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.

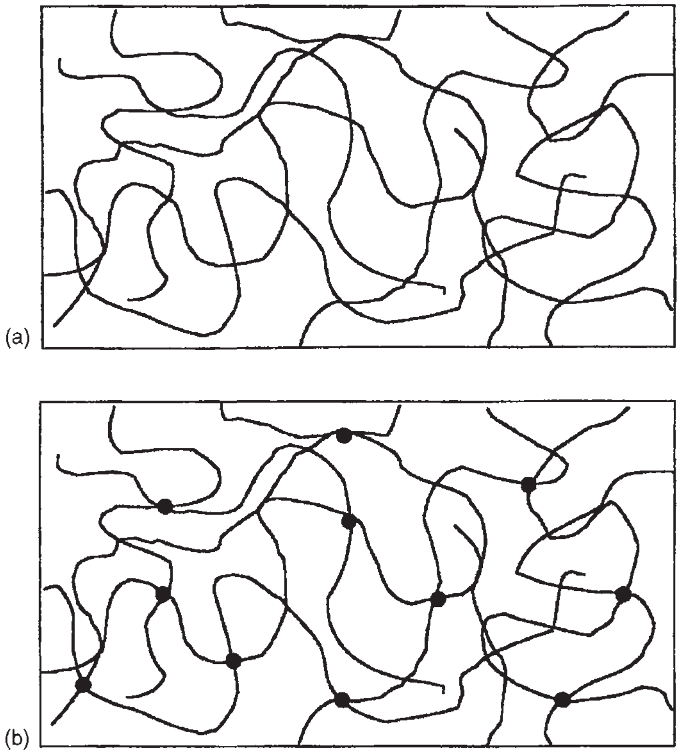

Figure 10.1 Schematic illustration of (a) an uncross-linked melt or concentrated solution of flexible chains and (b) the same material after cross-links are introduced.

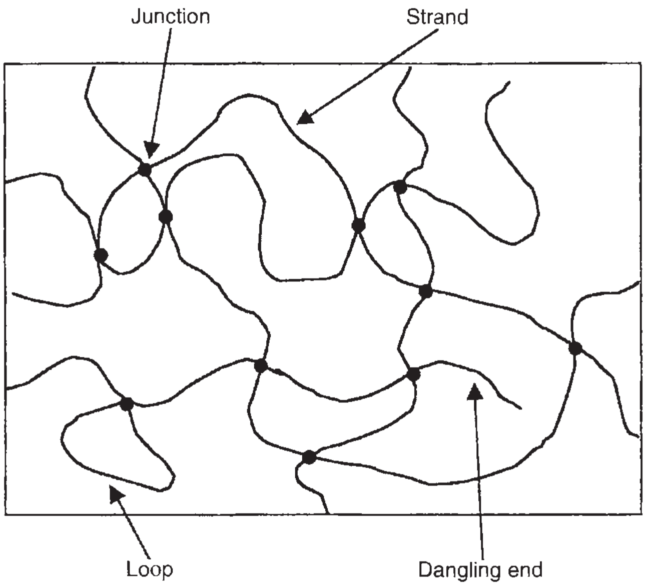

Figure 10.2 Schematic illustration of network elements defined in the text.

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 $x \to \infty$, and therefore we need $Np \geq 1$. Conversely, if $Np < 1$, $(Np)^x \to 0$ as $x \to \infty$. Consequently, the critical extent of reaction, p_c, at which an infinite network first appears, the *gel point*, is given by

$$p_c = \frac{1}{N-1} \approx \frac{1}{N} \tag{10.1.1}$$

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

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

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

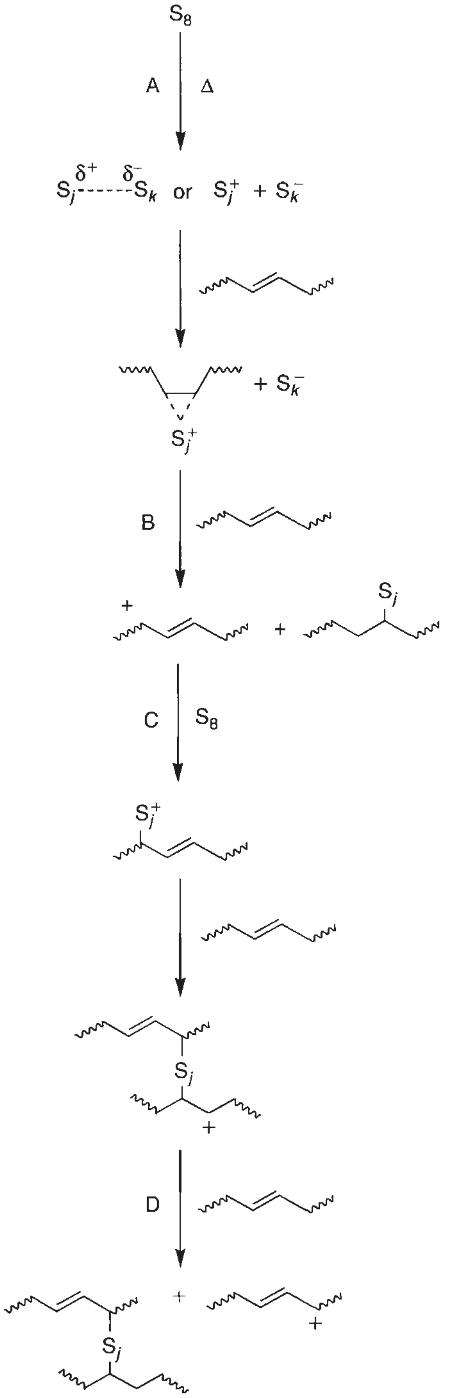

Figure 10.3 Possible mechanism for vulcanization of 1,4-polybutadiene with sulfur, following Odian. (From Odian, G., *Principles of Polymerization*, 2nd ed., Wiley, New York, 1981.)

we must raise 0.997 to the Nth 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

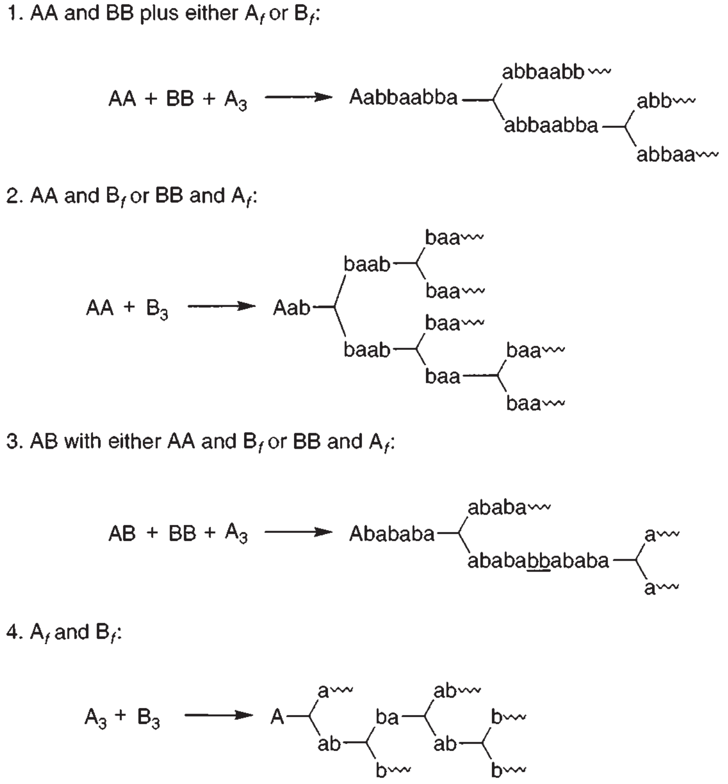

Figure 10.4 Possible reaction schemes for monomer mixtures containing A and B functional groups that can lead to network formation.

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 mulifunctional molecules is defined by the ratio

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

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:

   $A_{f-1}\text{abB} + \text{AA} \rightarrow A_{f-1}\text{abbaA}$

   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:

   $A_{f-1}\text{abbaA} + \text{BB} \rightarrow A_{f-1}\text{abbaabB}$

   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

   A_{f-1}abbaabB + AA + BB $\longrightarrow\longrightarrow\longrightarrow$ A_{f-1}a(bbaa)$_i$bB

   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:

   A_{f-1}a(bbaa)$_i$bB + A_f $\rightarrow$ A_{f-1}a(bbaa)$_i$bbaA_{f-1}

   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:

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

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

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

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

$$\alpha_c = \frac{1}{f-1} \tag{10.2.4}$$

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:

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

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

$$\langle f \rangle \equiv \frac{\sum_i n_i f_i}{\sum_i n_i} \tag{10.2.6}$$

where n_i and f_i are the number of molecules and the functionality of the ith 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:

$$N_n = \frac{n_0}{n} \tag{10.2.7}$$

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

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

Elimination of n between these expressions gives

$$N_n = \frac{2}{2 - p\langle f \rangle} \tag{10.2.9}$$

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/A_f 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 A_3 polymerization mixture is prepared in which $\nu_\text{A}^0 = \nu_\text{B}^0 = 3.00$ mol, with 10% of the A groups contributed by A_3. Use Equation 10.2.9 to calculate N_n for $p = 0.970$ and p for $N_\text{n} = 200$. 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 $3n_\text{AAA} + 2n_\text{AA} = 3.00$ and $3n_\text{AAA}/3 = 0.100$, we find that $n_\text{AA} = 1.350$ and $n_\text{AAA} = 0.1000$. Since $n_\text{BB} = 1.500$ 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 $\langle f \rangle = 2.034$:

$$N_\text{n} = \frac{2}{2 - 0.97(2.034)} = 73.8$$

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

$$N_\text{n} = \frac{1}{1-p} = \frac{1}{1-0.97} = 33.3$$

Solve Equation 10.2.9 with $N_\text{n} = 200$ and $\langle f \rangle = 2.034$:

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

Solve Equation 10.2.9 with $N_\text{n} = 200$ and $\langle f \rangle = 2$:

$$p = \left(1 - \frac{1}{N_\text{n}}\right) = \left(1 - \frac{1}{200}\right) = 0.995$$

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

$$N_n = \frac{2}{2 - \alpha f} \tag{10.2.10}$$

and

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

from which it follows that

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

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

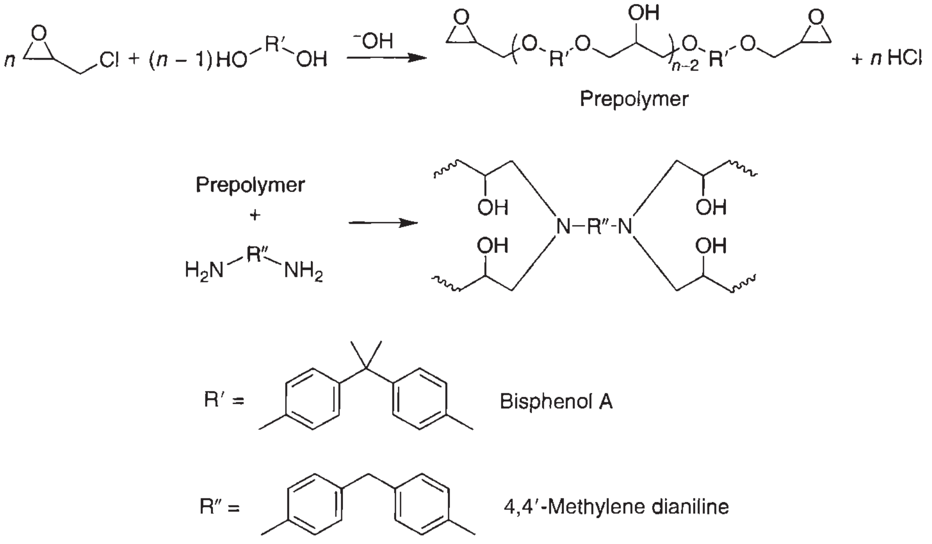

Figure 10.5 Illustration of an epoxy formulation. A prepolymer, formed by base-catalyzed condensation of an excess of epichlorohydrin with bisphenol A, is cured by cross-linking with 4,4′-methylene dianiline.

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

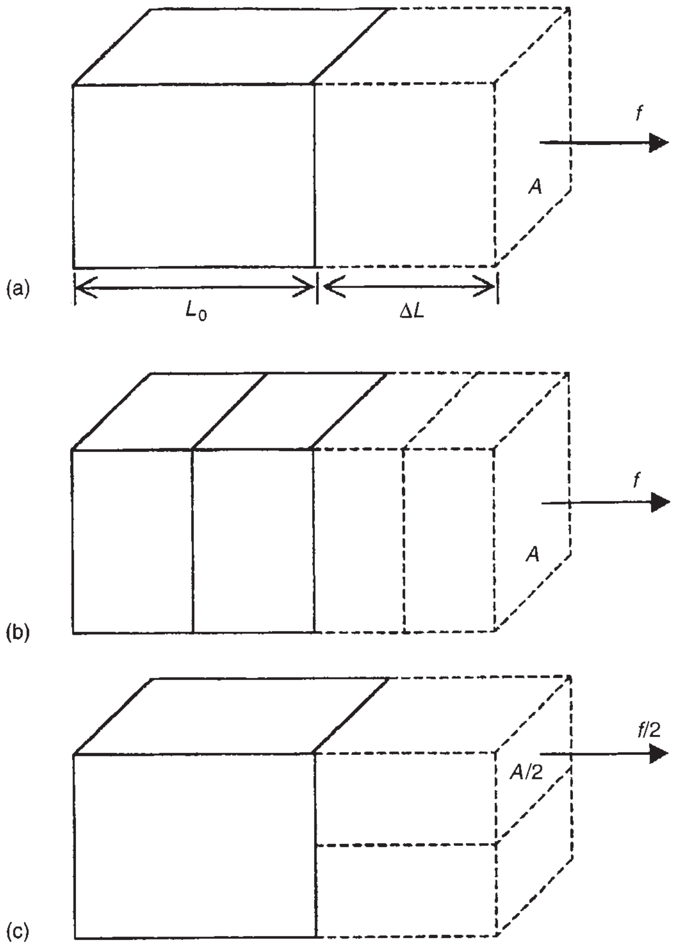

Figure 10.6 (a) A force f applied to area A extends the length of the sample from L_0 by an amount ΔL. Parts (b) and (c) illustrate the argument that $f/A \sim \Delta L/L_0$.

argument could be applied for any number of slices; hence it is the quantity $\Delta L/L_0$ that is proportional to the force.

2. 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 $\Delta L/L_0$.
3. 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

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

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/length^2, or N/m^2(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:

$$-\frac{\Delta d}{d} = -\frac{\Delta h}{h} = \nu\frac{\Delta L}{L_0} = \nu\varepsilon \tag{10.3.2}$$

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

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

where V is the volume of the sample (see Problem 9). Thus, if the volume does not change on elongation, the factional 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:

$$G2(1 + \nu) = E \tag{10.3.4a}$$

$$K3(1 - 2\nu) = E \tag{10.3.4b}$$

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 $\mathrm{d}L$ as

$$\mathrm{d}w = f\,\mathrm{d}L \tag{10.4.1}$$

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, $\mathrm{d}L$ and $\mathrm{d}w$ are all defined to be positive quantities. Thus $\mathrm{d}w$ 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 $\mathrm{d}U$ in the internal energy of a system as the sum of the heat absorbed by the system, $\mathrm{d}q$, plus the work done on the system, $\mathrm{d}w$:

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \tag{10.4.2}$$

The element of work is generally written $-p\,\mathrm{d}V$, where p is the external pressure, but with the possibility of an elastic contribution, it is $-p\,\mathrm{d}V + f\mathrm{d}L$. With this substitution, Equation 10.4.2 becomes

$$\mathrm{d}U = \mathrm{d}q - p\,\mathrm{d}V + f\,\mathrm{d}L \tag{10.4.3}$$

A consistent sign convention has been applied to the pressure–volume work term: a positive $\mathrm{d}V$ 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 $\mathrm{d}q$ as

$$\mathrm{d}S = \frac{\mathrm{d}q}{T} \tag{10.4.4}$$

This relationship can be used to replace $\mathrm{d}q$ by $T\,\mathrm{d}S$ 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:

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + f\,\mathrm{d}L \tag{10.4.5}$$

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

$$G = H - TS \tag{10.4.6}$$

where the enthalpy

$$H = U + pV \tag{10.4.7}$$

Combining the last two results and taking the derivative gives

$$\mathrm{d}G = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p - T\,\mathrm{d}S - S\,\mathrm{d}T \tag{10.4.8}$$

Comparing Equation 10.4.8 with Equation 10.4.5 enables us to replace several of these terms by $f\,\mathrm{d}L$

$$\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T + f\,\mathrm{d}L \tag{10.4.9}$$

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 $\mathrm{d}G$ is

$$\mathrm{d}G = \left(\frac{\partial G}{\partial p}\right)_{T,L}\mathrm{d}p + \left(\frac{\partial G}{\partial T}\right)_{p,L}\mathrm{d}T + \left(\frac{\partial G}{\partial L}\right)_{p,T}\mathrm{d}L \tag{10.4.10}$$

Comparing Equation 10.4.10 and Equation 10.4.9 enables us to write

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

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:

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

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

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

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

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

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

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

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

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

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

$$dA = dU - T\,dS \tag{10.4.17}$$

which may then be compared to Equation 10.4.5 to yield

$$dA = f\,dL - p\,dV \tag{10.4.18}$$

At both constant temperature and constant volume, therefore,

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

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

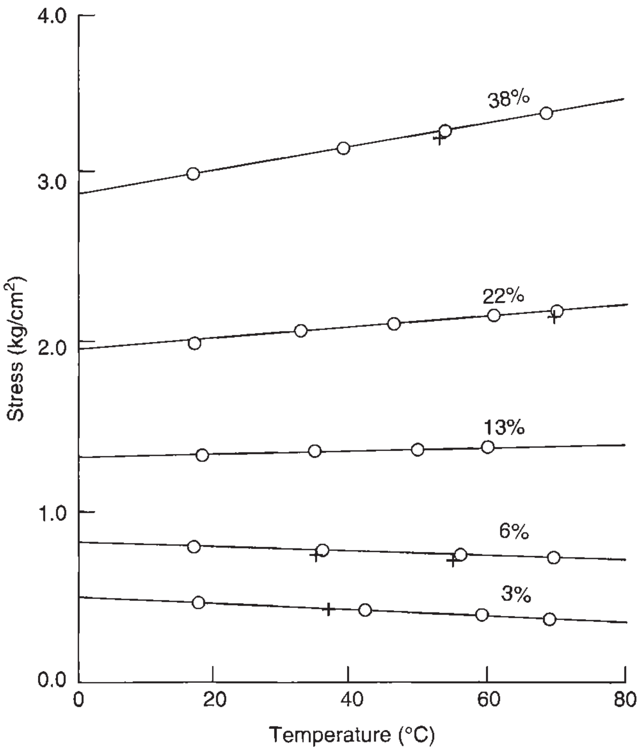

Figure 10.7 Stress at a constant length for natural rubber, at the indicated elongations, as a function of temperature. Thermoelastic inversion occurs below about 10% elongation. (Data from Anthony, R.L., Caston, R.H., and Guth, E., *J. Phys. Chem.*, 46, 826, 1942. With permission.)

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

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

and

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

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 $\mathrm{d}q = -\mathrm{d}w$. The work is given by Equation 10.4.1 and the heat by Equation 10.4.4; therefore the temperature change is

$$\Delta T = \frac{1}{C_\mathrm{L}} \int f\,\mathrm{d}L = -\frac{T}{C_\mathrm{L}} \int_{L_0}^{L} \left(\frac{\partial S}{\partial L}\right)_T \mathrm{d}L \tag{10.4.22}$$

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

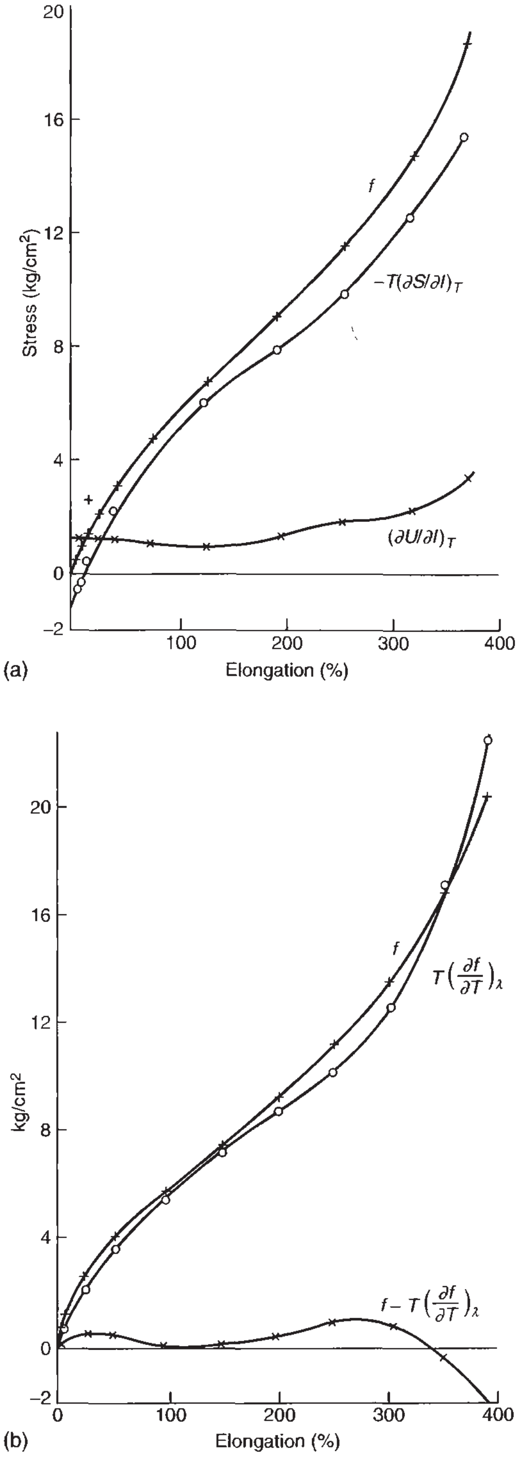

Figure 10.8 Stress versus elongation for natural rubber, resolved into internal energy and entropic contributions, at (a) constant temperature and (b) constant strain. (Data from Anthony, R.L., Caston, R.H., and Guth, E., *J. Phys. Chem.*, 46, 826, 1942. With permission.)

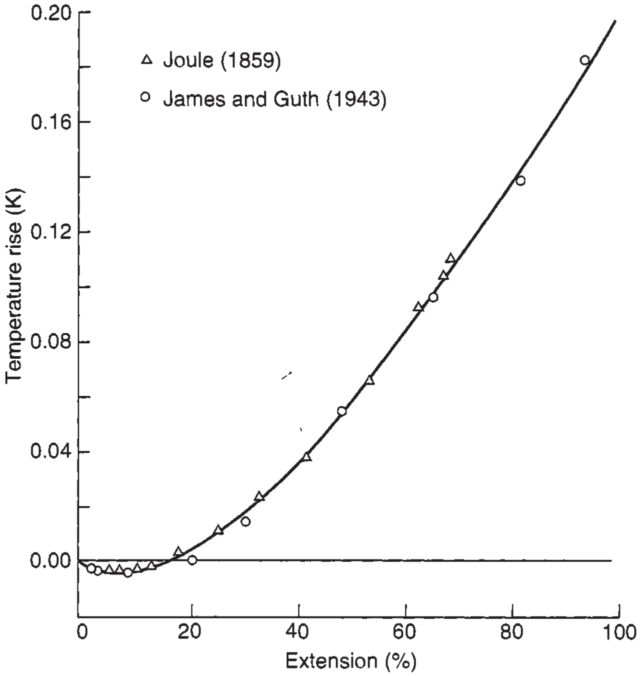

Figure 10.9 Temperature change during adiabatic extension of natural rubber. (Data from Joule, J.P., *Phil. Trans. R. Soc.*, 149, 91, 1859; James H.M. and Guth, E., *J. Chem Phys.*, 11, 455, 1943; 15, 669, 1947.) (From Treloar, L.R.G., *The Physics of Rubber Elasticity*, 3rd ed., Clarendon Press, Oxford,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

$$S = k \ln \Omega \tag{10.5.1}$$

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

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

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):

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

where we define the normalization factor, β as

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

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

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

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

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

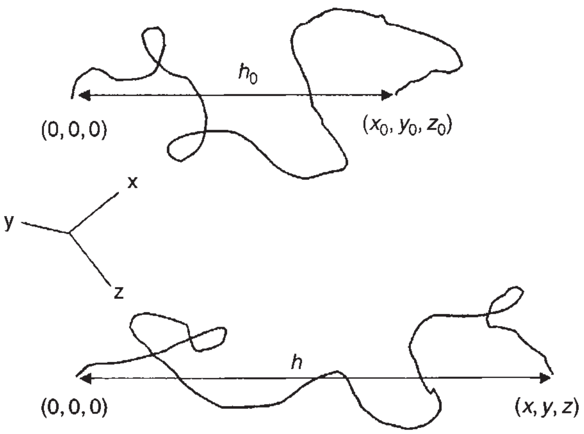

Figure 10.10 Extension of a single Gaussian chain from initial end-to-end distance h_0 to final end-to-end distance h.

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

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

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

$$V = L_xL_yL_z = V_0 = L_0^3; \quad \lambda_x\lambda_y\lambda_z = 1 \tag{10.5.8}$$

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

$$\begin{aligned}\Delta S_{\text{strand}} &= k\ln AP_{\text{f}} - k\ln AP_{\text{i}} = k\ln\left(\frac{P_{\text{f}}}{P_{\text{i}}}\right)\\ &= -k\pi\beta(x^2+y^2+z^2) - \left(-k\pi\beta(x_0^2+y_0^2+z_0^2)\right)\\ &= -k\frac{3}{2N_xb^2}\left(x_0^2(\lambda_x^2-1)+y_0^2(\lambda_y^2-1)+z_0^2(\lambda_z^2-1)\right)\end{aligned} \tag{10.5.9}$$

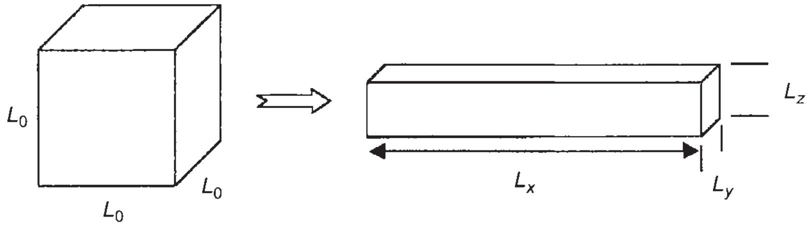

Figure 10.11 Deformation of a cube of material subjected to uniaxial elongation along x.

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

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

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

$$\Delta S = -\frac{\nu_{\text{e}} k}{2}\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right) \tag{10.5.11}$$

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

$$\Delta S = -\frac{\nu_{\text{e}} k}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right) \tag{10.5.12}$$

and the force is given by

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

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:

$$\sigma_{\text{t}} = \frac{f}{\text{area}} = \frac{\lambda f}{L_0^2} = kT\frac{\nu_{\text{e}}}{V}\left(\lambda^2 - \frac{1}{\lambda}\right) \tag{10.5.14}$$

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

$$\sigma_{\text{t}} = kT\frac{\nu_{\text{e}}}{V}\left(\lambda - \frac{1}{\lambda^2}\right) \tag{10.5.15}$$

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 $\mathrm{d}\lambda = \mathrm{d}\varepsilon$):

$$E = \lim_{\lambda \to 1} \frac{\partial \sigma_{\text{t}}}{\partial \lambda} = 3kT\frac{\nu_{\text{e}}}{V} \tag{10.5.16}$$

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):

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

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 $M_x = 10{,}000$ g/mol, Equation 10.5.17 gives a modulus of 2.5×10^6 dyn/cm^2, or 0.25 MPa. Typical values for elastomers fall within an order of magnitude of this number.

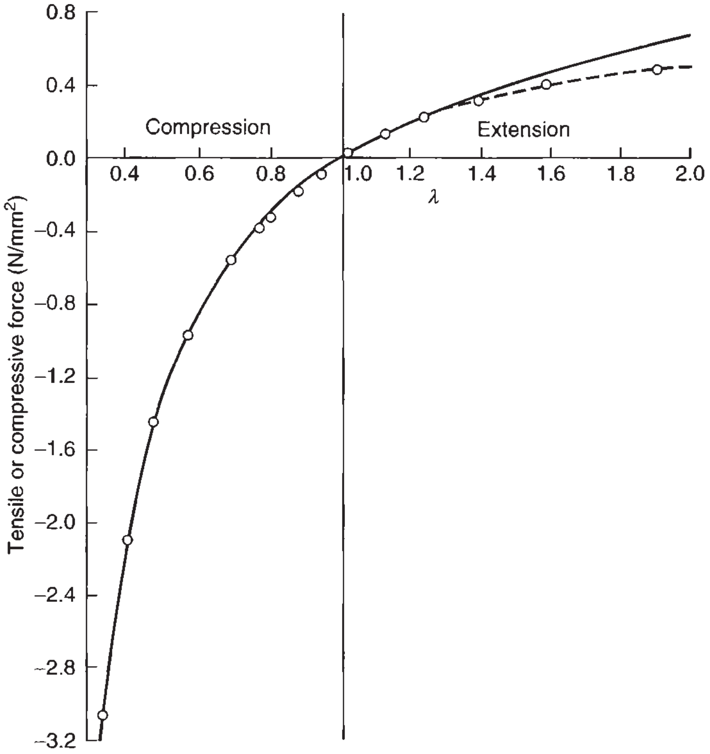

Figure 10.12 Stress for cross-linked natural rubber in compression and extension. (Data from Treloar, L.R.G., *Trans. Faraday Soc.*, 40, 59, 1944. With permission.)

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.

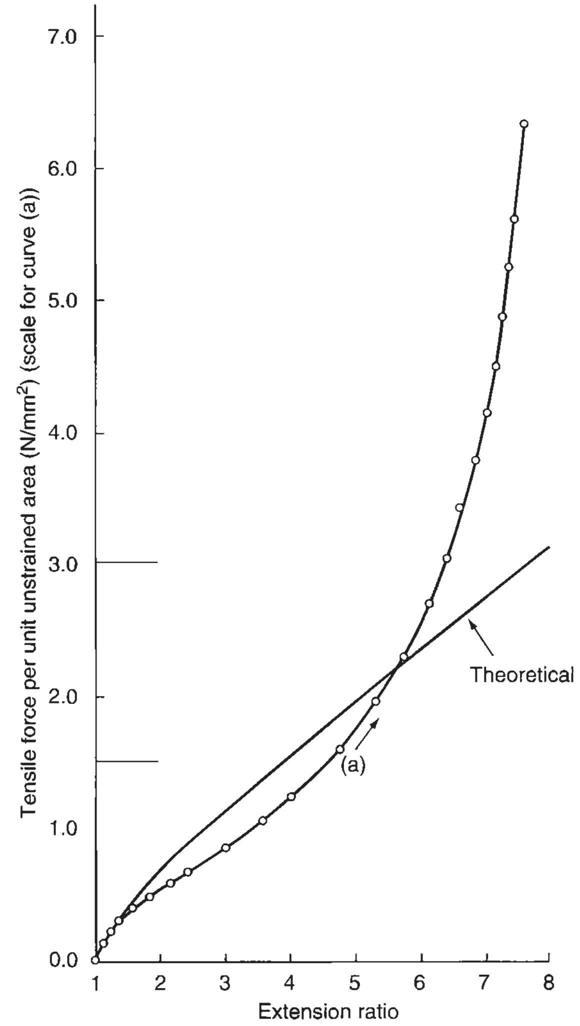

Figure 10.13 Same sample as in Figure 10.12, but now subjected to simple extension and much larger extension ratios (λ). (Data from Treloar, L.R.G., *Trans. Faraday Soc.*, 40, 59, 1944. With permission.)