elastomers and thermosets, but with an emphasis on the former. The reasons for this emphasis are that the phenomenon of rubber elasticity is unique to polymers and that it is an essential ingredient in understanding both the viscoelasticity of polymer liquids (see Chapter 11) and the swelling of single chains in a good solvent (see Chapter 7). In the first two sections we examine the two general routes to chemical formation of networks: cross-linking of preformed chains and polymerization with multifunctional monomers. In Section 10.3 through Section 10.6 we describe successively elastic deformations, thermodynamics of elasticity, the “ideal” molecular description of rubber elasticity, and then extensions to the idealized theory. In Section 10.7, we consider the swelling of polymer networks with solvent.

10.1.1 Definitions

Figure 10.1 provides a pictorial representation of a network polymer. In panel (a), there is a schematic representation of a collection of polymer chains, which could be either in solution or in the melt. In panel (b), a certain number of chemical linkages have been introduced between monomers on different chains (or on the same chain). If enough such *cross-links* are created, it becomes possible to start at one surface of the material and trace a course to the far side of the material by passing only along the covalent bonds of chain backbones or cross-links. In such a case an infinite *network* is formed, and we can say that the covalent structure *percolates* through the material. The network consists of the following elements, as illustrated in Figure 10.2:

1. *Strand*. A strand is a section of polymer chain that begins at one junction and ends at another without any intervening junctions.
2. *Junction*. A junction is a cross-link from which three or more strands emanate. The *functionality* of the junction is the number of strands that are connected; in the case of the random cross-linking pictured in Figure 10.1 the functionality is usually four. Note that a cross-link might simply connect two chains, but it would not be a junction until it becomes part of an infinite network.

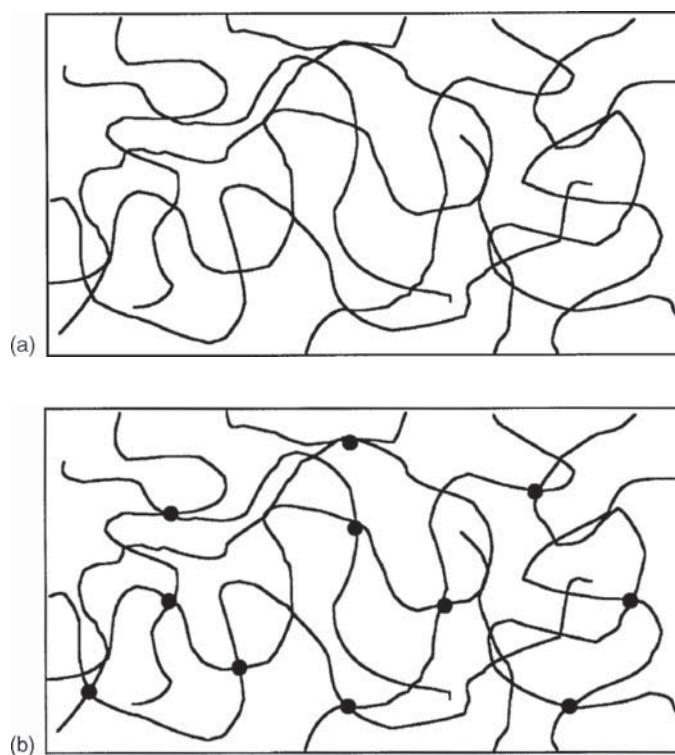


Figure 10.1 Schematic illustration of (a) an uncross-linked melt or concentrated solution of flexible chains and (b) the same material after cross-links are introduced.

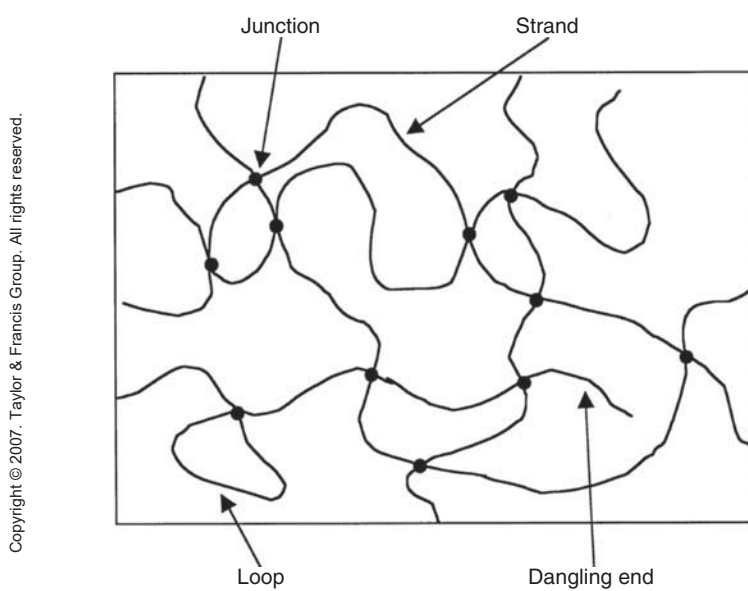


Figure 10.2 Schematic illustration of network elements defined in the text.

3. *Dangling end*. The section of the original polymer chain that begins at one chain terminus and continues to the first junction forms a dangling end. Because it is free to relax its conformation over time, it does not contribute to the equilibrium elasticity of the network, and as such it can be viewed as a defect in the structure.
4. *Loop*. Another defect is a loop, a section of chain that begins and ends at the same cross-link, with no intervening junctions. A loop might be formed by an intramolecular cross-linking reaction. Again, as with the dangling end, the loop can relax its conformation (at least in part) and is thus not fully elastically active.
5. *Sol fraction*. It is not necessary that every original polymer chain be linked into the network; a given chain may have no cross-links or it may be linked to a finite number of other chains to form a *cluster*. In either case, if the material were placed in a large reservoir of a good solvent the *sol fraction* could dissolve, whereas the network or *gel fraction* could not. Thus the sol fraction contains all the extractable material, including any solvent present.

The apparently synonymous terms network, infinite network, and gel have all appeared so far and it is time to say how we will use these terms from now on. We have used network and infinite network interchangeably; the modifier *infinite* just serves to emphasize that the structure percolates throughout a macroscopic sample and from now on we will omit it. The term *gel* is somewhat more problematic, as it is used by different workers in rather disparate ways. We will henceforth use it to refer to a material that contains a network, whereas the term network refers to the topology of the underlying molecular structure. Often, an elastomeric material containing little or no sol fraction is called a *rubber*, whereas a material containing an equivalent network structure plus a significant amount of solvent or low-molecular-weight diluent would be called a gel.

10.1.2 Gel Point

We now consider the following question: given a collection of polymer chains, how many random cross-links need to be introduced before a network will be formed? For simplicity, assume that all chains have the same degree of polymerization N , and that all monomers are equally likely to react. We will give examples of cross-linking chemistry in a moment, but for now we assume we can measure the extent of reaction, p , defined as the fraction of monomers that participate in cross-links. Suppose we start on a chain selected at random and find a cross-link; we now use it to cross over to the next chain. What is the probability that, as we move along the second chain, we will find a second cross-link? It is simply given by $(N-1)p \approx Np$. The probability of being able to hop from chain to chain x times in succession is therefore $(Np)^x$. (Recall that the probability of a series of independent events is given by the product of the individual probabilities.) For a network to be formed, we need this probability to be ≥ 1 as $x \rightarrow \infty$, and therefore we need $Np \geq 1$. Conversely, if $Np < 1$, $(Np)^x \rightarrow 0$ as $x \rightarrow \infty$. Consequently, the critical extent of reaction, p_c , at which an infinite network first appears, the *gel point*, is given by

$$p_c = \frac{1}{N-1} \approx \frac{1}{N} \quad (10.1.1)$$

This beautifully simple result indicates how effective polymers can be at forming networks; a polymer with $N \approx 1000$ only needs an average of 0.1% of the monomers to react to reach the gel point. Note that Equation 10.1.1 probably underestimates the true gel point because some fraction of cross-linking reactions will result in the formation of loops, which will not contribute to network formation.

Any real polymer will be polydisperse, so we should consider how this affects Equation 10.1.1. Let us return to our first chain, find the cross-link, and then ask, what is the average length of the next chain? As the cross-linking reaction was assumed to be random, then the chance that the next chain has degree of polymerization N_i is given by the weight fraction of N_i -mers, w_i . In other words, the probability that the neighboring monomer that forms the cross-link belongs to a chain of length N_i is proportional to N_i . (To see this argument, consider a trivial example: the sample

contains 1 mole of chains of length 100 and 1 mole of chains of length 200. Any monomer selected at random has a probability of 2/3 to be in a chain of length 200, and 1/3 to be in chain of length 100; 2/3 and 1/3 correspond to the weight fractions.) The critical probability therefore becomes

$$p_c = \frac{1}{\sum_{i=1}^{\infty} w_i (N_i - 1)} \approx \frac{1}{\sum_{i=1}^{\infty} w_i N_i} = \frac{1}{N_w} \quad (10.1.2)$$

and thus the critical extent of reaction is determined by the weight-average degree of polymerization, N_w .

Examples of postpolymerization cross-linking reactions are many. Free-radical initiators such as peroxides (see Chapter 3) can be used to cross-link polymers with saturated structures (i.e., no carbon-carbon double bonds), such as polyethylene or poly(dimethylsiloxane). Alternatively, high-energy radiation can be utilized for the same purpose. A prime example occurs in integrated circuit fabrication, where electron beam or UV radiation can be used to cross-link a particular polymer (called a negative resist) in desired spatial patterns. The uncross-linked polymer is then washed away, exposing the underlying substrate for etching or deposition. (In contrast, some polymers such as poly(methyl methacrylate) degrade rapidly on exposure to high-energy radiation, thereby forming a positive resist.) Of course, the classic example of cross-linking is that of polydienes cross-linked in the presence of sulfur. The use of sulfur dates back to 1839 and the work of Goodyear in the United States [1] and Macintosh and Hancock in the UK. The polymer of choice was natural rubber, a material extracted from the sap of rubber trees; the major ingredient is *cis*-1,4 polyisoprene. This basic process remains the primary commercial route to rubber materials, especially in the production of tires, and the cross-linking of polydienes is generically referred to as *vulcanization*. Remarkably, perhaps, the detailed chemical mechanism of the process remains elusive. For some time a free-radical mechanism was suspected, but current thinking favors an ionic route, as shown in Figure 10.3. The process is thought to proceed through formation of a sulfonium ion, whereby the naturally occurring eight-membered sulfur ring, S_8 , becomes polarized or opened (Reaction A). The next stage is abstraction of an allylic hydrogen from a neighboring chain to generate a carbocation (Reaction B), which subsequently can react with sulfur and cross-link to another chain (Reaction C). A carbocation is regenerated, allowing propagation of the cross-linking process (Reaction D). Termination presumably involves sulfur anions. In practice, the rate of vulcanization is greatly enhanced by a combination of additives, called accelerators and activators. Again, the mechanisms at play are far from fully understood, although the technology for producing an array of rubber materials with tunable properties is highly developed.

Example 10.1

A sample of polyisoprene with $M_w = 150,000$ is vulcanized until 0.3% of the double bonds are consumed, as determined by spectroscopy. Do you expect this sample to have formed a network, and what is the probability of finding a polyisoprene chain that is untouched by the reaction?

Solution

The nominal monomer molecular weight for polyisoprene is 68 g/mol, so for this sample the critical extent of reaction estimated by Equation 10.1.2 is

$$p_c \approx \frac{1}{N_w} = \frac{68}{150,000} = 0.00045$$

This is a factor of 6.7 less than the stated value of $p = 0.003$, so we may be reasonably confident that the sample has passed the gel point.

For an individual chain to be untouched, every monomer must be unreacted. The probability for each monomer to be unreacted is $1 - p = 0.997$ and for a chain of N monomers

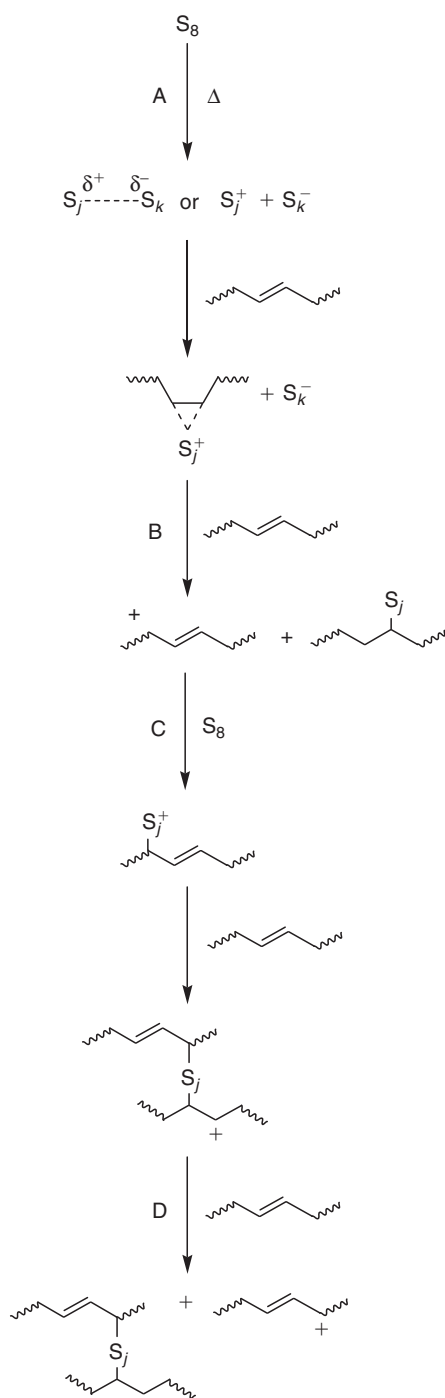


Figure 10.3 Possible mechanism for vulcanization of 1,4-polybutadiene with sulfur, following Odian. (From Odian, G., *Principles of Polymerization*, 2nd ed., Wiley, New York, 1981.)

we must raise 0.997 to the N th power. For simplicity, we assume all chains to have the same $N = 150,000/68 = 2200$; then $(0.997)^{2200} \approx 0.0013$ or there is about 0.1% chance that a chain is untouched.

10.2 Polymerization with Multifunctional Monomers

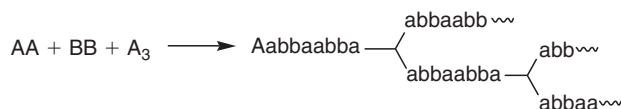
In this section we consider the other general approach to network formation or gelation, using polymerization of multifunctional monomers. Multifunctional, as noted in Chapter 2, means functionality greater than 2. We will build on the material in that chapter by considering step-growth or condensation polymerization of monomers containing A and B reactive groups. The resulting thermosets are widely used as engineering materials because their mechanical properties are largely unaffected by temperature variation.

For simplicity, we assume that the reaction mixture contains only A and B as reactive groups, but that either one (or both) of these is present (either totally or in part) in a molecule that contains more than two of the reactive groups. We use f to represent the number of reactive groups in a molecule when this quantity exceeds 2 and represent a multifunctional molecule as A_f or B_f . For example, if A were a hydroxyl group, a triol would correspond to $f=3$. Several reaction possibilities (all written for $f=3$) come to mind in the presence of multifunctional reactants, as shown in Figure 10.4. The lower case “a” and “b” refer to the corresponding groups that have reacted.

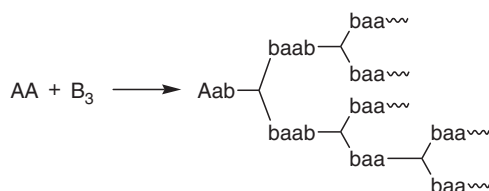
The third reaction is interesting inasmuch as either the AA or BB monomer must be present to produce cross-linking. Polymerization of AB with only A_f (or only B_f) introduces a single branch point, but no more, since all chain ends are unsuited for further incorporation of branch points. Including the AA or BB molecule reverses this. The bb unit that accomplishes this is underlined.

What we seek next is a quantitative relationship among the extent of the polymerization reaction, the composition of the monomer mixture, and the gel point. We shall base our discussion on the system described by the first reaction in Figure 10.4; other cases are derived by similar methods (see

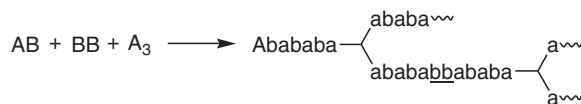
1. AA and BB plus either A_f or B_f :



2. AA and B_f or BB and A_f :



3. AB with either AA and B_f or BB and A_f :



4. A_f and B_f :

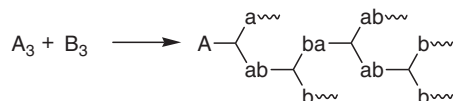


Figure 10.4 Possible reaction schemes for monomer mixtures containing A and B functional groups that can lead to network formation.

Problem 3). To further specify the system, we assume that A groups limit the reaction and that B groups are present in excess. Two parameters are necessary to characterize the reaction mixture:

1. The ratio of the initial number of A to B groups, ν_A^0/ν_B^0 , defines the factor r , as in Equation 2.7.1. The total number of A groups from both AA and A_f is included in this application of r .
2. The fraction of A groups present in multifunctional molecules is defined by the ratio

$$\rho = \frac{\nu_A(\text{from } A_f)}{\nu_A(\text{total})} \quad (10.2.1)$$

There are two additional useful parameters that characterize the reaction itself:

1. The extent of reaction p is based on the group present in limiting amount. For the system under consideration, p is therefore the fraction of A groups that have reacted. (Note that this p is slightly different from p in Section 10.1.)
2. The probability that a chain segment is capped at both ends by a branch unit is described by the *branching coefficient* α . The branching coefficient is central to the discussion of network formation, as the occurrence or nonoccurrence of gelation depends on what happens after capping a section of chain with a potential branch point.

10.2.1 Calculation of the Branching Coefficient

The methods we consider were initially developed by Stockmayer [2] and Flory [3] and have been applied to a wide variety of polymer systems and phenomena. Our approach proceeds through two stages: first we consider the probability that AA and BB polymerize until all chain segments are capped by an A_f monomer, and then we consider the probability that these are connected together to form a network. The actual molecular processes occur at random and not in this sequence, but mathematical analysis is more feasible if we consider the process in stages. As long as the same sort of structure results from both the random and the subdivided processes, this analysis is valid.

The arguments we employ are statistical, so we recall that the probability of a functional group reacting is given by the fraction of groups that have reacted at any point and that the probability of a sequence of events is the product of their individual probabilities (as used in developing Equation 10.1.1). As in Chapter 2 and Chapter 3, we continue to invoke the principle of equal reactivity, that is, that functional group activity is independent of the size of the molecule to which the group is attached. One additional facet of this assumption that enters when multifunctional monomers are considered is that all A groups in A_f are of equal reactivity.

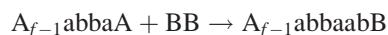
Now let us consider the probability that a section of polymer chain is capped at both ends by potential branch points:

1. The first step is the condensation of a BB monomer with one of the A groups of an A_f molecule: Since all A groups have the same reactivity by hypothesis, the probability of this occurrence is simply p .
2. The terminal B group reacts with an A group from AA rather than A_f :



The fraction of unreacted B groups is rp , so this gives the probability of reaction for B. Since ρ is the fraction of A groups on multifunctional monomers, rp must be multiplied by $1 - \rho$ to give the probability of B reacting with an AA monomer. The total probability for the chain shown is the product of the probabilities until now: $p[rp(1 - \rho)]$.

3. The terminal A groups react with another BB:



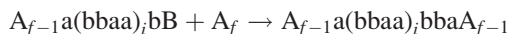
The probability of this step is again p , and the total probability is $p[rp(1 - \rho)p]$.

4. Additional AA and BB molecules condense into the chain to give a sequence of i bbaa units



We have just evaluated the probability of one such unit; the probability for a series of i units is just the product of the individual probabilities: $p[rp(1-\rho)p]^i$.

5. The terminal B groups react with an A group from a multifunctional monomer:



The probability of B reacting is rp and the fraction of these reactions that involve A_f molecules is $rp\rho$. The probability of the entire sequence is therefore $p[rp(1-\rho)p]^i rp\rho$.

6. In the general expression above, i can have any value from 0 to ∞ , so the probability for all possibilities is the sum of the individual probabilities. Note that a different procedure is used for compounding probabilities here: the sum instead of the product. This time we are interested in *either* $i=0$ *or* $i=1$ *or* $i=2$, and so forth, whereas previously we required the first A–B reaction *and* the second A–B reaction *and* the third A–B reaction, etc.

As the branching coefficient gives the probability of a chain segment being capped by potential branch points, the above development describes this situation:

$$\alpha = \sum_{i=0}^{\infty} rp^2 \rho [rp^2(1-\rho)]^i \quad (10.2.2)$$

The summation applies only to the quantity in brackets, since it alone involves i . Representing the bracketed quantity by Q , we note that $\sum_{i=0}^{\infty} Q^i = 1/(1-Q)$ (see Appendix) and therefore

$$\alpha = \frac{rp^2 \rho}{1 - rp^2(1-\rho)} \quad (10.2.3)$$

10.2.2 Gel Point

We have now completed the first (and harder) stage of the problem we set out to consider: we know the probability that a chain is capped at both ends by potential branch points. The second stage of the derivation considers the reaction between these chain ends via the remaining $f-1$ reactive A groups. (By hypothesis, the mixture contains an excess of B groups, so there are still unreacted BB monomers or other polymer chain segments with terminal B groups that can react with the A_{f-1} groups we have been considering.) By analogy with the discussion of the gel point in Section 10.1, we ask the question: if we choose an A_f group at random, and follow this chain to another A_f group, what is the probability that we can continue in this fashion forever? If this probability exceeds 1, we have a network, and the gel point corresponds to when it equals 1. The probability of there being a strand, that is, a chain segment between two junctions, is α . When we arrive at the next A_f , there are $f-1$ chances to connect to a new strand and the probability of there being a strand from any particular one of the $f-1$ groups is again α . Thus the total probability of keeping going from each A_f is just $(f-1)\alpha$. If we want to connect x strands in sequence, the probability that we can is $[(f-1)\alpha]^x$. Just as in the argument preceding Equation 10.1.1, therefore, the critical extent of reaction is simply given by

$$\alpha_c = \frac{1}{f-1} \quad (10.2.4)$$

which can be compared directly with Equation 10.1.1. Whenever the extent of reaction, p , is such that $\alpha > \alpha_c$, gelation is predicted to occur. Combining Equation 10.2.3 and Equation 10.2.4 and

rearranging gives the critical extent of reaction for gelation, p_c as a function of the properties of the monomer mixture r , ρ , and f :

$$p_c = \frac{1}{\sqrt{r + r\rho(f-2)}} \quad (10.2.5)$$

Corresponding equations for any of the reaction schemes depicted in Figure 10.4 can be derived in a similar fashion (see Problem 3 for an example).

Equation 10.2.5 is of considerable practical utility in view of the commercial importance of three-dimensional polymer networks. Some reactions of this sort are carried out on a very large scale: imagine the consequences of having a polymer preparation solidify in a large and expensive reaction vessel because the polymerization reaction went a little too far. Considering this kind of application, we might actually be relieved to know that Equation 10.2.5 errs in the direction of underestimating the extent of reaction at gelation. This comes about because some reactions of the multifunctional branch points result in intramolecular loops, which are wasted as far as network formation is concerned; the same comment applies to Equation 10.1.1. It is also not uncommon that the reactivity of the functional groups within one multifunctional monomer decreases with increasing p , which tends to favor the formation of linear structures over the branched ones.

As an example of the quantitative testing of Equation 10.2.5, consider the polymerization of diethylene glycol (BB) with adipic acid (AA) in the presence of 1,2,3-propane tricarboxylic acid (A_3). The critical value of the branching coefficient is 0.50 for this system by Equation 10.2.4. For an experiment in which $r = 0.800$ and $\rho = 0.375$, $p_c = 0.953$ by Equation 10.2.5. The critical extent of reaction was found experimentally to be 0.9907, determined in the polymerizing mixture as the point where bubbles fail to rise through it. Calculating back from Equation 10.2.3, the experimental value of p_c is consistent with the value $\alpha_c = 0.578$, instead of the theoretical value of 0.50.

10.2.3 Molecular-Weight Averages

It is apparent that numerous other special systems or effects could be considered to either broaden the range or improve the applicability of the derivation presented. Our interest, however, is in illustrating concepts rather than exhaustively exploring all possible cases, so we shall not pursue the matter of the gel point further here. Instead, we conclude this section with a brief examination of the molecular-weight averages in the system generated from AA, BB, and A_f . For simplicity, we restrict our attention to the case of $\nu_A^0 = \nu_B^0$. It is useful to define the average functionality of a monomer $\langle f \rangle$ as

$$\langle f \rangle \equiv \frac{\sum_i n_i f_i}{\sum_i n_i} \quad (10.2.6)$$

where n_i and f_i are the number of molecules and the functionality of the i th component in the reaction mixture, respectively. The summations are over all monomers. If n is the total number of molecules present at the extent of reaction p and n_0 is the total number of molecules present initially, then $2(n_0 - n)$ is the number of functional groups that have reacted and $\langle f \rangle n_0$ is the total number of groups initially present. Two conclusions immediately follow from these concepts:

$$N_n = \frac{n_0}{n} \quad (10.2.7)$$

where N_n is the number-average degree of polymerization, and

$$p = \frac{2(n_0 - n)}{\langle f \rangle n_0} \quad (10.2.8)$$

Elimination of n between these expressions gives

$$N_n = \frac{2}{2 - p\langle f \rangle} \quad (10.2.9)$$

This result is known as the *Carothers equation* [4]. It is apparent that this expression reduces to Equation 2.2.4 for the case of $\langle f \rangle = 2$, that is, the result for the most probable distribution in polycondensation reactions considered in Chapter 2. Furthermore, when $\langle f \rangle$ exceeds 2, as in the AA/BB/A₃ mixture under consideration, then N_n is increased over the value obtained at the same p for $\langle f \rangle = 2$. A numerical example will help clarify these relationships.

Example 10.2

An AA, BB, and A₃ polymerization mixture is prepared in which $\nu_A^0 = \nu_B^0 = 3.00$ mol, with 10% of the A groups contributed by A₃. Use Equation 10.2.9 to calculate N_n for $p = 0.970$ and p for $N_n = 200$. In each case, compare the results with what would be obtained if no multifunctional A were present.

Solution

Determine the average functionality of the mixture. The total number of functional groups is 6.00 mol, but the total number of molecules initially present must be determined. Using $3n_{AAA} + 2n_{AA} = 3.00$ and $3n_{AAA}/3 = 0.100$, we find that $n_{AA} = 1.350$ and $n_{AAA} = 0.1000$. Since $n_{BB} = 1.500$ the total number of moles initially present is $n_0 = 1.350 + 0.100 + 1.500 = 2.950$:

$$\langle f \rangle = \frac{3(0.100) + 2(1.350) + 2(1.500)}{2.950} = 2.034$$

Solving Equation 10.2.9 with $p = 0.970$ and $\langle f \rangle = 2.034$:

$$N_n = \frac{2}{2 - 0.97(2.034)} = 73.8$$

For comparison, solve Equation 10.2.9 with $p = 0.970$ and $\langle f \rangle = 2$:

$$N_n = \frac{1}{1 - p} = \frac{1}{1 - 0.97} = 33.3$$

Solve Equation 10.2.9 with $N_n = 200$ and $\langle f \rangle = 2.034$:

$$p = \frac{2(1 - 1/N_n)}{\langle f \rangle} = \frac{2(0.995)}{2.034} = 0.978$$

Solve Equation 10.2.9 with $N_n = 200$ and $\langle f \rangle = 2$:

$$p = \left(1 - \frac{1}{N_n}\right) = \left(1 - \frac{1}{200}\right) = 0.995$$

These results demonstrate how for a fixed extent of reaction, the presence of multifunctional monomers in an equimolar mixture of reactive groups increases the degree of polymerization. Conversely, for the same mixture a lesser extent of reaction is needed to reach a specific N_n with multifunctional reactants than without them. Remember that this entire approach is developed for the case of stoichiometric balance. If the numbers of functional groups are unequal, this effect works in opposition to the multifunctional groups.

The Carothers approach, as described above, is limited to the number-average degree of polymerization and gives no information concerning the breadth of the distribution. A statistical approach to the degree of polymerization yields expressions for both N_w and N_n . Ref. [4] contains a

derivation of these quantities for the self-polymerization of A_f monomers. Although this specific system might appear to be very different from the one we have considered, the essential aspects of the two different averaging procedures are applicable to the system we have considered as well. The results obtained for the A_f case are

$$N_n = \frac{2}{2 - \alpha f} \quad (10.2.10)$$

and

$$N_w = \frac{1 + \alpha}{1 - \alpha(f - 1)} \quad (10.2.11)$$

from which it follows that

$$\frac{N_w}{N_n} = \frac{(1 + \alpha)(1 - \alpha f/2)}{1 - \alpha(f - 1)} \quad (10.2.12)$$

The value of α to be used in these expressions is given by Equation 10.2.3 for the specific mixture under consideration. At the gel point $\alpha_c = 1/(f - 1)$ according to Equation 10.2.4, and thus Equation 10.2.11 predicts that N_w becomes infinite, whereas N_n remains finite. This is a very important point. It emphasizes that in addition to the network molecule, or gel fraction, of essentially infinite molecular weight, there are still many other molecules present at the gel point, the sol fraction. The ratio N_w/N_n also indicates a divergence of the polydispersity as $\alpha \rightarrow \alpha_c$. Expressions have also been developed to describe the distribution of molecules in the sol fraction beyond the gel point. We conclude this discussion with an example that illustrates application of some of these concepts to a common household product.

Example 10.3

The chemistry underlying an epoxy adhesive is illustrated in Figure 10.5. An excess of epichlorohydrin is reacted with a diol to form a linear *prepolymer*, terminated at each end with epoxide

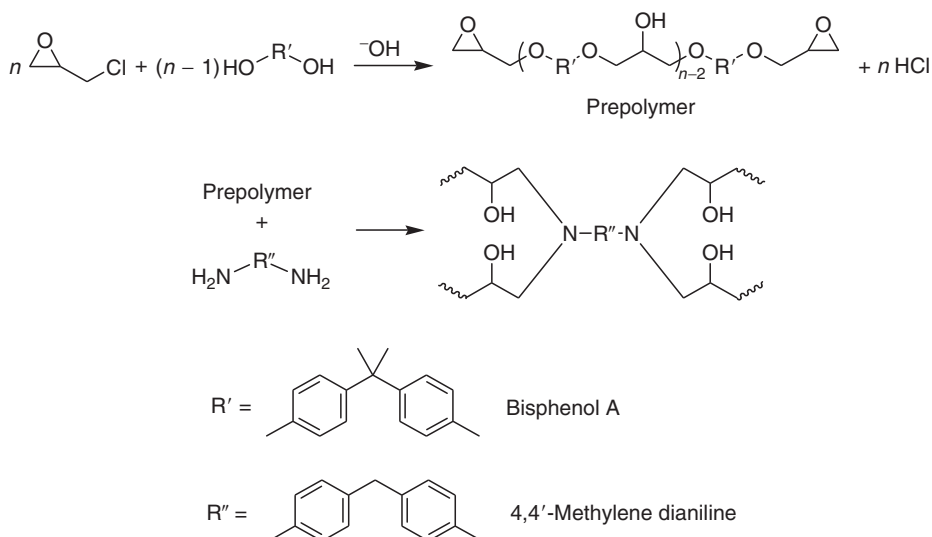


Figure 10.5 Illustration of an epoxy formulation. A prepolymer, formed by base-catalyzed condensation of an excess of epichlorohydrin with bisphenol A, is cured by cross-linking with 4,4'-methylene dianiline.

rings. For the example in Figure 10.5, the diol is based on bisphenol A. The prepolymer is then reacted (*cured*) with a multifunctional anhydride or amine (methyl dianiline in the figure) to form a highly cross-linked material. Adapt the analysis in the preceding section to find the gel point for this system, assuming that the two compounds are mixed in the weight ratio 1:10 diamine to prepolymer and that the prepolymer has $n = 4$ (see Figure 10.5). Then interpret the statement found in the instructions for a typical “two-part” epoxy that “the bond will set in 5 minutes, but that full strength will not be achieved until 6 hours.”

Solution

Following the reaction scheme in Figure 10.5, the prepolymer has functionality 2 whereas the diamine has functionality $f = 4$, so we will call the epoxide group “B” and the diamine A_4 . We now need to find out which group is in excess, that is, to calculate the ratio r . The molecular weight of the diamine is 198 g/mol and that of the prepolymer is 914 g/mol. If we mix 1 g of the diamine with 10 g of the prepolymer we have a molar ratio of $(1/198):(10/914)$ or 0.00505:0.0109. As there are four A groups per diamine and two B groups per prepolymer, the final ratio of A:B groups is 0.0101:0.0109 or 0.93:1. Thus the A group is limiting the reaction, albeit only just.

From Equation 10.2.1 we can see that $\rho = 1$, as all the A group are in A_4 units. This also makes the development of the branching coefficient quite simple, as every chain between two A_4 groups contains one and only one prepolymer (BB) unit. The addition of the first BB to an A_4 group takes place with probability p , and the addition of the subsequent A_4 has probability rp . Thus $\alpha = rp^2$, which we could also obtain from Equation 10.2.3 after inserting $\rho = 1$. The critical extent of reaction corresponds to $\alpha_c = 1/3$ from Equation 10.2.4, and from Equation 10.2.5 we have

$$p_c = \frac{1}{\sqrt{3r}} \approx 0.6$$

We can interpret the time for the bond to set as a time when the gel point is consistently exceeded, perhaps $p \approx 0.7$, so that the adhesive has solidified. The time to develop full mechanical strength reflects the time required for p to approach 1.

10.3 Elastic Deformation

For the remainder of this chapter we will emphasize elastomers rather than thermosets, and our primary focus will be the elasticity of such network materials. The various elastic phenomena we discuss in this chapter will be developed in stages. We begin with the simplest case: a sample that displays a purely elastic response when deformed by simple elongation. On the basis of Hooke's law, we expect that the force of deformation—related to the stress—and the distortion that results—related to the strain—will be directly proportional, at least for small deformations. In addition, the energy spent to produce the deformation is recoverable: the material snaps back when the force is released. We are interested in the molecular origin of this property for polymeric materials but, before we can get to that, we need to define the variables more precisely. One cautionary note is appropriate here. A full description of the elastic response of materials requires tensors, but we will avoid this complication by emphasizing one kind of deformation—uniaxial extension—and touching on another, shear.

A quantitative formulation of Hooke's law is facilitated by considering the rectangular sample shown in Figure 10.6a. If a force f is applied to the face of area A , the original length of the block L_0 will be increased by ΔL . Now consider the following variations:

1. Imagine subdividing the block into two portions perpendicular to the direction of the force, as shown in Figure 10.6b. Each slice experiences the same force as before, and the same net deformation results. A deformation $\Delta L/2$ is associated with a slice of length $L_0/2$. The same

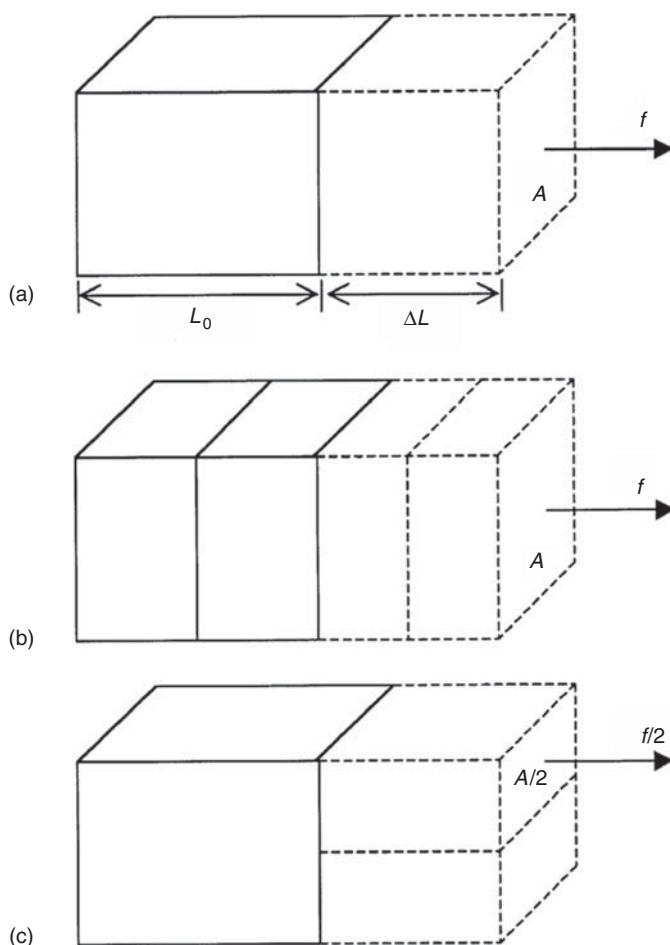


Figure 10.6 (a) A force f applied to area A extends the length of the sample from L_0 by an amount ΔL . Parts (b) and (c) illustrate the argument that $f/A \sim \Delta L/L_0$.

- argument could be applied for any number of slices; hence it is the quantity $\Delta L/L_0$ that is proportional to the force.
- Imagine subdividing the face of the block into two portions of area $A/2$. A force only half as large would be required for each face to produce the same net distortion. The same argument could be applied for any degree of subdivision; hence it is the quantity f/A that is proportional to $\Delta L/L_0$.
- The force per unit area along the axis of the deformation is called the uniaxial tension or stress. We shall use the symbol σ as a shorthand replacement for f/A and attach the subscript t to signify tension; we will use σ for the shear stress, as in Chapter 9 and Chapter 11. The elongation expressed as a fraction of the original length, $\Delta L/L_0$, is called the strain. We shall use ε as the symbol for the resulting extensional strain to distinguish it from the shear strain (γ) also discussed in Chapter 9 and Chapter 11.

With these considerations in mind, we write

$$\sigma_t = E\varepsilon = E\left(\frac{\Delta L}{L_0}\right) \quad (10.3.1)$$

where the proportionally constant E is called the tensile modulus or *Young's modulus*. Remember, it will be different for different substances and for a given substance at different temperatures. Since ε is dimensionless, E has the same units as f/A , namely, force/length², or N/m²(Pa) in the SI system. Note that for Equation 10.3.1 to be useful as a definition of E , the strain must be sufficiently small so that the stress remains proportional to the strain.

There is another aspect of tensile deformation to be considered. The application of a distorting force not only stretches a sample, but also causes the sample to contract at right angles to the stretch. If d and h represent the width and height of area A in Figure 10.6, both contract by the same fraction, a fraction that is related to the strain in the following way:

$$-\frac{\Delta d}{d} = -\frac{\Delta h}{h} = \nu \frac{\Delta L}{L_0} = \nu \varepsilon \quad (10.3.2)$$

where the minus signs indicate that Δd and Δh are negative when ΔL is positive. The constant ν is an important property of a material called *Poisson's ratio*; it may also be written as

$$\nu = \frac{1}{2} \left(1 - \frac{1}{V} \frac{dV}{d\varepsilon} \right) \quad (10.3.3)$$

where V is the volume of the sample (see Problem 9). Thus, if the volume does not change on elongation, the fractional contraction in each of the perpendicular directions is half the fractional increase in length and $\nu = 0.5$. In general two parameters, for example E and ν , are required to describe the response of a sample to tensile force. Poisson's ratio also provides a means to relate E to the shear modulus, G , and the compressional modulus, K :

$$G2(1 + \nu) = E \quad (10.3.4a)$$

$$K3(1 - 2\nu) = E \quad (10.3.4b)$$

For isotropic materials such as those we are considering in this chapter, the small strain elastic response can therefore be described by any two of the parameters of E , G , K , and ν . For elastomers, where the volume change on deformation tends to be very small, $\nu \approx 0.5$ and $E \approx 3G$. For example, polyisoprene has $\nu = 0.4999$, so this approximation is excellent; in contrast, for metals, ν typically lies between 0.25 and 0.35.

10.4 Thermodynamics of Elasticity

It is not particularly difficult to introduce thermodynamic concepts into a discussion of elasticity. We shall not explore all of the implications of this development, but shall proceed only to the point of establishing the connection between elasticity and entropy. Then in the next section we shall go from macroscopic thermodynamics to statistical thermodynamics, in pursuit of a molecular model to describe the elastic response of cross-linked networks.

10.4.1 Equation of State

We begin by remembering the mechanical definition of work and apply that definition to the stretching process of Figure 10.6. Using the notation of Figure 10.6, we can write the increment of elastic work associated with an increment in elongation dL as

$$dw = f dL \quad (10.4.1)$$

It is necessary to establish some conventions concerning signs before proceeding further. When the applied force is a tensile force and the distortion is one of stretching, f , dL and dw are all defined to be positive quantities. Thus dw is positive when elastic work is done on the system. The work done by the sample when the elastomer snaps back to its original size is a negative quantity.

The first law of thermodynamics defines the change dU in the internal energy of a system as the sum of the heat absorbed by the system, dq , plus the work done on the system, dw :

$$dU = dq + dw \quad (10.4.2)$$

The element of work is generally written $-p dV$, where p is the external pressure, but with the possibility of an elastic contribution, it is $-p dV + f dL$. With this substitution, Equation 10.4.2 becomes

$$dU = dq - p dV + f dL \quad (10.4.3)$$

A consistent sign convention has been applied to the pressure–volume work term: a positive dV corresponds to an expanded system, and work is done by the system to push back the surrounding atmosphere.

The second law of thermodynamics gives the change in entropy associated with the isothermal, reversible absorption of an element of heat dq as

$$dS = \frac{dq}{T} \quad (10.4.4)$$

This relationship can be used to replace dq by $T dS$ in Equation 10.4.3, since the infinitesimal increments implied by the differentials mean that the system is only slightly disturbed from equilibrium and the process is therefore reversible:

$$dU = T dS - p dV + f dL \quad (10.4.5)$$

We now turn to the Gibbs free energy G (recall the treatment of mixtures in Chapter 7) defined as

$$G = H - TS \quad (10.4.6)$$

where the enthalpy

$$H = U + pV \quad (10.4.7)$$

Combining the last two results and taking the derivative gives

$$dG = dU + p dV + V dp - T dS - S dT \quad (10.4.8)$$

Comparing Equation 10.4.8 with Equation 10.4.5 enables us to replace several of these terms by $f dL$

$$dG = V dp - S dT + f dL \quad (10.4.9)$$

thus establishing the desired connection between the stretching experiment and thermodynamics.

Since G is a state variable and forms exact differentials, an alternative expression for dG is

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,L} dp + \left(\frac{\partial G}{\partial T}\right)_{p,L} dT + \left(\frac{\partial G}{\partial L}\right)_{p,T} dL \quad (10.4.10)$$

Comparing Equation 10.4.10 and Equation 10.4.9 enables us to write

$$f = \left(\frac{\partial G}{\partial L}\right)_{p,T} \quad (10.4.11)$$

Note this is the same derivation that yields the important results $V = (\partial G / \partial p)_T$ and $S = -(\partial G / \partial T)_p$ when no elastic work is considered; these will arise in the discussion of the glass transition in Chapter 12.

We differentiate Equation 10.4.6 with respect to L , keeping p and T constant:

$$\left(\frac{\partial G}{\partial L}\right)_{p,T} = \left(\frac{\partial H}{\partial L}\right)_{p,T} - T\left(\frac{\partial S}{\partial L}\right)_{p,T} \quad (10.4.12)$$

The left-hand side of this equation gives f according to Equation 10.4.11; therefore

$$f = \left(\frac{\partial H}{\partial L}\right)_{p,T} - T\left(\frac{\partial S}{\partial L}\right)_{p,T} \quad (10.4.13)$$

This expression is sometimes called the *equation of state for an elastomer*, by analogy to

$$-p = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T \quad (10.4.14)$$

the thermodynamic equation of state for a fluid. Note the parallel roles played by length and volume in these two expressions.

10.4.2 Ideal Elastomers

Equation 10.4.12 shows that the force required to stretch a sample can be broken into two contributions: one that measures how the enthalpy of the sample changes with elongation and one that measures the same effect on entropy. The pressure of a system also reflects two parallel contributions, except that the coefficients are associated with volume changes. It will help to pursue the analogy with a gas a bit further. For an ideal gas, the molecules are noninteracting and so it makes no difference how far apart they are. Therefore, for an ideal gas $(\partial U/\partial V)_T = 0$ and the thermodynamic equation of state becomes

$$-p = -T\left(\frac{\partial S}{\partial V}\right)_T \quad (10.4.15)$$

By analogy, an *ideal elastomer* is defined as one for which $(\partial H/\partial L)_{p,T} = 0$; in this case Equation 10.4.13 reduces to

$$f = -T\left(\frac{\partial S}{\partial L}\right)_{p,T} \quad (10.4.16)$$

Although defined by analogy to an ideal gas, the justification for setting $(\partial H/\partial L)_{p,T} = 0$ cannot be the same for an elastomer as for an ideal gas. All molecules attract one another and this attraction is not negligible in condensed phases (recall the cohesive energy density in Chapter 7). What the ideality condition requires in an elastomer is that there is no change in the enthalpy of the sample as a result of the stretching process. This has two implications. On the one hand, the average energy of interaction between different molecules cannot change. For a given material this intermolecular contribution is determined primarily by the density, and therefore for a deformation that does not change the volume it may be a good approximation. The intramolecular contribution arises from the conformational energy of each chain, which is determined by the relative population of *trans* and *gauche* conformers (recall Chapter 6). In fact, moderate changes in the end-to-end distance of a chain can be accomplished with the expenditure of relatively little energy. For large deformations, or for networks with strong interactions—say, hydrogen bonds instead of dispersion forces—the approximation of an ideal elastomer may be very poor. There is certainly an enthalpy change associated with crystallization (see Chapter 13), so $(\partial H/\partial L)_{p,T}$ would not vanish if stretching induced crystal formation (which can occur, e.g., in natural rubber).

We have presented this development of the ideal elastomer in terms of the Gibbs free energy, which is generally the most appropriate for processes of importance in chemistry: p and T (and

number of moles) are the natural independent variables. However, in the majority of texts the Helmholtz free energy, $A = U - TS$ is employed, so it is worthwhile to take a moment and compare the answers. For an experiment at constant temperature, we can write

$$dA = dU - T dS \quad (10.4.17)$$

which may then be compared to Equation 10.4.5 to yield

$$dA = f dL - p dV \quad (10.4.18)$$

At both constant temperature and constant volume, therefore,

$$f = \left(\frac{\partial A}{\partial L} \right)_{T,V} = \left(\frac{\partial U}{\partial L} \right)_{T,V} - T \left(\frac{\partial S}{\partial L} \right)_{T,V} \quad (10.4.19)$$

and the criterion for an ideal elastomer becomes $(\partial U / \partial L)_{T,V} = 0$. Because the volume changes on elastomer deformation are typically so small, a deformation carried out at constant T and p is very close to one done at constant T and V .

10.4.3 Some Experiments on Real Rubbers

Before proceeding to the statistical theory of rubber elasticity, it is instructive to examine some of the classical experiments conducted on rubbers. An example is shown in Figure 10.7, where the tensile stress (proportional to f) was measured as a function of temperature at the indicated constant

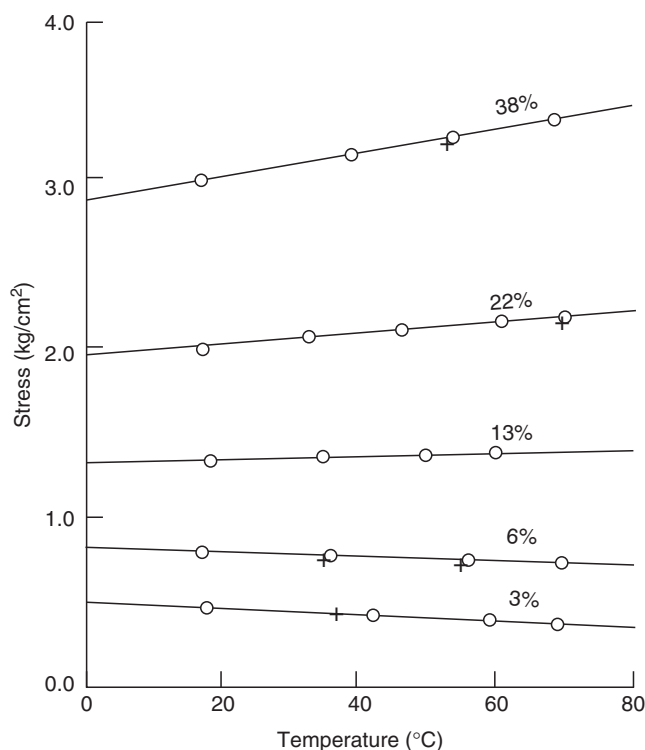


Figure 10.7 Stress at a constant length for natural rubber, at the indicated elongations, as a function of temperature. Thermoelastic inversion occurs below about 10% elongation. (Data from Anthony, R.L., Caston, R.H., and Guth, E., *J. Phys. Chem.*, 46, 826, 1942. With permission.)

length. These data show an interesting feature, known as *thermoelastic inversion*, whereby at elongations below about 10%, the stress decreases with temperature, in contrast to the larger strain behavior. As we are anticipating that the elasticity is primarily due to entropy, we expect the force to increase with temperature. The reason for the behavior at small elongation is actually quite simple; it is due to thermal expansion. The unstrained length increases with temperature due to expansion and thus the actual strain at fixed length decreases with increased temperature and consequently the force decreases. Thus the thermoelastic inversion can be eliminated by comparing the data at constant strain.

This kind of thermoelastic data can be further analyzed in terms of the thermodynamic contributions. From Equation 10.4.19 we can write

$$\left(\frac{\partial f}{\partial T}\right)_L = -\left(\frac{\partial S}{\partial L}\right)_T \quad (10.4.20)$$

and

$$\left(\frac{\partial U}{\partial L}\right)_T = f - T\left(\frac{\partial f}{\partial T}\right)_L \quad (10.4.21)$$

These expressions are useful because they permit extraction of information about S and U from the measured behavior of f . Figure 10.8a shows data for f versus elongation and the decomposition into an entropic and an internal energy contribution, following Equation 10.4.20 and Equation 10.4.21. Clearly at large elongation, the entropic part of the force dominates, but at low elongations the internal energy contribution is larger. Again, however, this effect is largely eliminated by plotting the data at constant strain, as shown in Figure 10.8b. These results and many others confirm, to a good approximation, that there is only a modest internal energy contribution to the force for a deformation at constant volume.

One further example of a “model-free” thermodynamic interpretation of rubber elasticity is given by the temperature increase observed in adiabatic extension of a rubber band. This underlies the standard classroom demonstration of the entropic origin of rubber elasticity, whereby a rubber band is rapidly extended and placed in contact with a (highly temperature-sensitive) upper lip. This kind of experiment goes back at least as far as Gough [5] and Joule [6], and some of Joule’s data are shown in Figure 10.9 along with some from James and Guth [7]. At low extensions, the temperature actually decreases slightly, but then increases steadily. The interpretation of the experiment is as follows. In the adiabatic extension of an ideal elastomer, the work done on the sample is retained entirely as heat; there is a loss of entropy but no change of internal energy and $dq = -dw$. The work is given by Equation 10.4.1 and the heat by Equation 10.4.4; therefore the temperature change is

$$\Delta T = \frac{1}{C_L} \int f dL = -\frac{T}{C_L} \int_{L_0}^L \left(\frac{\partial S}{\partial L}\right)_T dL \quad (10.4.22)$$

where C_L is the appropriate heat capacity at constant length. As in the previous examples, the negative change in temperature at small extensions is due to the positive entropy of deformation, that is, it corresponds to the thermoelastic inversion.

10.5 Statistical Mechanical Theory of Rubber Elasticity: Ideal Case

We now proceed to use a molecular model to derive predictions for the stress–strain behavior of an ideal elastomer. In the subsequent section, we will consider various nonidealities that could occur in a real material, but even granted the existence of some or all of these nonidealities, the

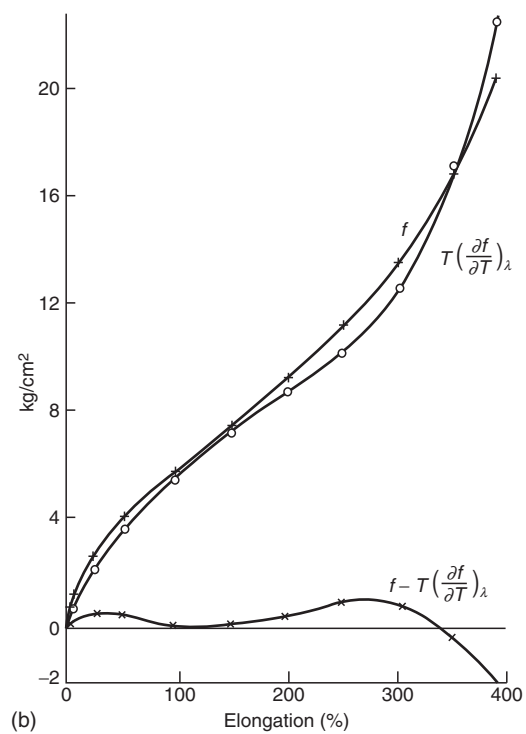
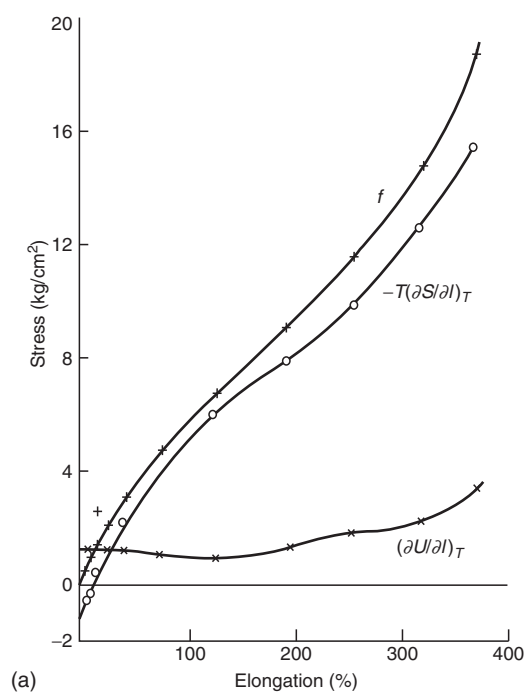


Figure 10.8 Stress versus elongation for natural rubber, resolved into internal energy and entropic contributions, at (a) constant temperature and (b) constant strain. (Data from Anthony, R.L., Caston, R.H., and Guth, E., *J. Phys. Chem.*, 46, 826, 1942. With permission.)

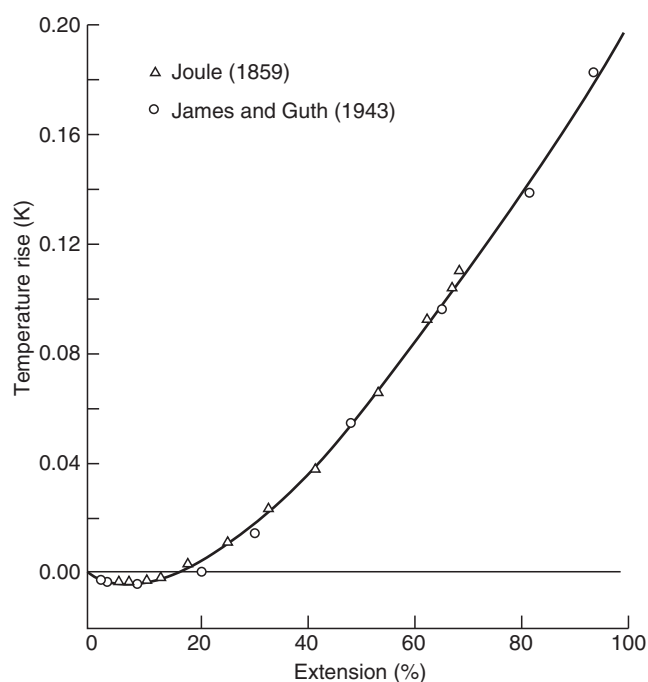


Figure 10.9 Temperature change during adiabatic extension of natural rubber. (Data from Joule, J.P., *Phil. Trans. R. Soc.*, 149, 91, 1859; James H.M. and Guth, E., *J. Chem Phys.*, 11, 455, 1943; 15, 669, 1947.) (From Treloar, L.R.G., *The Physics of Rubber Elasticity*, 3rd ed., Clarendon Press, Oxford, 1975. With permission.)

qualitative success of the ideal model is really a remarkable triumph of statistical mechanics. We have already considered the most famous equation of state, that of the ideal gas. That simple result is illuminating, but only describes the behavior of very dilute gases with any reliability and dilute gases are of limited significance from the point of view of materials science. In contrast, the ideal elastomer equations will provide a reasonable description of a practically important, but extremely complex, amorphous condensed phase, even though the derivation is not appreciably more elaborate than that for the ideal gas. We will begin by considering the force required to extend a single Gaussian chain, an example that already arose in the context of chain swelling in Section 7.7 and that will resurface in the bead-spring model of viscoelasticity in Section 11.4. Then we will apply this result to an entire ensemble of cross-linked chains.

10.5.1 Force to Extend a Gaussian Chain

Since entropy plays the determining role in the elasticity of an ideal elastomer, let us review some ideas about this important thermodynamic variable. We used a probabilistic interpretation of entropy extensively in Chapter 7 to formulate the entropy of mixing. The starting point was the Boltzmann relation:

$$S = k \ln \Omega \quad (10.5.1)$$

where k is Boltzmann's constant and Ω is the number of possible states. As then, the difference in entropy between two states of different thermodynamic probability is

$$\Delta S = S_2 - S_1 = k \ln \left(\frac{\Omega_2}{\Omega_1} \right) \quad (10.5.2)$$

so that ΔS is positive when $\Omega_2 > \Omega_1$ and negative when $\Omega_2 < \Omega_1$.

In the previous section, we identified the force of extension with the associated change in free energy (Equation 10.4.11 or Equation 10.4.19). Then, if the change in free energy is entirely due to the entropy, the material is an ideal elastomer. Figure 10.8 provides an example of how reasonable this assumption is for a material; now we apply it to one chain. Consider extending a single Gaussian chain of N units, with statistical segment length b (recall Section 6.3). The chain has one end fixed at the origin $(0, 0, 0)$ and the other is held in the infinitesimal cube between (x_0, y_0, z_0) and $(x_0 + dx_0, y_0 + dy_0, z_0 + dz_0)$, as shown in Figure 10.10. The imposed end-to-end distance is $h_0 = (x_0^2 + y_0^2 + z_0^2)^{1/2}$, which may be compared to the equilibrium mean square end-to-end distance $\langle h^2 \rangle = Nb^2$. The number of ways that this chain can satisfy the imposed constraint is given by the Gaussian distribution (recall Equation 6.7.1):

$$P_i(N, \vec{h}_0) = \left(\frac{3}{2\pi\langle h^2 \rangle} \right)^{3/2} \exp \left[-\frac{3h_0^2}{2\langle h^2 \rangle} \right] = \beta^{3/2} \exp[-\pi\beta h_0^2] \quad (10.5.3)$$

where we define the normalization factor, β as

$$\beta \equiv \frac{3}{2\pi\langle h^2 \rangle} = \frac{3}{2\pi Nb^2} \quad (10.5.4)$$

and the subscript “i” on P denotes the “initial” state. We then extend the chain to a new end-to-end distance, h , with coordinates between (x, y, z) and $(x + dx, y + dy, z + dz)$. The corresponding “final” state distribution function P_f is

$$P_f(N, \vec{h}) = \beta^{3/2} \exp[-\pi\beta h^2] \quad (10.5.5)$$

We now associate the number of possible conformations with the entropy defined by Equation 10.5.1, that is, we take $\Omega = AP$, with A as some unspecified proportionality constant. Then we can say

$$\begin{aligned} \Delta S_{\text{chain}} &= k \ln AP_f - k \ln AP_i = k \ln \left(\frac{P_f}{P_i} \right) \\ &= -k\pi\beta(h^2 - h_0^2) \end{aligned} \quad (10.5.6)$$

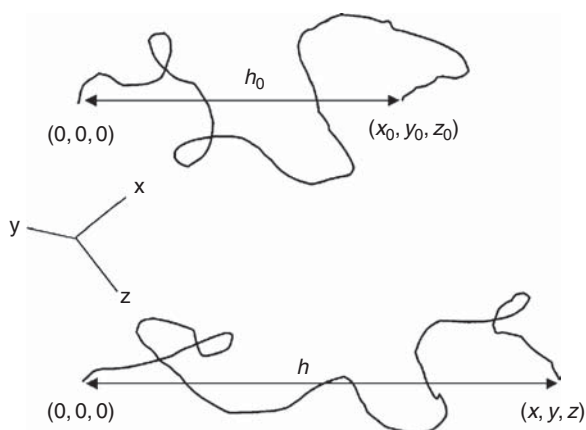


Figure 10.10 Extension of a single Gaussian chain from initial end-to-end distance h_0 to final end-to-end distance h .

where we use the subscript “chain” to emphasize that this is a single chain calculation. The unknown constant A cancels out when we calculate the change in entropy. The force to extend the chain to h is given by

$$f = -T \left(\frac{\partial \Delta S_{\text{chain}}}{\partial h} \right) = \frac{3kT}{\langle h^2 \rangle} h \quad (10.5.7)$$

This is a fundamental result, and one we will use extensively in modeling the viscoelastic properties of polymer liquids in Chapter 11. Equation 10.5.7 indicates that a single Gaussian chain behaves like a Hooke’s law spring, with force constant $3kT/\langle h^2 \rangle$ and zero rest-length. Note the interesting result that this spring will stiffen as T increases, in contrast to intuitive expectation for a metal spring; this is a direct result of its entropic basis. Equation 10.5.7 contains most of the physical concepts that are required to describe rubber elasticity from a molecular viewpoint.

10.5.2 Network of Gaussian Strands

We now consider an ideal network made up of Gaussian strands. If the cross-links were introduced to a melt of Gaussian chains, for example, by vulcanization, it is plausible that the strands will be more or less Gaussian as well. For simplicity, we will assume that all strands contain an identical number of statistical segment lengths, N_x ; this simplification will subsequently be removed. We now impose a macroscopic deformation on the network; for example, we might stretch it in the x direction. However, to be more general, we describe the deformation by three *extension ratios* λ_x , λ_y , and λ_z , given by L_x/L_0 , L_y/L_0 , and L_z/L_0 , respectively. If we begin with a cube of material of length L_0 on each side, that cube will be deformed to a three-dimensional volume element with sides L_x , L_y , and L_z , as shown in Figure 10.11. We assume that there is no volume change on deformation, and thus

$$V = L_x L_y L_z = V_0 = L_0^3; \quad \lambda_x \lambda_y \lambda_z = 1 \quad (10.5.8)$$

This is a reasonable approximation for bulk elastomers, where Poisson’s ratio is nearly 0.5, but is not appropriate, for example, when the network is swollen with solvent. The removal of this assumption will be discussed in Section 10.7.

We now make a final, very important assumption, the so-called *affine junction assumption*: each junction point moves in proportion to the macroscopic deformation. Consequently, the end-to-end vector of each strand is deformed so that the coordinates of one end transform $x_0 \rightarrow x = \lambda_x x_0$, $y_0 \rightarrow y = \lambda_y y_0$, $z_0 \rightarrow z = \lambda_z z_0$, when we take the other end as the origin. We already know the entropy change per strand associated with this process: it is simply the result for a single chain, see Equation 10.5.6, applied to a single strand. Writing it out in more detail, we have

$$\begin{aligned} \Delta S_{\text{strand}} &= k \ln AP_f - k \ln AP_i = k \ln \left(\frac{P_f}{P_i} \right) \\ &= -k\pi\beta(x^2 + y^2 + z^2) - (-k\pi\beta(x_0^2 + y_0^2 + z_0^2)) \\ &= -k \frac{3}{2N_x b^2} (x_0^2(\lambda_x^2 - 1) + y_0^2(\lambda_y^2 - 1) + z_0^2(\lambda_z^2 - 1)) \end{aligned} \quad (10.5.9)$$

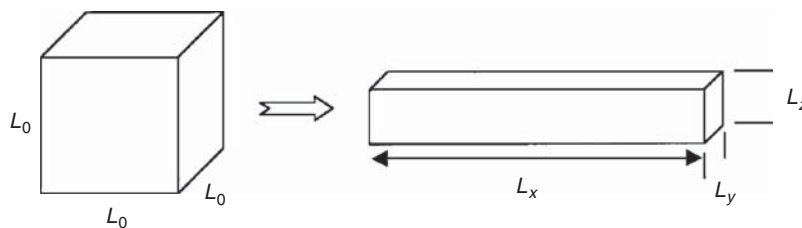


Figure 10.11 Deformation of a cube of material subjected to uniaxial elongation along x .

We now note that on average $x_0^2 = N_x b^2/3$, and the same for y_0 and z_0 , so that

$$\langle \Delta S_{\text{strand}} \rangle = -\frac{k}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (10.5.10)$$

In this rather simple result, N_x does not appear, so the assumption of constant N_x was actually not necessary. To obtain the total entropy change for the material, we simply need the number of strands per unit volume. For our ideal network this is given by $\rho N_{\text{av}}/M_x$, where M_x is the (number average) molecular weight between cross-links, but in anticipation of defects such as dangling ends and loops in real networks, we will just define the total *number of elastically effective strands*, ν_e . The number of strands per unit volume is thus ν_e/V and the total entropy change becomes

$$\Delta S = -\frac{\nu_e k}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (10.5.11)$$

This equation represents the principal result of this molecular network theory. We will now consider a specific deformation to obtain expressions for the modulus, but the necessary manipulations are all results of continuum elasticity theory and require no further assumptions about what the molecules are doing.

10.5.3 Modulus of the Gaussian Network

We begin with a uniaxial extension, say along x , by a stretch ratio λ . Thus $\lambda_x = \lambda$, and by volume conservation (see Equation 10.5.8) $\lambda_y = \lambda_z = 1/\sqrt{\lambda}$. Furthermore, $\varepsilon = \lambda - 1$. In this case, then

$$\Delta S = -\frac{\nu_e k}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \quad (10.5.12)$$

and the force is given by

$$f = -T \left(\frac{\partial \Delta S}{\partial L} \right) = -\frac{T}{L_0} \left(\frac{\partial \Delta S}{\partial \lambda} \right) = \frac{\nu_e k T}{L_0} \left(\lambda - \frac{1}{\lambda^2} \right) \quad (10.5.13)$$

Note that the force changes sign, as it should, when $\lambda = 1$. If we now divide both sides by the cross-section area normal to the stretching direction, $L_y L_z = L_0^2/\lambda$, we obtain the tensile stress:

$$\sigma_t = \frac{f}{\text{area}} = \frac{\lambda f}{L_0^2} = kT \frac{\nu_e}{V} \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (10.5.14)$$

Alternatively, it is often experimentally more convenient to divide by the initial cross-sectional area, L_0^2 , which leads to the following result:

$$\sigma_t = kT \frac{\nu_e}{V} \left(\lambda - \frac{1}{\lambda^2} \right) \quad (10.5.15)$$

The stress given by Equation 10.5.14 is sometimes called the *true stress* to distinguish it from the quantity given Equation 10.5.15, which is known as the *engineering stress* or the nominal stress.

We can now obtain an expression for Young's modulus, E , recalling Equation 10.3.1 (and that $d\lambda = d\varepsilon$):

$$E = \lim_{\lambda \rightarrow 1} \frac{\partial \sigma_t}{\partial \lambda} = 3kT \frac{\nu_e}{V} \quad (10.5.16)$$

Note that the same result is obtained if we use either the true stress or the engineering stress because they coincide in the small strain limit.

We finally obtain an expression for the shear modulus, G , using the approximate relation $G = E/3$ (Equation 10.3.4a):

$$G = kT \frac{\nu_e}{V} = \frac{\rho RT}{M_x} \quad (10.5.17)$$

where in the last step we have substituted the ideal value for ν_e/V in terms of the molecular weight between cross-links, M_x . From these equations (Equation 10.5.14 through Equation 10.5.17) we can extract some important conclusions:

1. The modulus increases with temperature, just as with the spring constant of a single chain, due to its entropic origin.
2. The modulus increases as a function of cross-link density, because M_x decreases; a “tighter” network is “stiffer.”
3. The modulus is independent of the functionality of the cross-links.
4. The extensional stress is not a linear function of the strain, even though the individual network strands are supposed to be Hookean. (In contrast, the shear stress turns out to be linear in the strain, but we will not take the time to derive this relation.)
5. Assuming a density of 1 g/cm^3 at room temperature, and $M_x = 10,000 \text{ g/mol}$, Equation 10.5.17 gives a modulus of $2.5 \times 10^6 \text{ dyn/cm}^2$, or 0.25 MPa . Typical values for elastomers fall within an order of magnitude of this number.

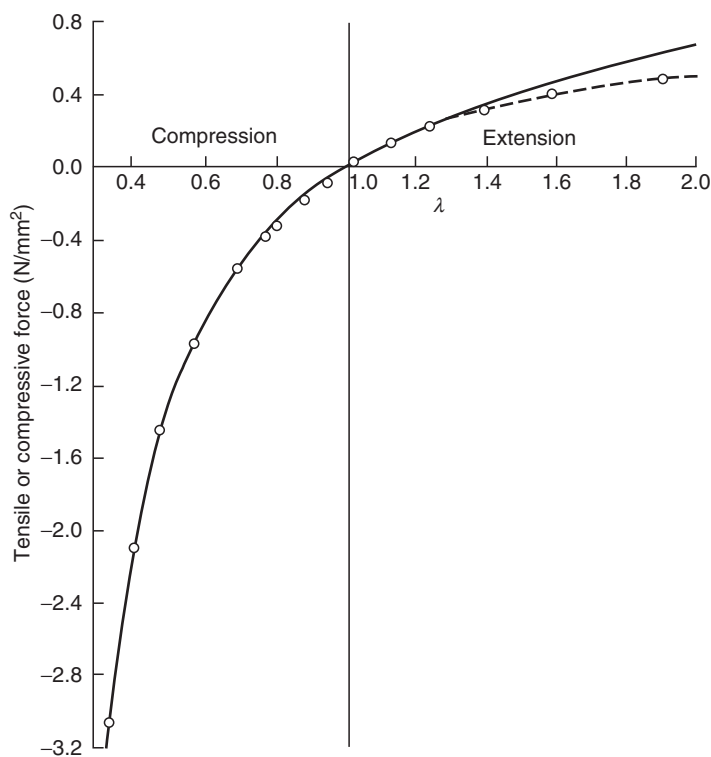


Figure 10.12 Stress for cross-linked natural rubber in compression and extension. (Data from Treloar, L.R.G., *Trans. Faraday Soc.*, 40, 59, 1944. With permission.)

An example of a test of the theory, and Equation 10.5.14 in particular, is shown in Figure 10.12. Both extensional and compressive stresses were determined as a function of λ for a piece of vulcanized rubber. The agreement between experiment and theory is impressive, particularly in compression. The same sample was subsequently extended up to its breaking point, near $\lambda \approx 7.5$, and the results are shown in Figure 10.13. The data at low extension ratios were fit to the theory to obtain the modulus of 0.39 MPa. The theory and the data are not in perfect agreement in this case; the main difference is the sharp increase in experimental stress at high λ . This is primarily due to the failure of the Gaussian assumption for large extensions; when the end-to-end distance becomes an appreciable fraction of the contour length, the Gaussian distribution no longer applies. This point will be considered again in the next section.

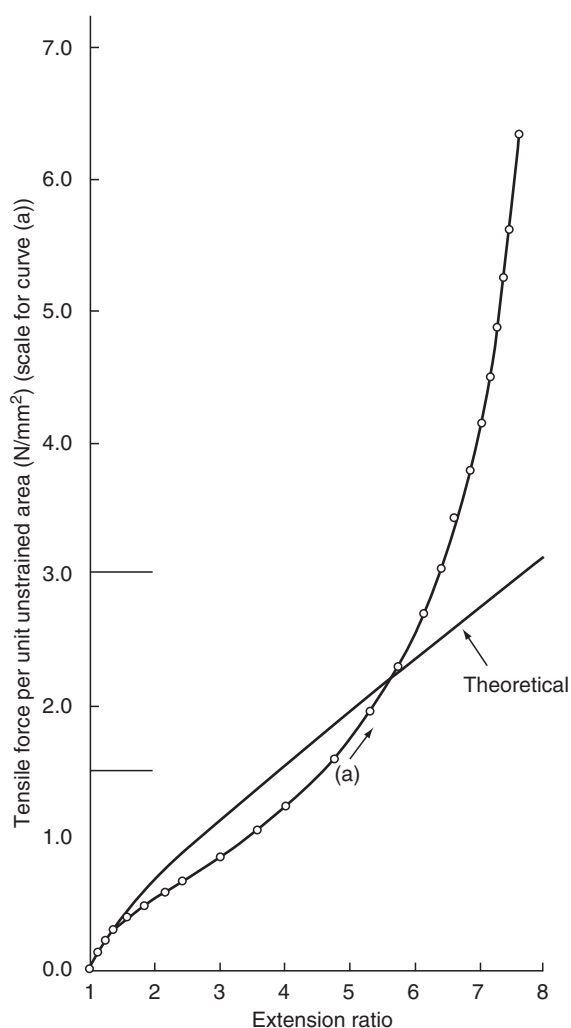


Figure 10.13 Same sample as in Figure 10.12, but now subjected to simple extension and much larger extension ratios (λ). (Data from Treloar, L.R.G., *Trans. Faraday Soc.*, 40, 59, 1944. With permission.)

10.6 Further Developments in Rubber Elasticity

The development of a statistical thermodynamic approach to rubber elasticity in the previous section involved a series of assumptions that could be questioned. In this section we touch briefly on some of these and give an indication of how they might be addressed. To begin with, we recall the central result of the theory (see Equation 10.5.11):

$$\Delta S = -\frac{\nu_e k}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (10.6.1)$$

from which the stress and modulus can be computed for any deformation. The main assumptions invoked in the development and application of this equation are summarized below:

1. There is no change in internal energy, U , upon deformation at constant T and p .
2. There is no change in volume, V , upon deformation at constant T and p .
3. The number of conformations available to the strands both before and after deformation is given by a Gaussian distribution.
4. The number of conformations available to the strands before deformation is the same as for equivalent chains in the uncross-linked state.
5. The junction points deform affinely with the macroscopic deformation.
6. The number of elastically effective strands per unit volume, ν_e/V , is given by $\rho N_{av}/M_x$ for a perfect network.

It turns out that refinement or relaxation of almost any of these assumptions has generated significant amounts of controversy over the years, and to address these issues thoroughly would require an entire book. Accordingly, we will have to be content with a few examples.

10.6.1 Non-Gaussian Force Law

The approximate validity of the first two assumptions was suggested in the previous section and the effects of deviations from these assumptions should be reasonably transparent. Accordingly, except for the issue of solvent swelling, which will be taken up in the following section, we will not consider these further. The third assumption is more interesting from a molecular point of view. One violation of this assumption can be readily imagined: upon large extensions, say beyond 100% (recall Figure 10.13), a strand may no longer be Gaussian. Clearly as we approach the limit of full extension, when the end-to-end distance becomes a significant fraction of the contour length, the Gaussian force law (Equation 10.5.7) will not apply. This problem has been addressed theoretically and a reasonable solution is known. Specifically, Kuhn and Gr $\ddot{u}$ n [8] showed that when a freely jointed chain of N_x links of length b is extended to an end-to-end distance h , the distribution function is not the familiar Gaussian, but rather

$$P(N_x, h) \propto \exp \left(-N_x \left[\frac{h}{N_x b} \beta + \ln \left(\frac{\beta}{\sinh \beta} \right) \right] \right) \quad (10.6.2)$$

where the quantity β is the so-called inverse Langevin function, $L^{-1}(x)$:

$$\beta = L^{-1}(h/N_x b) \quad (10.6.3)$$

This formulation is not particularly transparent, but it turns out that the exponential in Equation 10.6.2 can be expanded as a power series in $(h/N_x b)$ as follows:

$$P(N_x, h) \propto \exp \left(-N_x \left[\frac{3}{2} \left(\frac{h}{N_x b} \right)^2 + \frac{9}{20} \left(\frac{h}{N_x b} \right)^4 + \frac{99}{350} \left(\frac{h}{N_x b} \right)^6 \cdots \right] \right) \quad (10.6.4)$$

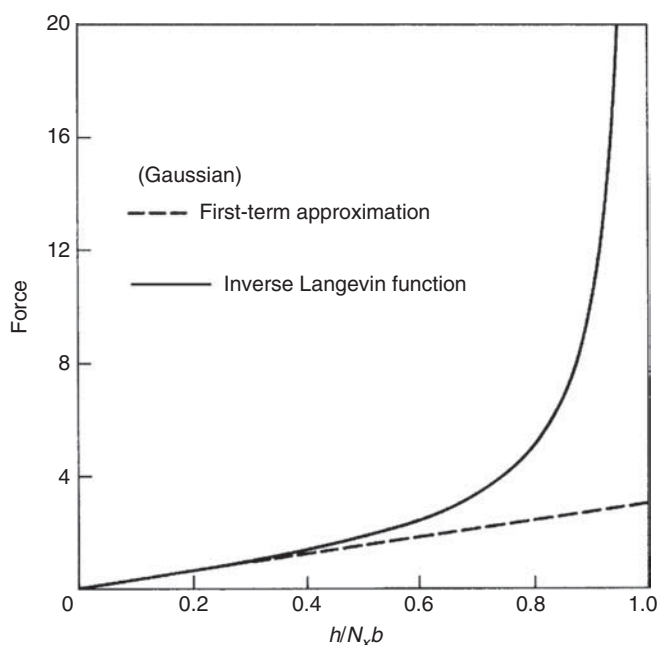


Figure 10.14 Force versus extension for a Gaussian chain (first-term approximation) and for the full inverse Langevin function.

from which we can see that the Gaussian result is just the first term in a series. When the argument $(h/N_x b)$ is small, the Gaussian function is adequate, but at large extensions Equation 10.6.4 is more accurate. This result can be carried through the analysis of the previous section (see Equation 10.5.6 and Equation 10.5.7) to obtain the corresponding force law and the result is illustrated in Figure 10.14. The main new feature is that for extensions such that $(h/N_x b) > 0.4$, the force increases rather sharply. This is in excellent qualitative agreement with the data in Figure 10.13. In fact, recent experiments have been able to measure the force of extension of single DNA molecules and the inverse Langevin function provides a good account of the results (see Problem 12), so although this approach is mathematically unwieldy, it is successful.

A second difficulty with the Gaussian assumption arises from the inevitable distribution of strand lengths. In the development leading up to Equation 10.5.10, we argued that because the quantity N_x cancels out of the final expression for ΔS , the assumption of monodisperse strands was benign. In reality the cross-linking process, however it is carried out, will leave some distribution of N_x . Consequently, the non-Gaussian character of the distribution function will become apparent at different values of the macroscopic extension; shorter strands will sooner become more fully stretched than longer ones. For example, an average strand begins with an unperturbed $h/b = \sqrt{N_x}$, which is then stretched to $\lambda\sqrt{N_x}$. The smaller the N_x , the smaller the value of λ required for $\lambda\sqrt{N_x}$ to approach N_x . This problem is much more difficult to deal with, not least because of the difficulty in characterizing the distribution of N_x .

10.6.2 Front Factor

The fourth assumption above represents a reasonable simplification, but it need not hold, even for rubbers lightly cross-linked in the melt state. Under some circumstances, such as cross-links introduced while the material is under stress, it certainly would not apply. The first step in lifting this assumption is to assume that in the undeformed state the elastomer is isotropic and the mean

square strand length is $\langle h_i^2 \rangle$, where the subscript “i” denotes initial. If we return to Equation 10.5.9, we would replace $x_0^2 = y_0^2 = z_0^2$ with $x_i^2 = y_i^2 = z_i^2$, and the expression for the strand entropy (Equation 10.5.10) would be replaced by

$$\langle \Delta S_{\text{strand}} \rangle = -\frac{k}{2} \frac{\langle h_i^2 \rangle}{\langle h_0^2 \rangle} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (10.6.5)$$

The ratio of mean square end-to-end distances in the undeformed network relative to that in a melt of the same strands is known as the *front factor*. As it is a constant, it carries through the subsequent development and therefore appears in the expressions for the stress and the modulus.

Alternatives to Assumption 5—that the junction points deform affinely with the macroscopic strain—have also been proposed. In the most common approach only the junctions on the edges of the material are so constrained; those in the bulk of the network are free to fluctuate about their mean positions [7]. This model is sometimes referred to as the *phantom network*. This modification cannot be applied to the entropy of a single strand, as in Equation 10.6.5, but must be applied to the network as a whole. The result is a reduction in the net stress, which is determined by the number of junctions, ν_x ; Equation 10.5.11 so modified becomes

$$\Delta S = -(\nu_e - \nu_x) \frac{k}{2} \frac{\langle h_i^2 \rangle}{\langle h_0^2 \rangle} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (10.6.6)$$

Again, this new front factor is a constant and would carry through to the expressions for the stress and the modulus. For the particular case of a regular network in which f strands emerge from each junction, then $\nu_e = \nu_x f/2$, and $(\nu_e - \nu_x) = \nu_e(f - 2)/f$. For a network made by vulcanization, therefore, $f = 4$ and this term is equal to $\nu_e/2$.

10.6.3 Network Defects

Any real network will contain defects in the structure, as suggested at the beginning of the chapter. These include loops, dangling ends, and the sol fraction. We have finessed this issue, in part, by using the concept of *elastically effective strands*, ν_e , which suggests that the contribution from such defects has been removed. However, it is not a straightforward matter to account for these in practice. Consider two general approaches. By NMR spectroscopy, for example, we might monitor the conversion of double bonds in a polydiene. From this information we could estimate M_x and thus ν_e by Assumption 6. But the NMR experiment could not tell us about loops or distinguish sol fraction from gel fraction (and, in fact, for modest degrees of cross-linking it is hard to even quantify that reliably). The next option is to measure the modulus itself and fit the results to the model. But, because all of these various effects contribute proportionally to the modulus, there is no easy way to resolve them from measurements on a single sample. In general, these three particular kinds of defects are treated in the following way: (a) loops are ignored, (b) dangling ends are corrected for, and (c) the conversion is high enough that the sol fraction is negligible, or it is extracted before measurement. Under (b), the number of dangling ends can be estimated from M_x , because each prenetwork chain had two ends. Therefore each prenetwork chain will contribute two dangling ends to the network, and the average length of these dangling ends will be M_x . Accordingly, the fraction of these dangling ends will be $2M_x/M$, where M is the molecular weight of the prenetwork chain and the number of effective strands may be estimated as

$$\frac{\nu_e}{V} = \frac{\rho N_{\text{av}}}{M_x} \left(1 - \frac{2M_x}{M} \right) \quad (10.6.7)$$

Another contribution to the modulus, the so-called *trapped entanglement*, although not strictly a topological defect has been considered extensively. We will see in Section 11.6 that the viscoelastic properties of high-molecular-weight polymers are dominated by the phenomenon of

entanglement, which results from the intertwining of different chains. These entanglements act like temporary cross-links, imparting a rubber-like modulus to the liquid at intermediate times, before eventual relaxation and flow. By exploiting the expression for the shear modulus of an ideal elastomer, Equation 10.5.17, a molecular weight between entanglements can be defined, M_e . Now imagine we have a high-molecular-weight melt, with $M \gg M_e$, and we cross-link it enough to produce a network. (Recall from Equation 10.1.1 that we only need a few cross-links, $\sim 1/N$, to pass the gel point.) At this stage the modulus must be about the same, or perhaps slightly higher than it was before cross-linking, but $M_x \gg M_e$. In other words, we expect a modulus of about $\rho RT/M_e$, but the theory of rubber elasticity says it should be only $\rho RT/M_x$. Therefore these entanglements contribute to the modulus, but they are trapped; full stress relaxation, or flow, is eliminated by the cross-linking. Thus at low degrees of cross-linking, trapped entanglements should make the experimental modulus larger than expected by ideal elastomer theory. As the degree of cross-linking goes up, so that $M_x < M_e$, then this contribution should become progressively less important. A variety of approaches have been taken to this issue, all of which have the general effect just described; for example, the modulus could be expressed as

$$G = G_{\text{network}} + xG_{\text{entanglements}} = \rho RT \left(\frac{1}{M_x} + x \frac{1}{M_e} \right) \quad (10.6.8)$$

where x is just a parameter between 0 and 1, depending on the degree to which the entanglements are effective as cross-links. However, it is likely that the importance of this effect varies with extension as well. For example, imagine that the cross-linking process has created a “loose knot”: two different strands are irreversibly intertwined, but not influencing each other very much. At low degrees of extension, this constraint on the strand conformations plays no particular role, but as the deformation increases, the “knot” might be pulled tight. This would have the effect of increasing the number of cross-links with deformation, and therefore act in the same direction as the non-Gaussian force law.

10.6.4 Mooney–Rivlin Equation

The preceding discussion of modifications to the ideal elastomer theory has emphasized additional molecular contributions and particularly ones that modify the prefactor. Following Equation 10.5.15, we may represent the tensile stress from these models as

$$\sigma_t = 2C_1 \left(\lambda - \frac{1}{\lambda^2} \right) \quad (10.6.9)$$

where the prefactor, now labeled “ $2C_1$,” is given by

$$2C_1 = \frac{f - 2 \langle h_i^2 \rangle}{f \langle h_o^2 \rangle} \frac{\rho RT}{M_x} \left(1 - \frac{2M_x}{M} \right) \quad (10.6.10)$$

where we have incorporated the modifications discussed above. Before the development of the statistical theory, however, Mooney and Rivlin [9] used continuum arguments to propose that

$$\sigma_t = 2C_1 \left(\lambda - \frac{1}{\lambda^2} \right) + 2C_2 \left(1 - \frac{1}{\lambda^3} \right) = \left(2C_1 + \frac{2C_2}{\lambda} \right) \left(\lambda - \frac{1}{\lambda^2} \right) \quad (10.6.11)$$

where C_1 and C_2 are unknown parameters of the material, but not functions of the deformation. The first term in this Mooney–Rivlin equation, therefore, has exactly the form of the statistical theory, and the second term can be viewed as a correction. The second form of Equation 10.6.11 suggests plotting the following quantity versus $1/\lambda$:

$$\frac{\sigma_t}{\left(\lambda - \frac{1}{\lambda^2} \right)} = 2C_1 + \frac{2C_2}{\lambda} \quad (10.6.12)$$

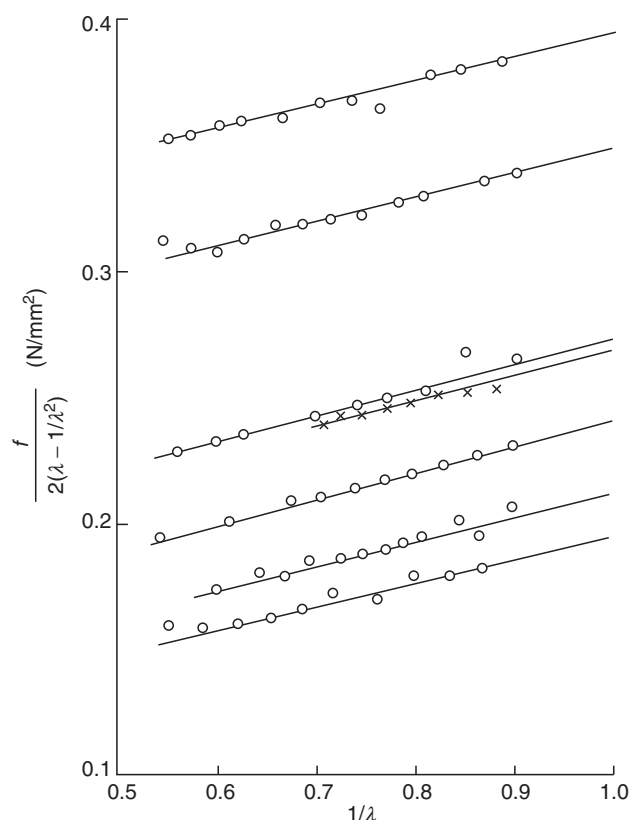


Figure 10.15 A “Mooney plot” for various rubbers in simple extension. (Data from Gumbrell, S.M., Mullins, L., and Rivlin, R.S., *Trans. Faraday Soc.*, 49, 1495, 1953. With permission.)

which should give a straight line with intercept $2C_1$ and slope $2C_2$. Adherence to the ideal theory should give a horizontal line. Examples from a variety of rubbers are shown in Figure 10.15; clearly Equation 10.6.12 gives a good description of the data, with nonzero values of C_2 . There are other cases, however, such as swollen rubbers or networks prepared by cross-linking in solution, where $C_2 \approx 0$. A convincing and generally applicable molecular explanation for C_2 has proven elusive. Furthermore, for some materials the values of C_2 are even found to depend on the kind of experimental deformation employed, which suggests that Equation 10.6.11 is not the universally correct functional form.

10.7 Swelling of Gels

One of the distinguishing features of a lightly cross-linked polymer material is its ability to imbibe and retain a large volume of solvent. Examples include:

1. *Hot melt adhesives.* In this family of adhesives, the glue is applied as a liquid at high temperature and solidifies upon cooling. A typical formulation could include about 30% of a “thermoplastic elastomer,” a styrene–isoprene–styrene triblock copolymer. At low temperatures, the styrene segments segregate from the isoprene blocks to form roughly spherical styrene aggregates that act as cross-links. At high temperatures, however, the segregation is disrupted and the polymer flows. The remaining 70% of the material consists of low-molecular-weight species, largely to dilute the isoprene segments and make the resulting gel

softer, but also in part to plasticize the styrene domains and lower their glass transition temperature (see Section 12.6).

2. *Soft contact lenses.* Soft contact lenses are an example of a hydrogel—a network in which the polymer is either water soluble or at least water compatible. The original soft contact lenses were made largely from cross-linked poly(hydroxyethyl methacrylate), and were developed in the late 1960s.
3. *Diapers.* Clearly, the major function of a diaper material is to imbibe and retain a large quantity of aqueous solution, without dissolving. Diaper materials can absorb up to several hundred times their own weight. A typical ingredient is poly(acrylic acid) or (sodium polyacrylate). In this instance the network strands bear charged groups, which have the effect of greatly increasing the osmotic drive for water to enter the polymer and swell it.
4. *Biological tissue.* Much of biological tissue is essentially network material, although of course very complex. For example, in the “extra cellular matrix” collagen molecules intertwine in triple helices, which in turn aggregate to form fibrils, which in turn cross-link with the assistance of certain proteins to form three-dimensional gels.

Clearly, swollen networks are of fundamental importance in many areas of materials and biological science. In this section we will briefly address two aspects of the swelling phenomenon. First, we consider how the expression for the modulus of an ideal elastomer changes when solvent is incorporated. Then we consider swelling equilibrium; how much solvent can a network take up?

10.7.1 Modulus of a Swollen Rubber

We begin with a network formed at volume V_0 and then swollen with solvent to a new volume V . The volume fraction of polymer in the resulting gel is $\phi_2 = V_0/V$ (assuming additivity of volumes). We assume that the swelling is isotropic, so that the x , y , and z components of the end-to-end vector of each strand are increased by a factor of $(V/V_0)^{1/3} = \phi_2^{-1/3}$. We will reference the deformation of the already swollen network to the isotropically swollen dimensions so that the reference state terms (x_0^2 , y_0^2 , and z_0^2) in Equation 10.5.9 should each be multiplied by a factor of $\phi_2^{-2/3}$. Thus Equation 10.5.11 describing the entropy of deformation becomes

$$\Delta S = -\frac{\nu_e}{2} k \phi_2^{-2/3} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (10.7.1)$$

(The same result could be obtained by taking the front factor of Equation 10.6.5, $\langle h_i^2 \rangle / \langle h_0^2 \rangle$, and realizing that $\langle h_i^2 \rangle$ is increased by the same factor of $\phi_2^{-2/3}$.) Now let us apply an elongation along the x direction, so $\lambda_x = \lambda$, and $\lambda_y = \lambda_z = 1/\sqrt{\lambda}$, and compute the force as in Equation 10.5.13:

$$f = -T \left(\frac{\partial \Delta S}{\partial L} \right) = -\frac{T}{L_s} \left(\frac{\partial \Delta S}{\partial \lambda} \right) = \frac{\nu_e k T}{L_s} \phi_2^{-2/3} \left(\lambda - \frac{1}{\lambda^2} \right) \quad (10.7.2)$$

where now L_s refers to the swollen but unstrained network. To compute the stress, again referenced to the swollen but otherwise undeformed network, we divide by L_s^2 , recognizing that $L_s^3 = V$, not V_0 .

$$\begin{aligned} \sigma_t &= \frac{f}{L_s^2} = kT \frac{\nu_e}{V} \phi_2^{-2/3} \left(\lambda - \frac{1}{\lambda^2} \right) \\ &= kT \frac{\nu_e}{V_0} \phi_2^{1/3} \left(\lambda - \frac{1}{\lambda^2} \right) \end{aligned} \quad (10.7.3)$$

Comparing this result with Equation 10.5.15, the main result of swelling is that the stress in the swollen network is reduced by a factor of $\phi_2^{1/3}$ compared to the original network, and the modulus is reduced by the same factor when computed for constant cross-sectional area.

10.7.2 Swelling Equilibrium

Now we address the question of how much solvent a network can take up. Imagine we have a piece of lightly cross-linked polymer and we immerse it in a beaker of solvent. We have actually considered a very similar situation before. In Section 7.7 we treated a single polymer coil as an osmotic pressure experiment and saw how the good solvent exponent, $\nu = 3/5$, could be obtained from balancing the osmotic swelling of the coil (the solvent wants to dilute the monomers) and elastic resistance to swelling (loss of conformational entropy as the chain stretches out). Essentially the same balance will occur here. The chemical potential gradient will drive solvent into the piece of network, but the elasticity of the network will resist unlimited deformation. A state of *swelling equilibrium* will be reached, from which it is possible to determine both χ and the average molecular weight between cross-links.

The earliest theory of swelling equilibrium was that of Flory and Rehner [10], and we will now rederive their main result. We begin by considering the free energy of the swollen network to be composed of two parts, one due to the mixing of solvent and polymer and the other due to distortion of the network:

$$\Delta G = \Delta G_m + \Delta G_{el} \quad (10.7.4)$$

The former part can be represented by the Flory–Huggins theory expression (Equation 7.3.13), but with the network contributing no entropy of mixing ($N \rightarrow \infty$):

$$\Delta G_m = RT\{n_1 \ln \phi_1 + \chi n_1 \phi_2\} \quad (10.7.5)$$

In this case χ represents a combination of interaction energies between solvent and monomer and between solvent and cross-linking unit, but for low cross-link densities and/or systems such as styrene/divinylbenzene where the monomer and the cross-linker are chemically very similar, this complication is not important. The elastic part of ΔG is assumed to be purely entropic ($\Delta G_{el} = -T\Delta S_{el}$) and we simply invoke the rubber elasticity result (Equation 10.5.11):

$$\Delta S_{el} = \frac{-k\nu_e}{2} \{\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\} \quad (10.7.6)$$

where ν_e is the number of effective strands. However, it is time to address a complication. By a different analysis than that used in this chapter, Flory [4] obtained an expression for the entropy that contains an additional logarithmic term not present in Equation 10.7.6:

$$\Delta S_{el} = \frac{-k\nu_e}{2} \{\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 - \ln(\lambda_x \lambda_y \lambda_z)\} \quad (10.7.7)$$

A simple and very qualitative way to understand the origin of such a term is that there is an additional entropy gain for the placement of the end of each strand in space, as the volume of the network plus solvent increases. In this way the new term (which could be written as $-\ln \phi_2$) is equivalent to an ideal entropy of mixing contribution as derived in Section 7.3.1. Flory's analysis included a more explicit calculation of the entropy change associated with the cross-linking process, but in fact the appropriateness of the new logarithmic term in Equation 10.7.7 has not been without controversy [11]. Because the product of the three extension ratios is unity for a constant volume deformation, this term drops out in the unswollen network, so we have not missed anything by omitting it in the previous sections. We retain it now to be consistent with the Flory–Rehner result and we note that the factor of α^3 in Equation 7.7.10 from the Flory–Krigbaum theory for excluded volume also originates from inclusion of this term.

As in the consideration of the swollen network modulus above, we call the volume of the initial piece of polymer V_0 and the swollen volume V , but now the extension ratios are

$$\lambda_x = \lambda_y = \lambda_z = \lambda = \left(\frac{V}{V_0}\right)^{1/3} \quad (10.7.8)$$

Thus

$$\Delta S_{\text{el}} = \frac{-k\nu_e}{2} \{3\lambda^2 - 3 - \ln \lambda^3\} \quad (10.7.9)$$

At the point of swelling equilibrium, the chemical potential of the solvent inside the swollen network will equal that in the surrounding pure solvent, and so we have

$$\begin{aligned} \mu_1 - \mu_1^0 &= \Delta\mu_1 = \left(\frac{\partial \Delta G}{\partial n_1} \right)_{T,p} \\ &= \left(\frac{\partial \Delta G_{\text{m}}}{\partial n_1} \right)_{T,p} + \left(\frac{\partial \Delta G_{\text{el}}}{\partial \lambda} \right) \left(\frac{\partial \lambda}{\partial n_1} \right)_{T,p} \end{aligned} \quad (10.7.10)$$

If we assume no volume change on mixing as before, then the volume fraction of polymer in the swollen gel, ϕ_2 , is simply given by

$$\frac{1}{\phi_2} = \frac{V}{V_0} = \lambda^3 = \frac{(V_0 + n_1 \hat{V}_1)}{V_0} \quad (10.7.11)$$

where $\hat{V}_1$ is the molar volume of the solvent. If we differentiate this expression with respect to n_1 we obtain

$$3\lambda^2 \left(\frac{\partial \lambda}{\partial n_1} \right) = \frac{\hat{V}_1}{V_0} \quad (10.7.12)$$

The other two derivatives on the right-hand side of Equation 10.7.10 are also straightforward. The first is the solvent chemical potential of the Flory–Huggins theory (Equation 7.4.14) in the infinite molecular weight limit:

$$\left(\frac{\partial \Delta G_{\text{m}}}{\partial n_1} \right)_{T,p} = RT \{ \ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2 \} \quad (10.7.13)$$

The second is just

$$\left(\frac{\partial \Delta G_{\text{el}}}{\partial \lambda} \right)_{T,p} = \frac{RT\nu_e}{N_{\text{av}}} \left(3\lambda - \frac{3}{2\lambda} \right) \quad (10.7.14)$$

where we have multiplied and divided by Avogadro's number to put this term on a molar basis. By combining Equation 10.7.10 and Equation 10.7.12 through Equation 10.7.14 we obtain

$$\Delta\mu_1 = 0 = RT \left\{ \ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2 + \frac{\nu_e}{N_{\text{av}}} \frac{\hat{V}_1}{V_0} \left(\frac{1}{\lambda} - \frac{1}{2\lambda^3} \right) \right\} \quad (10.7.15)$$

or, using Equation 10.7.8 to eliminate λ , we obtain

$$\ln(1 - \phi_e) + \phi_e + \chi \phi_e^2 = \frac{\nu_e}{N_{\text{av}}} \frac{\hat{V}_1}{V_0} \left(\frac{\phi_e}{2} - \phi_e^{1/3} \right) \quad (10.7.16)$$

where $\phi_e = \phi_2$ is used to emphasize that we have swelling equilibrium. The prefactor on the right-hand side includes the number of strands per unit volume in the original network, ν_e/V_0 , and from Equation 10.6.7 this can be written as

$$\frac{\nu_e}{V_0} = \frac{\rho N_{\text{av}}}{M_x} \left(1 - \frac{2M_x}{M} \right) \quad (10.7.17)$$

where M_x is the average molecular weight between cross-links. Thus if χ is known, Equation 10.7.16 and Equation 10.7.17 can be solved for M_x using the measured value of V (although in practice it is more common to actually weigh the dry and swollen polymer, and convert to volume through the known densities of polymer and solvent). The following numerical example gives an idea of the magnitude of the swelling.

Example 10.4

Calculate the predicted volumetric swelling for the polyisoprene network of Example 10.1, when exposed to a reservoir of cyclohexane at room temperature.

Solution

The polyisoprene chains had $M = 150,000$ with the extent of vulcanization $= 0.003$. The monomer molecular weight is 68 g/mol, so the average number of cross-links per chain is $(150,000 \times 0.003)/68 = 6.6$, and thus $M_x \approx 150,000/(6.6) = 23,000$. Utilizing Equation 10.7.17 and a density of 0.91 g/cm^3 for polyisoprene gives

$$\frac{\nu_e}{N_{av}V_0} = \frac{0.91}{23,000} \left(1 - \frac{46,000}{150,000} \right) = 2.7 \times 10^{-5} \text{ mol strands/cm}^3$$

The last ingredient we need in order to apply the Flory–Rehner expression is a value for χ . Back in Section 7.6.2 we considered ways to estimate χ using solubility parameters, and the necessary values were given in Table 7.1. Using Equation 7.6.6 we have

$$\chi = \frac{\hat{V}_1}{RT} (\delta_1 - \delta_2)^2 \approx \frac{108}{2 \times 300} (8.2 - 8.1)^2 \approx 0.002$$

where 108 cm^3 is the molar volume of cyclohexane.

Returning to the Flory–Rehner expression, that is, Equation 10.7.16, we have values for all the quantities except the desired ϕ_e , but the equation does not reduce to a simple algebraic expression. To proceed we anticipate that $\phi_e \ll 1$, and then the left-hand side can be simplified to $(\chi - 0.5) \phi_e^2$ using the expansion $\ln(1 - \phi_e) \approx -\phi_e - \phi_e^2/2$. Similarly, on the right-hand side we can expect $\phi_e^{1/3} \gg \phi_e/2$. This gives

$$\phi_e^{5/3} \approx \frac{108 \times 2.7 \times 10^{-5}}{0.5 - 0.002} = 0.0058$$

or $\phi_e \approx 0.046$. This gives a volumetric expansion of $1/0.046 = 22$ times. This value also justifies the small ϕ_e approximation that we have used to simplify the algebra. However, see Problem 15 for a numerically more realistic version of this calculation.

A test of the Flory–Rehner theory (Equation 10.7.16) is provided by the data in Figure 10.16. A variety of butyl rubbers with differing degrees of cross-linking were swollen to equilibrium and then extended to $\lambda = 4$. The results show a power law dependence of force on $\phi_e^{-5/3}$. This is consistent with Equation 10.7.16 in the limit of $\phi_e \rightarrow 0$, as can be seen by taking this limit on both sides of the equation as in the preceding example. (Note that force $\sim G \sim 1/M_x$.)

10.8 Chapter Summary

In this chapter we have considered two routes to network formation, cross-linking of preformed chains and direct polymerization including multifunctional monomers. The former is the preferred route to elastomers, or lightly cross-linked, low T_g materials, and the latter is commonly employed to produce thermosets for high-temperature applications. We then developed the theory of rubber elasticity in some detail, covering general thermodynamic aspects, the statistical theory in the ideal

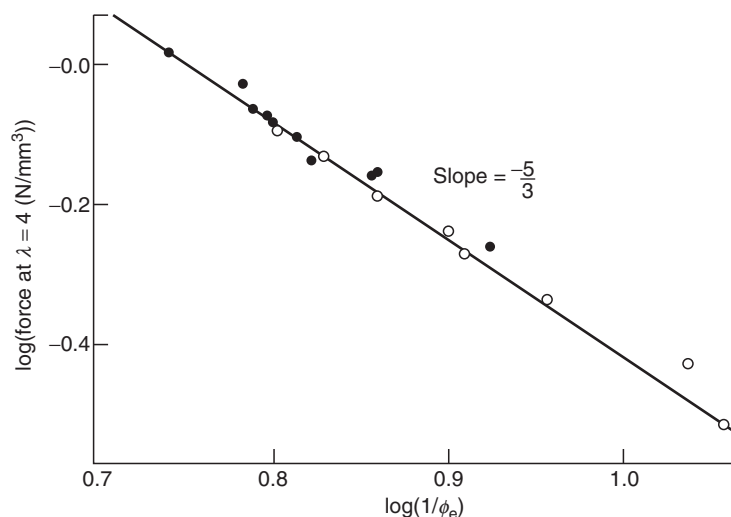


Figure 10.16 Force at constant extension ($\lambda = 4$) versus equilibrium swelling for butyl rubbers with different degrees of cross-linking, showing the predicted dependence on $\phi_e^{5/3}$. (Data from Flory, P.J., *Ind. Engng. Chem.*, 38, 417, American Chemical Society, 1948. Reproduced from Treloar, L.R.G., *The Physics of Rubber Elasticity*, 3rd ed., Clarendon Press, Oxford, 1975. With permission.)

case, some modifications to account for nonideal features of the response of real materials, and the case of networks swollen with solvent. The main points may be summarized as follows:

1. When cross-linking preformed chains with weight-average degree of polymerization N_w , the “gel point” is predicted to occur when the fraction of monomers participating in cross-links is equal to $1/N_w$. In practice, this tends to underestimate the necessary extent of reaction.
2. For multifunctional monomers, explicit predictions for the gel point can be developed using the principle of equal reactivity and probability arguments appropriate to the particular polymerization mechanism and combination of monomers. In practice, these expressions also tend to underestimate the extent of reaction needed to reach the gel point.
3. Analysis of rubber elasticity via macroscopic thermodynamics is relatively straightforward, the main new ingredient being the incorporation of the work of deformation into the free energy. An ideal elastomer is defined as one for which the force resisting deformation is entirely entropic, which is a reasonable approximation for many rubbery materials.
4. The molecular basis of rubber elasticity rests in the reduction of conformational degrees of freedom when a single Gaussian chain is extended. A single Gaussian chain acts as a Hooke’s law spring, with a stiffness that is proportional to absolute temperature.
5. Straightforward expressions for the force required to deform an ideal elastomer are obtained by modeling the network as a collection of Gaussian strands and by making an assumption as to how the macroscopic deformation is transmitted to each strand. The resulting shear and extensional moduli are proportional to the number of strands per unit volume.
6. Networks or gels are often capable of absorbing more than 100 times their own weight in solvent, a phenomenon that is central to many applications, and that can be understood as a simple balance between the osmotic drive to dilute the polymer and the entropic resistance to strand extension.
7. Although the statistical theory of rubber elasticity captures the main features of a wide variety of experimental phenomenology, attempts to bring the theory into quantitative agreement with experiment have met with rather mixed success.

Problems

1. A constant force is applied to an ideal elastomer, assumed to be a perfect network. At an initial temperature T_i the length of the sample is L_i . The temperature is raised to T_f and the final length is L_f . Which is larger: L_i or L_f (remember F is a constant and $T_f > T_i$)? Suppose a wheel were constructed with spokes of this same elastomer. From the viewpoint of an observer, the spokes are heated near the 3 o'clock position—say, by exposure to sunlight—while other spokes are shaded. Assuming the torque produced can overcome any friction at the axle, would the observer see the wheel turn clockwise or counterclockwise? How would this experiment contrast, in magnitude and direction, with an experiment using metal spokes?
2. An important application of Equation 10.5.15 is the evaluation of M_x ; P.J. Flory, N. Rabjohn, and M.C. Shaffer measured the tensile force required for 100% elongation of synthetic rubber with variable cross-linking at 25°C.[†] The molecular weight of the uncross-linked polymer was 225,000, its density was 0.92 g/cm³, and the average molecular weight of a repeat unit was 68. Use Equation 10.5.15 to estimate M_x for each of the following samples and compare the calculated value with that obtained from the known fraction of repeat units cross-linked:

Fraction cross-linked	0.005	0.010	0.015	0.020	0.025
F/A (lb-force/in. ²)	61.4	83.2	121.8	148.0	160.0

- How important for this system is the end group correction introduced in Equation 10.6.7?
3. Develop the equivalent to Equation 10.2.3 and Equation 10.2.5 for the third system in Figure 10.4, that is, $AB + BB + A_3$.
 4. The Carothers equation (Equation 10.2.9) can also be used as the basis of an estimate of the extent of reaction at gelation. Consider the value implied for each of the parameters in the Carothers equation at the threshold of gelation, and derive a relationship between p_c and f on the basis of this consideration. Compare the predictions of the equation you have derived with those of Equation 10.2.5 for a mixture containing 2 mol A_3 , 7 mol AA , and 10 mol BB . Criticize or defend the following proposition: the Carothers equation gives higher value for p_c than Equation 10.2.5 because the former is based on the fraction of reactive groups that have reacted and hence considers wasted loops that the latter disregards.
 5. Categorize the following mixtures as to whether they can form linear, branched, or network structures:

(a) $A_2 + B_2 + AB$	(b) $AB_2 + A_2$
(c) $AB + AB_2$	(d) $A_3 + B_2 + A_2$
(e) $AB + B_3$	(f) $A_2B_2 + A_2 + B_2$
 6. Suppose you have a balloon made of an ideal elastomer that is inflated to a reasonable size with an ideal gas at room temperature. If the temperature of the balloon plus gas system is then increased to 100°C, will the balloon expand, contract, or stay the same size? Justify your answer.
 7. Find the relation between the (true) stress σ and the strain λ for a piece of ideal rubber in biaxial extension. Assume the rubber has initial area A_0 and thickness d_0 , and let the final area be $A = \lambda^2 A_0$.
 8. Use the result from the previous problem to calculate the relation between the pressure of an ideal gas, p , inside a balloon made from an ideal elastomer, expanded to a radius $R = \lambda R_0$, where R_0 is the initial radius. Use a version of the Young–Laplace equation to relate the excess pressure (inside the balloon minus outside) to the stress in the rubber, $p = 2d\sigma/R$, where d is the thickness of the balloon skin. Empirically, it often seems harder to “get started” blowing up a balloon, than to blow it up further beyond a certain point. Explain this observation based on your result for p versus λ .

[†] P.J. Flory, N. Rabjohn, and M.C. Shaffer, *J. Polym. Sci.*, 4, 225 (1949).

9. Show that Equation 10.3.2 and Equation 10.3.3 are equivalent definitions of Poisson's ratio.
10. Use Equation 10.4.22 and the data in Figure 10.8a to assess whether or not the heat capacity at constant length, C_L , is comparable to typical values of C_p for rubber of 2 J/g/K. Be careful with the stated units of stress (kg/cm²) in Figure 10.8a.
11. Estimate the temperature increase in a rubber band when extended to $\lambda = 8$ at room temperature. Assume C_L is 2 J/g/K and $\rho = 1$ g/cc.
12. The following data represent force (f , in piconewtons) versus extension (h , in microns) for a single λ -DNA molecule, measured at room temperature in salt solutions.[†] These data therefore represent an opportunity to test basic assumptions of the theory of rubber elasticity. Try to fit these data in three ways. First, use the Gaussian expression; restrict the fit to the low extension part of the curve. Second, try the inverse Langevin function, approximated in Equation 10.6.4. Third, try the following formula derived for the worm-like chain (recall Chapter 6) in C. Bustamante et al.[‡]

h (μm)	f (pN)	h (μm)	f (pN)	h (μm)	f (pN)
10.1	0.0338	25.0	0.367	30.3	3.03
10.8	0.0335	25.6	0.364	31.2	5.57
17.6	0.102	26.4	0.486	31.3	6.82
18.2	0.102	27.1	0.604	31.7	11.9
22.4	0.218	28.5	1.08	32.0	12.2
23.0	0.217	29.0	1.53	32.1	18.3
24.3	0.382	30.3	3.39	32.2	17.0

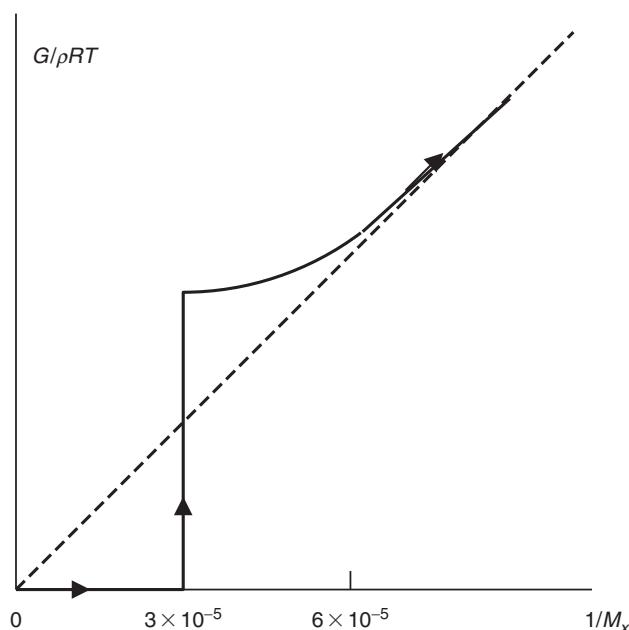
$$f = \frac{kT}{\ell_p} \left(\frac{1}{4(1 - h/L)^2} - \frac{1}{4} + \frac{h}{L} \right)$$

Comment on the success or failure of the various expressions and provide values for the contour length, L , and the persistence length.

13. A rubber band, made of a styrene-butadiene random copolymer, is swollen to equilibrium in toluene; the volume increases by a factor of 5. Taking $\chi \approx 0.4$, estimate the number of strands per unit volume, and therefore the extent of cross-linking. Estimate Young's modulus for both the dry and swollen rubber bands.
14. According to the Flory-Rehner theory, what value of χ would be required to get absolutely no uptake of solvent for a typical rubber? What value of χ would restrict the uptake to less than 5% by volume?
15. In Example 10.4, the estimated value of χ was 0.002, which is not realistic. Revisit the discussion in Section 7.6, and use a more realistic estimate for χ . How much does the rubber swell at equilibrium in this case? Is it significantly different from the answer in Example 10.4?
16. On the following plot of a normalized equilibrium shear modulus ($G/\rho RT$) versus an inverse "effective" molecular weight between cross-links ($1/M_x$) are two curves. The first is a straight dashed line with unit slope to "guide the eye" (and the brain). The second represents the modulus of a real polymer as it undergoes progressive cross-linking (the arrow represents the course of the modulus with extent of reaction). Why does the modulus shoot up at $1/M_x \approx 3 \times 10^{-5}$ mol/g? Why does the modulus exceed the unit slope line, just after $1/M_x \approx 3 \times 10^{-5}$ mol/g? Estimate M_c for this polymer. (Note that the last two questions will be easier to answer after reading Section 11.6.)

[†] S.B. Smith, L. Finzi, and C. Bustamante, *Science*, 258, 1122 (1992).

[‡] C. Bustamante, J. Marko, E. Siggia, and S. Smith, *Science*, 265, 1599 (1994).



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