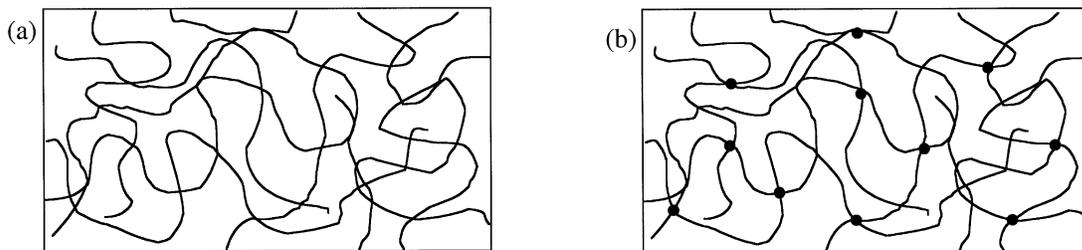


# 10

## 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 Chapters 12 and 13, respectively. We will define the term network more precisely shortly, 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 crosslinked 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 crosslinking 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: crosslinking of preformed chains, and polymerization with multifunctional monomers. In Sections 3-6 we describe successively elastic deformations, thermodynamics of elasticity, the “ideal” molecular description of rubber elasticity, and then extensions to the idealized theory. In the final section we consider the swelling of polymer networks with solvent.



**Figure 10.1**

Schematic illustration of (a) an uncrosslinked melt or concentrated solution of flexible chains, and (b) the same material after crosslinks are introduced.

### 10.1A Definitions

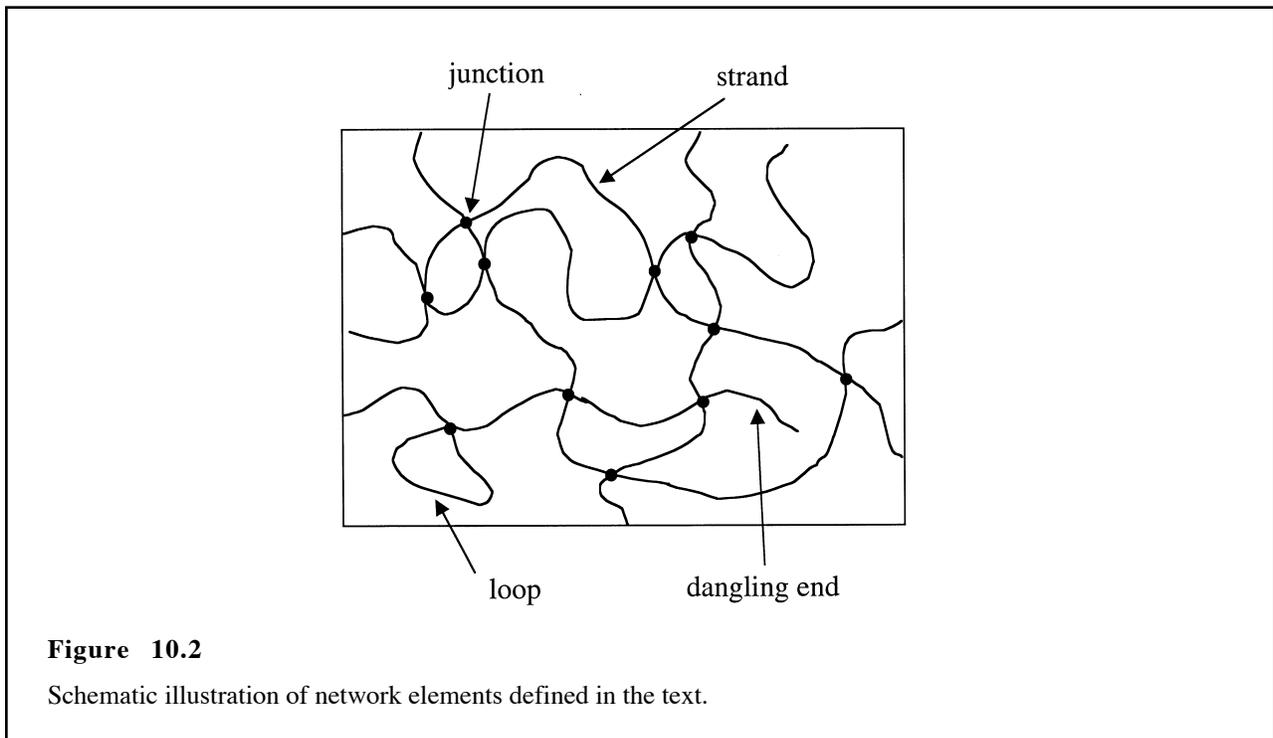
Figure 10.1 provides a pictorial representation of a network polymer. In panel (a) there is a schematic representation of a collection of polymer chains, which could be either in solution or in the melt. In panel (b), a certain number of chemical linkages have been introduced between monomers on different chains (or on the same chain). If enough such *crosslinks* have been 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 crosslinks. 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 *crosslink* 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 crosslinking pictured in Figure 10.1 the functionality is usually four. Note that a crosslink might simply connect two chains, but it would not be a junction until it became part of an infinite network.

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 crosslink, with no intervening junctions. A loop might be formed by an intramolecular crosslinking 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 crosslinks, 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 served 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.

### 10.1B The gel point

We now consider the following question: given a collection of polymer chains, how many random crosslinks 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 crosslinking 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 crosslinks. Suppose we start on a chain selected at random, and find a crosslink; 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 crosslink? 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  $\geq 1$  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 eq 10.1.1 probably underestimates the true gel point, because some fraction of crosslinking 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 eq 10.1.1. Let us return to our first chain, find the crosslink, and then ask, what is the average length of the next chain? As the crosslinking 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 crosslink 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,  $N_w$ .

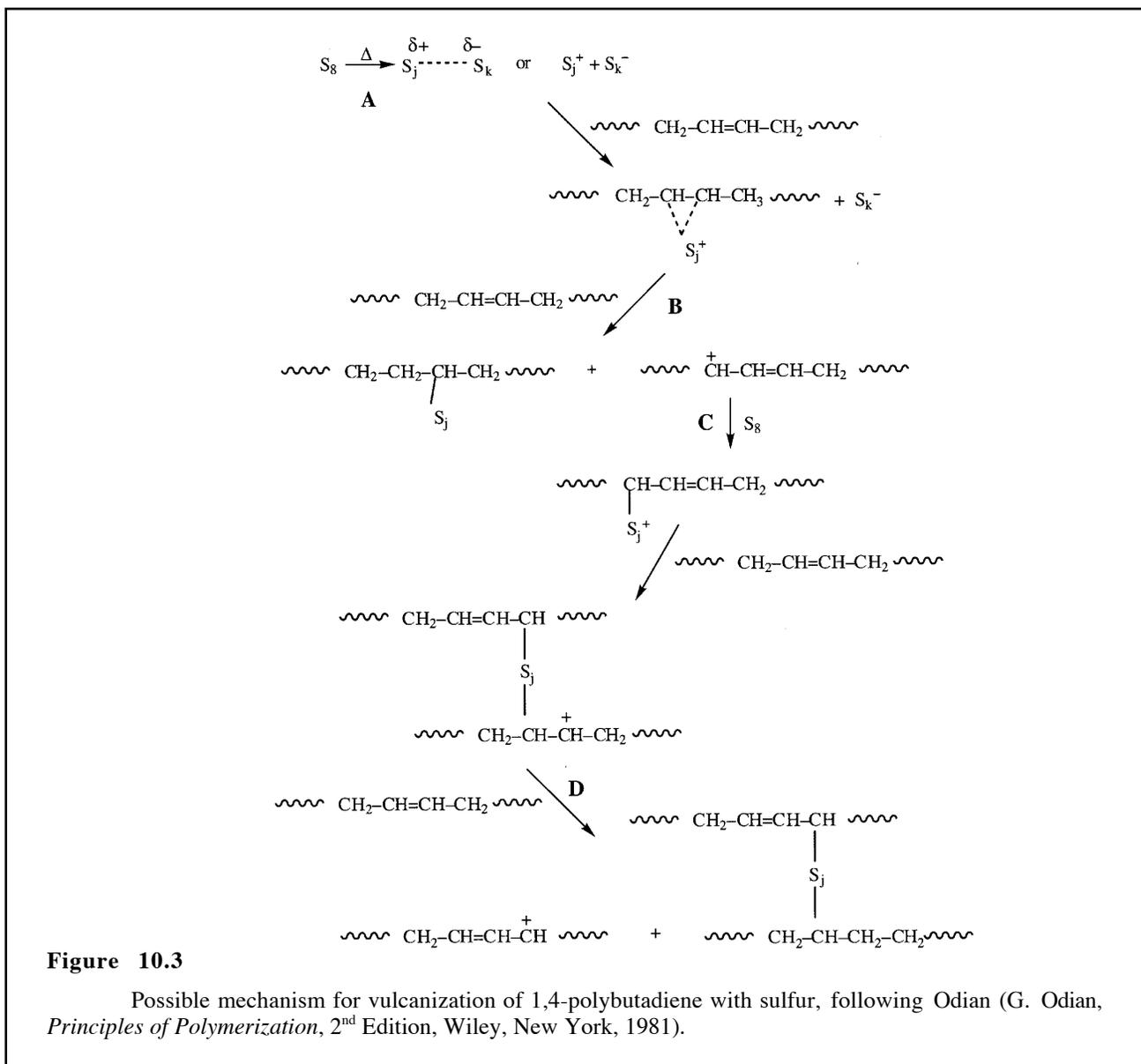
Examples of post-polymerization crosslinking reactions are many. Free radical initiators such as peroxides (see Chapter 3) can be used to crosslink polymers with saturated structures (i.e., no carbon-carbon double bonds), such as polyethylene or polydimethylsiloxane. Alternatively, high

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 crosslink a particular polymer (called a *negative resist*) in desired spatial patterns. The uncrosslinked polymer is then washed away, exposing the underlying substrate for etching or deposition. (In contrast, some polymers such as polymethylmethacrylate degrade rapidly on exposure to high energy radiation, thereby forming a *positive resist*.) Of course, the classic example of crosslinking is that of polydienes crosslinked in the presence of sulfur. The use of sulfur dates back to 1839 and the work of Goodyear in the US [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 crosslinking 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<sub>8</sub>, becomes polarized or opened (Reaction A). The next stage is abstraction of an allylic hydrogen from a neighboring chain to generate a carbocation (B), which subsequently can react with sulfur and crosslink to another chain (C). A carbocation is regenerated, allowing propagation of the crosslinking process (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 eq 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  $p = 0.003$ , so we may be reasonably confident that the sample has passed the gel point.

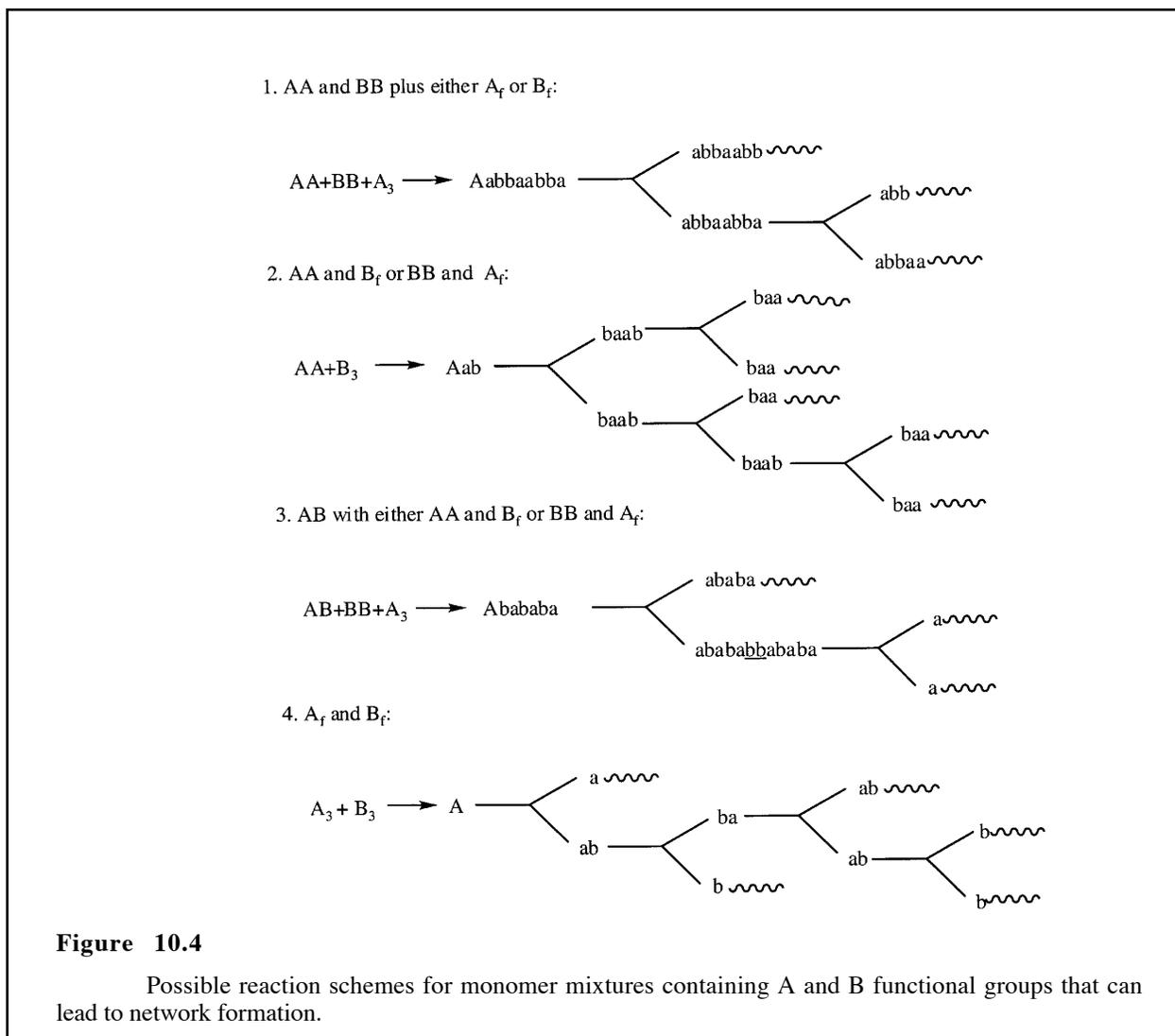
For an individual chain to be untouched, every monomer must be unreacted. The probability for each monomer to be unreacted is  $1-p = 0.997$ , and for a chain of  $N$  monomers we must raise 0.997 to the  $N$ th power. For simplicity, assume all chains have the same  $N = 150,000/68 = 2200$ ; then  $(0.997)^{2200} \approx 0.0013$ , or there is about a tenth of one percent chance that a chain is untouched.

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## 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 means functionality greater than 2, as noted in Chapter 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 crosslinking. 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 which accomplishes this is underlined.

What we seek next is a quantitative relationship between 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 Problem 10.3). 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,  $v_A^0/v_B^0$ , defines the factor  $r$ , as in eq 2.7.1. The total number of A groups from both AA and  $A_f$  are included in this application of  $r$ .
2. The fraction of A groups present in multifunctional molecules is defined by the ratio

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

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

3. 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).
4. The probability that a chain segment is capped at both ends by a branch unit is described by the *branching coefficient*  $\alpha$ . The branching coefficient is central to the discussion of network formation, since whether gelation occurs or not depends on what happens after capping a section of chain with a potential branch point.

### 10.2A Calculation of the branching coefficient

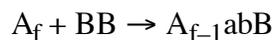
The methods we consider were initially developed by Stockmayer [2] and Flory [3] and have been applied to a wide variety of polymer systems and phenomena. Our approach proceeds through two stages: first we consider the probability that AA and BB polymerize until all chain segments are capped by an  $A_f$  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 eq 10.1.1). As in Chapters 2 and 3, we continue to invoke the *principle of equal reactivity*, i.e., 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 chains 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  $p$ .

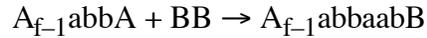
2. The terminal B group reacts with an A group from AA rather than  $A_f$ :



The fraction of unreacted B groups is  $r_p$ , so this gives the probability of reaction for B. Since  $p$  is the fraction of A groups on multifunctional monomers,  $r_p$  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 reacts with another BB:



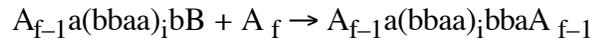
The probability of this step is again  $p$ , and the total probability is  $p[rp(1-\rho)p]$ .

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 reacts with an A group from a multifunctional monomer:



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

6. In the general expression above,  $i$  can have any value from 0 to  $\infty$ , 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.

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

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

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

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

### 10.2B The 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 which 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 chain at random, and follow a chain to another  $A_f$  group, what is the probability that we can continue in this fashion for ever? 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, i.e., a chain segment between two junctions, is  $\alpha$ . 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  $\alpha$ . 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 eq 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 eq 10.1.1. Whenever the extent of reaction,  $p$ , is such that  $\alpha > \alpha_c$ , gelation is predicted to occur. Combining eqs 10.2.3 and 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  $r$ ,  $\rho$ , 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 10.3 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 eq 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 applied to eq 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 branched ones.

As an example of the quantitative testing of eq 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 eq 10.2.4. For an experiment in which  $r = 0.800$  and  $\rho = 0.375$ ,  $p_c = 0.953$  by eq 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 eq 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.

### 10.2C 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 follow immediately 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 eq 2.2.4 for the case of  $\langle f \rangle = 2$ , i.e., 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<sub>f</sub> 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<sub>3</sub> polymerization mixture is prepared in which  $v_A^0 = v_B^0 = 3.00$  mol, with 10% of the A groups contributed by A<sub>3</sub>. Use eq 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  $n_0 = 1.350 + 0.100 + 1.500 = 2.950$ :

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

Solve eq 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 eq 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 eq 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 eq 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.

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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  $N_n$ . Reference 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

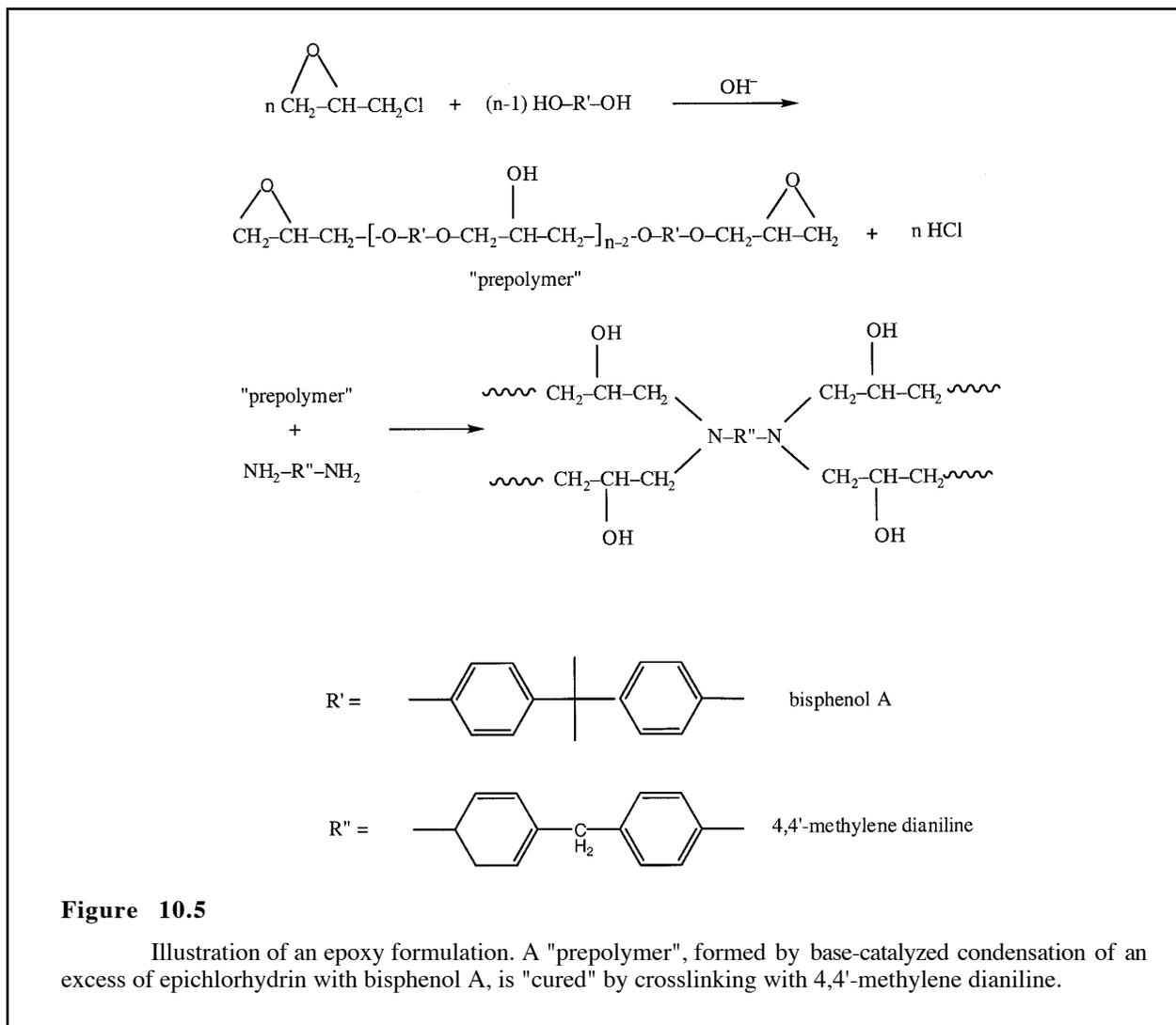
$$\frac{N_w}{N_n} = \frac{(1 + \alpha)(1 - \alpha f / 2)}{1 - \alpha (f - 1)} \quad (10.2.12)$$

The value of  $\alpha$  to be used in these expressions is given by eq 10.2.3 for the specific mixture under consideration. At the gel point  $\alpha_c = 1/(f-1)$  according to eq 10.2.4, and thus eq 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 rings. For the example in the figure 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 crosslinked 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  $n = 2$  (see Figure). 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, i.e., 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 2 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 eq 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 eq 10.2.3 after inserting  $\rho = 1$ . The critical extent of reaction corresponds to  $\alpha_c = 1/3$  from eq 10.2.4, and from eq 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.

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Suggestions for further reading on networks and rubber elasticity:

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### 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 eq 10.5.15 is the evaluation of  $M_c$ . P. J. Flory, N. Rabjohn, and M. C. Shaffer measured the tensile force required for 100% elongation of synthetic rubber with variable crosslinking at 25 °C (*J. Polym. Sci.*, 4, 225, 1949). The molecular weight of the un-cross-linked polymer was 225,000, its density was 0.92 g cm<sup>-3</sup>, and the average molecular weight of a repeat unit was 68. Use 10.5.15 to estimate  $M_c$  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. <sup>-2</sup> )	61.4	83.2	121.8	148.0	160.0

How important is the end group correction introduced in eq 10.6.7 for this system?

3. Develop the equivalent to eqs 10.2.3 and 10.2.5 for the third system in Figure 10.4, i.e., AB + BB+A<sub>3</sub>.
4. The Carothers equation (eq 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 eq 10.2.5 for a mixture containing 2 mol A<sub>3</sub>, 7 mol AA, and 10 mol BB. Criticize or defend the following proposition: the Carothers equation gives higher value for  $p_c$  than eq 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.