1

Introduction to chain molecules

1.1 Introduction

“I am inclined to think that the development of polymerization is perhaps the biggest thing chemistry has done, where it has had the biggest impact on everyday life” [1]. This assessment of the significance of polymer chemistry to modern society was offered twenty-five years ago by Lord Todd (President of the Royal Society and 1957 Nobel Laureate in Chemistry), and subsequent developments have only reinforced this sentiment. There is hardly an area of modern life in which polymer materials do not play an important role. Applications span the range from the mundane (e.g., packaging, toys, fabrics, diapers, non-stick cookware, pressure sensitive adhesives…) to demanding specialty uses (e.g., bullet-proof vests, stealth aircraft, artificial hip joints, resorbable sutures …). In many instances polymers are the main ingredients, and the ingredients whose characteristic properties are essential to the success of a particular technology: rubber tires, foam cushions and insulation, high-performance athletic shoes, clothing, and equipment are good examples. In other cases, polymers are used as additives at the level of a few percent by volume, but which nevertheless play a crucial role in the properties of the final material; illustrations of this can be found in asphalt (to suppress brittle fracture at low temperature and flow at high temperature), shampoo and other cosmetics (to impart “body”), automobile windshields (to prevent shattering), and motor oil (to reduce the dependence of viscosity on temperature and to suppress crystallization).

For those polymer scientists “of a certain age”, the 1967 movie “The Graduate” [2] provided an indelible moment that still resonates today. At his college graduation party, the hero Benjamin Braddock (played by Dustin Hoffmann) is offered the following advice by Mr. McGuire (played by Walter Brooke):

Mr. McGuire: “I want to say one word to you. Just one word.”

Benjamin: “Yes, sir”.

Mr. McGuire: “Are you listening?”

Benjamin: “Yes I am”.

Mr. McGuire: “Plastics”.

In that period, the term “plastic” was often accompanied by negative connotations, including “artificial”, as opposed to “natural”, and “cheap”, as opposed to “valuable”. Today, in what we might call the “post-Graduate era”, the situation has changed. To the extent that the advice offered to Benjamin was pointing him to a career in a particular segment of the chemical industry, it was probably very sound advice. The volume of polymer materials produced annually has grown rapidly over the intervening years, to the point where today several hundred pounds of polymer materials are produced each year for each person in the United States. More interesting than shear volume, however, is the breadth of applications for polymers. Not only do they continue to encroach into the domains of “classical” materials such as metal, wood, and glass, (note the inexorable transformation of polymers from minor to major components in automobiles) but they also play a central role in many emerging technologies. Examples include “plastic electronics”, gene therapy, artificial prostheses, optical data storage, electric cars, and fuel cells. In short, a reasonable appreciation of the properties of chain molecules, and how these result in the many desirable attributes of polymer-containing materials, is a necessity for a well trained chemist, materials scientist, or chemical engineer today.

Science tends to be plagued by cliches which make invidious comparison of its efforts; “they can cure such and such a dreaded disease, but they cannot do anything about the common cold” or “we know more about the surface of the moon than the bottom of the sea.” If such comparisons were popular in the 1920s, the saying might have been, “we know more about the structure of the atom than about those messy, sticky substances called polymers.” Indeed, Millikan's determination of the charge of an electron, Rutherford's idea of the nuclear atom, and

Bohr's model of the hydrogen atom were all well-known concepts before the notion of truly covalent macromolecules was accepted. This was the case in spite of the great importance of polymers to human life and activities. Our bodies, like all forms of life, depend on polymer molecules: carbohydrates, proteins, nucleic acids, and so on. From the earliest times, polymeric materials have been employed to satisfy human needs: wood and paper; hides; natural resins and gums; fibers such as cotton, wool, and silk.

Attempts to characterize polymeric substances had been made, of course, and high molecular weights were indicated, even if they were not too accurate. Early workers tended to be more suspicious of the interpretation of the colligative properties of polymeric solutions than to accept the possibility of high molecular weight compounds. Faraday had already arrived at C_5H_8 as the empirical formula of "rubber" in 1826, and isoprene was identified as the product resulting from the destructive distillation of rubber in 1860. The idea that a natural polymer such as rubber somehow “contained” isoprene emerged, but the nature of its involvement was more elusive.

During the early years of the twentieth century, organic chemists were enjoying success in determining the structures of ordinary-sized organic molecules, and this probably contributed to their reluctance to look beyond structures of convenient size. Physical chemists were interested in intermolecular forces during this period, and the idea that polymers were the result of some sort of association between low molecular weight constituent molecules prevailed for a long while. Staudinger is generally credited as being the father of modern polymer chemistry, although a foreshadowing of his ideas can be traced through older literature. In 1920 Staudinger proposed the chain formulas we accept today, maintaining that structures are held together by covalent bonds which are equivalent in every way to those in low molecular weight compounds. There was a decade of controversy before this "macromolecular hypothesis" began to experience widespread acceptance. Staudinger was awarded the Nobel Prize in 1953 for his work with polymers. By the 1930s Carothers began synthesizing polymers using well-established reactions of organic chemistry such as esterification and amidation. His products were not limited to single ester or amide linkages, however, but contained many such groups: they were *poly*esters and *poly*amides. Physical chemists also got in on the act. Kuhn, Guth, Mark and others were soon applying statistics and crystallography to describe the multitude of forms a long-chain molecule could assume [3].

Our purpose in this introduction is not to trace the history of polymer chemistry beyond the sketchy version above; interesting and extensive treatments are available [4,5]. Rather, the primary objective is to introduce the concept of chain molecules, which stands as the cornerstone of all polymer chemistry. In the next few sections we shall explore some of the categories of polymers, some of the reactions that produce them, and some aspects of isomerism which multiply the structural possibilities. A common feature of all synthetic polymerization reactions is the statistical nature of the individual polymerization steps. This leads inevitably to a distribution of molecular weights, which we would like to describe. As a consequence of these considerations, another important part of this chapter is an introduction to some of the statistical concepts which also play a central role in polymer chemistry.

1.2 How big is big?

The term *polymer* is derived from the Greek words *poly* and *meros*, meaning many parts. We noted in the last section that the existence of these parts was acknowledged before the nature of the interaction which held them together was known. Today we realized that ordinary covalent bonds are the intramolecular forces which keep the polymer molecule intact. In addition, the usual types of intermolecular forces — hydrogen bonds, dipole-dipole interactions, London forces, etc. — hold assemblies of these molecules together in the bulk state. The only thing that is remarkable about these molecules is their size, but that feature is remarkable indeed. Another useful term is *macromolecule*, which of course simply means “large molecule”. Some practitioners draw a distinction between the two: all polymers are macromolecules, but not all macromolecules are polymers. For example, a protein is not made by repeating one or two chemical units many times, but involves a precise selection from among 20 different amino acids; thus it is a macromolecule, but not a polymer. In this text we will not be sticklers for formality, and will use the terms rather interchangeably, but the reader should be aware of the distinction.

1.2A Molecular weight

One of the first things we must consider is what we mean when we talk about the “size” of a polymer molecule. There are two possibilities: one has to do with the number of repeat units, and the other to the spatial extent. In the former case, the standard term is *molecular weight* (although again the reader must be aware that *molar mass* is often preferred). A closely related concept, the *degree of polymerization*, is also commonly used in this context. A variety of experimental techniques are available for determining the molecular weight of a polymer. We shall discuss a few such methods in Section 1.8 and postpone others until the appropriate chapters. The expression molecular weight and molar mass should always be modified by the word *average*. This, too, is something we shall take up presently. For now, we assume that a polymer molecule has a molecular weight M, which can be anywhere in the range 10^3–10^7 or more. (We shall omit units when we write molecular weights in this book, but the student is advised to attach the units g/mol to these quantities when they appear in problem calculations).

Since polymer molecules are made up of chains of repeating units, after the chain itself comes the repeat unit as a structural element of importance. Many polymer molecules are produced by covalently bonding together only one or two types of repeating units. These units are the parts from which chains are generated; as a class of compounds they are called monomers. Throughout this book we shall designate the molecular weight of a repeat unit as M_o.

The degree of polymerization of a polymer is simply the number of repeat units in a molecule. The degree of polymerization N is given by the ratio of the molecular weight of the polymer to the molecular weight of the repeat unit:

$$N = \frac{M}{M_o} \tag{1.2.1}$$

One type of polymerization reaction is the addition reaction in which successive repeat units add on to the chain. No other product molecules are formed, so the molecular weight of the monomer and that of the repeat unit are identical in this case. A second category of polymerization reaction is the condensation reaction, in which one or two small molecules such as water or HC1 are eliminated for each chain linkage formed. In this case the molecular weight of the monomer and the repeat unit are somewhat different. For example, suppose an acid (subscript A) reacts with an alcohol (subscript B) to produce an ester linkage and a water molecule. The molecular weight of the ester — the repeat unit if an entire chain is built up this way — differs from the combined weight of the reactants by twice the molecular weight of the water; therefore,

$$N = \frac{M}{M_o} = \frac{M}{M_A + M_B - 2M_{H_2O}} \tag{1.2.2}$$

The end units in a polymer chain are inevitably different from the units that are attached on both sides to other repeat units. We see this situation in the *n*-alkanes: each end of the chain is a methyl group and the middle parts are methylene groups. Of course, the terminal group does not have to be a hydrogen as in alkanes; indeed, it is often something else. Our interest in end groups is concerned with the question of what effect they introduce into the evaluation of N through eq (1.2.2). The following example examines this through some numerical calculations.

Example 1.1

As a polymer prototype consider an *n*-alkane molecule consisting of N–2 methylenes and 2 methyl groups. How serious an error is made in M for different N's if the difference in molecular weight between methyl and methylene groups is ignored?

Solution

The effect of different end groups on M can be seen by comparing the true molecular weight with an approximate molecular weight, calculated on the basis of a formula $(CH_2)_N$. These M's and the percentage difference between them are listed here for several values of N:

N	M	M_{approx}	% difference
3	44	42	4.5
7	100	98	2.0
12	170	168	1.2
52	730	728	0.3
102	1,430	1,428	0.14
502	7,030	7,028	0.028
1002	14,030	14,028	0.014

Although the difference is almost 5% for propane, it is closer to 0.1% for the case of N ≈ 100, which is about the threshold for polymers. The precise values of these numbers will be different, depending on the specific repeat units and end groups present. For example, if

$M_o = 100$ and $M_{end} = 80$, the difference would be 0.39% in a calculation such as that above for $N \approx 100$.

The example shows that the contribution of the ends becomes progressively less important as the number of repeat units in a structure increases. By the time polymeric molecular sizes are reached, the error associated with failure to distinguish between segments at the end and those within the chain is generally less than experimental error. In Section 1.8B we shall consider a method for polymer molecular weight determination which is based on chemical analysis for the end groups in a polymer. A corollary of the present discussion is that the method of end group analysis is applicable only in the case of relatively low molecular weight polymers.

As suggested above, not all polymers are constructed by bonding together a single kind of repeating unit. For example, although protein molecules are polyamides in which N amino acid repeat units are bonded together, the degree of polymerization is a less useful concept, since an amino acid unit might be any one of the 20-odd molecules that are found in proteins. In this case the molecular weight itself, rather than the degree of polymerization, is generally used to describe the molecule. When the actual content of individual amino acids is known, it is their sequence that is of special interest to biochemists and molecular biologists.

1.2B Spatial extent

We began this section with an inquiry into how to define the size of a polymer molecule. In addition to the molecular weight or the degree of polymerization, some linear dimension which characterizes the molecule could also be used for this purpose. As an example, consider a hydrocarbon molecule stretched out to its full length but without any bond distortion. There are several features to note about this situation:

1. The tetrahedral geometry at the carbon atoms gives bond angles of 109.5°.

2. The equilibrium bond length of a carbon-carbon single bond is 0.154 nm or 1.54Å.

3. Because of the possibility of rotation around carbon-carbon bonds, a molecule possessing many such bonds will undergo many twists and turns along the chain.

4. The fully extended molecular length is not representative of the spatial extension that a molecule actually displays. The latter is sensitive to environmental factors, however, so the extended length is convenient for our present purposes to provide an idea of the spatial size of polymer molecules.

A fully extended hydrocarbon molecule will have the familiar all-trans zigzag profile in which the hydrogens extend in front of and in back of the plane containing the carbons, also making an angle of 109.5° between them at the carbon atoms. The chain may be pictured as a row of triangles resting corner to corner. The length of the row equals the product of the number of triangles and the length of the base of each. Although it takes three carbons to define one of these triangles, one of these atoms is common to two triangles; therefore the number of triangles is the same as the number of *pairs* of carbon atoms, except where this breaks down at the ends of the molecule. If the chain is sufficiently long, this end effect is inconsequential. The law of cosines can be used to calculate the length of the base of each of these triangles: $\left[2(0.154)^2(1 - \cos 109.5°)\right]^{1/2}$ = 0.252 nm. If the repeat unit of the molecule contributes two carbon atoms to the backbone of the polymer—as is the case for vinyl polymers—the fully extended chain length is given by N(0.252)nm. For a polymer with $N = 10^4$, this corresponds to 2.52 μm. Objects which actually display linear dimensions of this magnitude can be seen in an ordinary microscope, provided that they have suitable optical properties to contrast with their surroundings; an example will be given in Figure 1a. Note that the distance between every other carbon atom we have used here is also the distance between the substituents on these carbons for the fully extended chains.

We shall see in Chapter 6 that, because of all the twists and turns a molecule undergoes, the actual average end-to-end distance of the jumbled molecules increases as $N^{1/2}$. With the same repeat distance calculated above, but the square root dependence on N, the actual end-to-end distance of the coiled chain with N = 10^4 is closer to $\left(10^4\right)^{1/2}$ x 0.252 nm $\approx$ 25 nm. If we picture one end of this jumbled chain at the origin of a coordinate system, the other end might be anywhere on the surface of a sphere whose radius is given by this end-to-end distance. This spherical geometry comes about because the random bends occurring along the chain length can take the end of the chain anywhere in a spherical domain whose radius depends on $N^{1/2}$.

The above discussion points out the difficulty associated with using the linear dimensions of a molecule as a measure of its size: it is not the molecule alone that determines its dimensions, but also the shape or *conformation* in which it exists. Fully extended, linear arrangements of the sort described above exist in polymer crystals, at least for some distance, although usually not over the full length of the chain. We shall take up the structure of polymer crystals in Chapter 13. In the solution and bulk states, many polymers exist in the coiled form we have also described. Still other structures are important, notably the rod or semiflexible chain, which we shall discuss in Chapter 6. The overall shape assumed by a polymer molecule can be greatly affected by the environment. The shape of a molecule in solution plays a key role in determining many properties of polymer solutions. From a study of these solutions, some conclusions can be drawn regarding the shape of the molecule in the environment. Relevant aspects of polymer solutions are taken up in Chapters 6-9.

Figures 1.1a and b are rather striking images of individual polymer molecules. Figure 1.1a shows single molecules of DNA that have been heavily labeled with fluorescent dyes; the dyes intercalate between the base pairs along the chain, without seriously altering the conformation of the molecule. Under illumination the resulting fluorescence provides a good representation of the molecules themselves. In this particular image the DNA molecules are spread out in two dimensions, on a cationically charged imitation lipid membrane. DNA, as it turns out, is an excellent example of a semiflexible chain, which can actually be inferred from these images; the molecules are not straight rods, but neither are they heavily coiled around themselves. The scale bar corresponds to 10 μm, indicating that these molecules are of very high molecular weight indeed. In Figure 1.1b the image is of a star-shaped polymer, but one in which each arm of the star is a heavily branched comb or "bottlebrush". The molecule is thus akin to a kind of starfish, with very hairy arms. This picture was obtained by atomic force microscopy (AFM), one of a series of surface-sensitive analysis techniques with exquisite spatial resolution. The molecules themselves were deposited from a Langmuir-Blodgett trough onto a mica substrate. Both situations depicted in Figures 1a and 1b raise the question of the relationship between the conformation observed on the surface and that at equilibrium in solution. In Chapters 6-9 we will encounter several ways in which the solution conformation can be determined reliably, which can serve to confirm the impression derived from figures such as these.

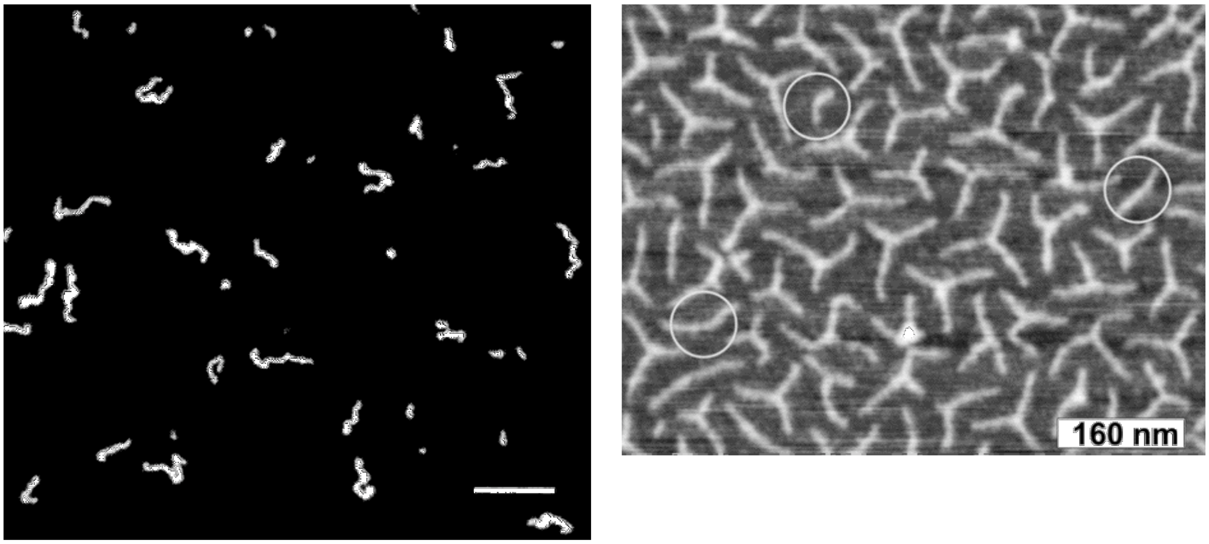


Figure 1.
(a) Individual molecules of DNA of various sizes, spread on a fluid positively charged surface, imaged by fluorescence. The scale bar is 10 μm. Reproduced with permission from B. Maier and J. O. Rädler, *Macromolecules* 33, 7185 (2000). (b) Atomic force microscopy images of 3-arm star polymers, where each arm is a heavily branched comb. The circles indicate linear molecules. Reproduced with permission from K. Matyjaszewski, S. Qin, J. R. Boyce, D. Shirvanyants, and S. S. Sheiko, *Macromolecules* 36, 1843 (2003).

We conclude this section by questioning whether there is a minimum molecular weight or linear dimension that must be met for a molecule to qualify as a polymer. Although a dimer is a molecule for which N = 2, no one would consider it a polymer. The term *oligomer* has been coined to designate molecules for which N < 10. If they require a special name, apparently the latter are not full-fledged polymers either. At least as a first approximation, we shall take the attitude that there is ordinarily no discontinuity in behavior with respect to observed properties as we progress through a homologous series of compounds with different N values. At one end of the series we may be dealing with a simple low molecular weight compound, and at the other end with a material that is unquestionably polymeric. The molecular weight and chain length increase monotonically through this series, and a variety of other properties vary smoothly also. This point of view emphasizes continuity with familiar facts concerning the properties of low molecular weight compounds. There are some properties, on the other hand, which follow so closely from the chain structure of polymers that the property is simply not observed until a certain critical molecular size has been reached. This critical size is often designated by a threshold molecular weight. The elastic behavior of rubber and several other mechanical properties fall into this latter category. In theoretical developments, large values of N are often assumed to justify neglecting end effects, using certain statistical methods and other mathematical approximations. With these ideas in mind, M = 1000 seems to be a convenient round number for designating a compound to be a polymer, although it should be clear that this cutoff is arbitrary (and on the low side).

1.3 Linear and branched polymers, homopolymers and copolymers

1.3A Branched structures

Most of the preceding section was based on the implicit assumption that polymer chains are linear (with the striking exception of Figure 1b!). In evaluating both the degree of polymerization and the extended chain length, we assumed that the chain had only two ends. While linear polymers are important, they are not the only type of molecules possible: branched and cross-linked molecules are also common. When we speak of a branched polymer, we refer to the presence of additional polymeric chains issuing from the backbone of a linear molecule. (Small substituent groups such as methyl or phenyl groups on the repeat units are generally not considered branches, or, if they are, they should be specified as "short chain branches"). Branching can arise through several routes. One is to introduce into the polymerization reaction some monomer with the capability of serving as a branch. Consider the formation of a polyester. The presence of difunctional acids and difunctional alcohols allows the polymer chain to grow. These difunctional molecules are incorporated into the chain with ester linkages at both ends of each. Trifunctional acids or alcohols, on the other hand, produce a linear molecule by reacting two of their functional groups. If the third reacts and the resulting chain continues to grow, a branch has been introduced into the original chain. A second route is through adventitious branching, for example as a result of an atom being abstracted from the original linear molecule, with chain growth occurring from the resulting active site. This is quite a common occurrence in the free-radical polymerization of ethylene, for example. A third route is *grafting*, whereby pre-formed but still reactive polymer chains can be added to sites along an existing backbone (so-called "grafting to"), or where multiple initiation sites along a chain can be exposed to monomer (so-called "grafting from").

The amount of branching introduced into a polymer is an additional variable that must be specified for the molecule to be fully characterized. When only a slight degree of branching is present, the concentration of junction points is sufficiently low that these may be simply related to the number of chain ends. For example, two separate linear molecules have a total of four ends. If the end of one of these linear molecules attaches itself to the middle of the other to form a T, the resulting molecule has three ends. It is easy to generalize this result. If a molecule has ν branches, it has $\nu + 2$ chain ends if the branching is relatively low. Two limiting cases to consider, illustrated in Figure 1.2, are *combs* and *stars*. In the former, a series of relatively uniform branches emanate from along the length of a common backbone; in the latter, all branches radiate from a central junction. Figure 1b gave an example of both of these features.

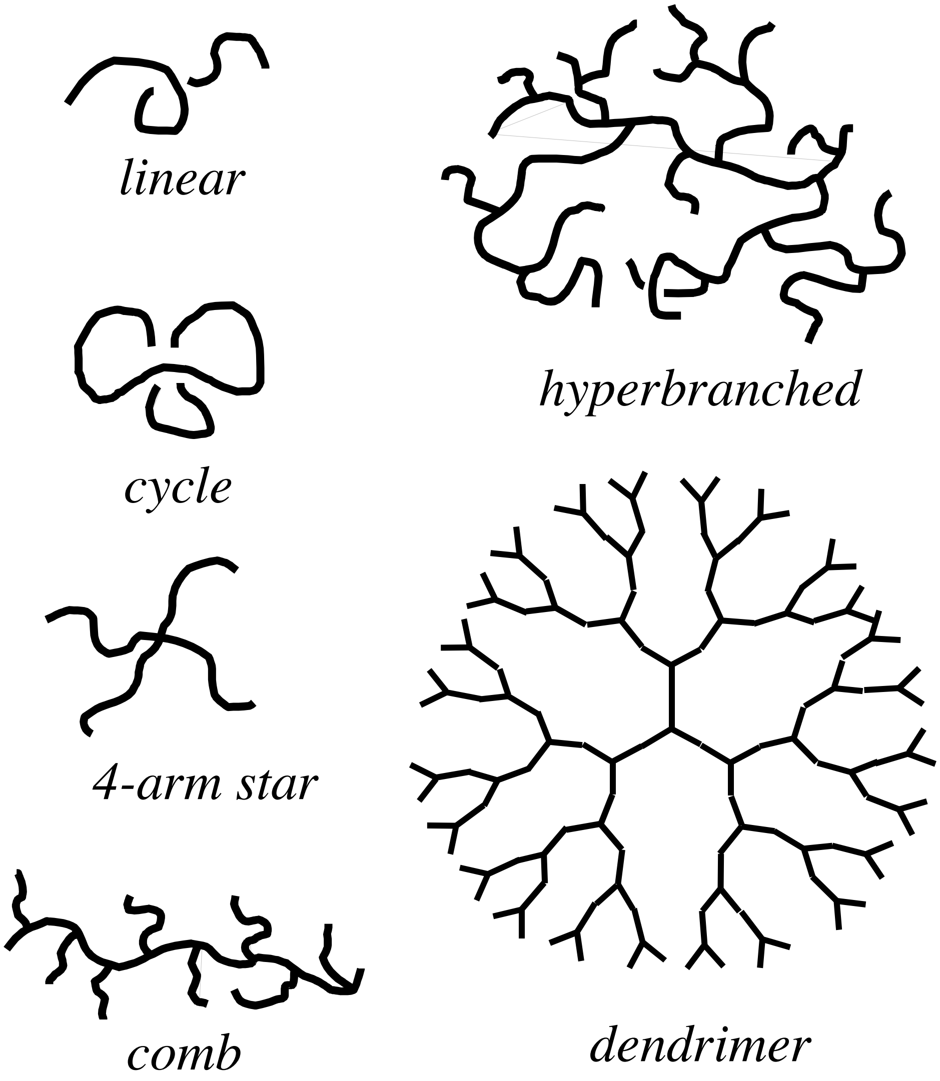


Figure 1.2
Illustration of various polymer architectures

If the concentration of junction points is high enough, even branches will contain branches. Eventually a point can be reached at which the amount of branching is so extensive that the polymer molecule becomes a giant three-dimensional network. When this condition is achieved, the molecule is said to be cross-linked. In this case, an entire macroscopic object may be considered to consist of essentially one molecule. The forces which gives cohesiveness to such a body are covalent bonds, not intermolecular forces. Accordingly, the mechanical behavior of cross-linked bodies is much different from those without cross-linking. This will be discussed at length in Chapter 10. However, it is also possible to suppress cross-linking such that the highly branched molecules remain as discrete entities, known as *hyperbranched polymers* (see Figure 1.2). Another important class of highly branched polymers illustrated in Figure 1.2 are *dendrimers*, or tree-like molecules. These are completely regular structures, with well-defined molecular weights, that are made by the successive condensation of branched monomers. For example, begin with a trifunctional monomer “B_3”, or “generation 0”. This is reacted with an excess of AB_2 monomers, leading to a generation 1 dendrimer with 6 B groups. A second reaction with AB_2 leads to generation 2 with 12 pendant B groups. Eventually, perhaps at generation 6 or 7, the surface of the molecule becomes so congested that addition of further complete generations is impossible. Note that the “B” part of the AB_2 monomer needs to be protected in some way so that only one generation can be added at one time.

A final class of non-linear polymers to consider are *cycles* or *rings*, whereby the two ends of the molecule react to close the loop. Such polymers are currently more of academic interest than commercial importance, as they are tricky to prepare, but they can shed light on various aspects of polymer behavior. Interestingly, nature makes use of this architecture; the DNA of the Lambda bacteriophage reversibly cyclizes and uncyclizes during gene expression.

1.3B Copolymers

Just as it is not necessary for polymer chains to be linear, it is also not necessary for all repeat units to be the same. We have already mentioned proteins, where a wide variety of different repeat units are present. Among synthetic polymers, those with a single kind of repeat unit are called *homopolymers*, and those containing more than one kind of repeat unit are *copolymers*. Note that these definitions are based on the repeat unit, not the monomer. An ordinary polyester is not really a copolymer, even though two different monomers, acids and alcohols, are its monomers. By contrast, copolymers result when different monomers bond together in the same way to produce a chain in which each kind of monomer retains its respective substituents in the polymer molecule. The unmodified term copolymer is generally used to designate the case where two different repeat units are involved. Where three kinds of repeat units are present, the system is called a *terpolymer*; where there are more than three, the system is called a multicomponent copolymer. The copolymers we discuss in this book will be primarily two-component molecules; we shall explore aspects of the synthesis and characterization of copolymers in both Chapters 4 and 5.

The moment we admit the possibility of having more than one kind of repeat unit, we require additional variables to describe the polymer. First, we must know how many kinds of repeat units are present and what they are. To describe the copolymer quantitatively, the relative amounts of the different kinds of repeat units must be specified. Thus the empirical formula of a copolymer may be written A_xB_y, where A and B signify the individual repeat units and x and y indicate the relative number of each. From a knowledge of the molecular weight of the polymer, the molecular weights of A and B, and the values of x and y, it is possible to calculate the number of each kind of monomer unit in the copolymer. The sum of these values gives the degree of polymerization of the copolymer. The following example illustrates some of the ways of describing a copolymer.

Example 1.2

A terpolymer is prepared from vinyl monomers A, B, and C; the molecular weights of the repeat units are 104, 184, and 128, respectively. A particular polymerization procedure yields a product with the empirical formula $A_{3.55}B_{2.20}C_{1.00}$. The authors of this research state that the terpolymer has “an average unit weight of 134” and “the average molecular weight per angstrom of 53.5.” (A. Ravve and J. T. Khamis, *Additions and Condensation of Polymerization Processes.*

Advances in Chemistry Series, Vol. 91, American Chemical Society Publications, Washington, D.C., 1969). Verify these values.

Solution

The empirical formula gives the relative amounts of A, B, and C in the terpolymer. The total molecular weight of this empirical formula unit is given by adding the molecular weight contributions of A, B, and C: 3.44(104) + 2.20(184) + 1.00(128) = 902 g/mol per empirical formula unit. The total amount of chain repeat units possessing this total weight is 3.55 + 2.20 + 1.00 = 6.75 repeat units per empirical formula unit. The ratio of the total molecular weight to the total number of repeat units gives the average molecular weight per repeat unit:

$$\frac{902}{6.75} = 134 \text{ g/mol per repeat unit}$$

Since the monomers are specified to be vinyl monomers, each contributes two carbon atoms to the polymer backbone, with the associated extended length of 0.252 nm per repeat unit. Therefore the total extended length of the empirical formula unit is

$$6.75(0.252 \text{ nm}) = 1.79 \text{ nm} = 17.0 \text{ Å}$$

The ratio of the total weight to the total extended length of the empirical formula unit gives the average molecular weight per length of chain:

$$\frac{902}{17} = 53 \text{ g/mol per Å}$$

Note that the average weight per repeat unit could be used to evaluate the overall degree of polymerization of this terpolymer. For example, if the molecular weight were 43,000, the corresponding degree of polymerization would be

$$\frac{43{,}000}{134} = 321 \text{ repeat units per molecule}$$

With copolymers, it is far from sufficient merely to describe the empirical formula to characterize the molecule. Another question that must be asked concerns the location of the different kinds of repeat units within the molecule. Starting from monomers A and B, the following distribution patterns can be obtained in linear polymers:

1. *Random* (or *statistical*). The A—B sequence is governed strictly by chance, subject only to the relative abundances of repeat units. For equal proportions of A and B we might have structures like:

   –AAABABAABBABBB–

   Such a polymer could be called poly(A-*stat*-B) or poly(A-*ran*-B).

2. *Alternating*. A regular pattern of alternating repeat units in poly(A-*alt*-B):

   –ABABABABABAB–

3. *Block*. Long, uninterrupted sequences of each monomer is the pattern:

–AAAAAAAAAAAAAABBBBBBBBBBBBBAAAAAAAAA–

The above structure has three blocks, and is called poly(A-*block*-B-*block*-A), or an ABA triblock copolymer. If a copolymer is branched with different repeat units occurring in the branches and the backbone, we can have the following:

4. *Graft*. This segregation is often accomplished by first homopolymerizing the backbone. This is dissolved in the second monomer, with sites along the original chain becoming the origin of the comonomer side-chain growth:

```
             BBBBBBBBBB–
             |
    –AAAAAAAAAAAAAAAAA–
          |        |
–BBBBBBBBBB        BBBBBBB–
```

In a cross-linked polymer, the junction units are different kinds of monomers than the chain repeat units, so these molecules might be considered to be still another comonomer. While the chemical reactions which yield such cross-linked substances are technically copolymerizations, the products are described as cross-linked rather than as copolymers. In this instance, the behavior due to cross-linking takes precedence over the presence of an additional type of monomer in the structure.

It is apparent from items (1)-(3) above that linear copolymers – even those with the same proportions of different kinds of repeat units – can be very different in structure and properties.

In classifying a copolymer as random, alternating, or block, is should be realized that we are describing the average character of the molecule; accidental variations from the basic patterns may be present. Furthermore, in some circumstances nominally "random" copolymers can have substantial sequences of one monomer or the other. In Chapter 5 we shall see how an experimental investigation of the sequence of repeat units in a copolymer is a valuable tool for understanding copolymerization reactions.

1.4 Addition, condensation, and natural polymers

In the last section we examined some of the categories into which polymers can be classified. Various aspects of molecular structure were used as the basis for classification in that section. Next we shall consider the chemical reactions that produce the molecules as a basis for classification. The objective of this discussion is simply to provide some orientation and to introduce some typical polymers. For this purpose many polymers may be classified as being either addition or condensation polymers; both of these classes are discussed in detail in Chapters 2 and 3, respectively. Even though these categories are based on the reactions which produce the polymers, it should not be inferred that only two types of polymerization reactions exist. We have to start somewhere, and these two important categories are the usual place to begin.

1.4A Addition and condensation polymers

These two categories of polymer can be developed along several lines. For example, in addition-type polymers the following statements apply:

1. The repeat unit in the polymer and the monomer have the same composition, although, of course, the bonding is different in each.

2. The mechanism of these reactions places addition polymerizations in the kinetic category of *chain reactions*, with either free radicals or ionic groups responsible for propagating the chain reaction.

3. The product molecules often have an all-carbon chain backbone, with pendant substituent groups.

In contrast, for condensation polymers:

4. The polymer repeat unit arises from reacting together two different functional groups which usually originate on different monomers. In this case the repeat unit is different from either of the monomers. In addition, small molecules are often eliminated during the condensation reaction. Note the words *usual* and *often* in the previous statements; exceptions to both statements are easily found.

5. The mechanistic aspect of these reactions can be summarized by saying that the reactions occur in steps. Thus the formation of an ester linkage between two small molecules is not essentially different from that between a polyester and a monomer.

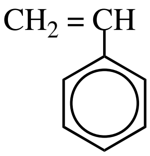
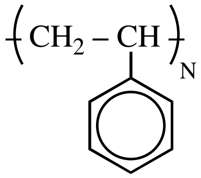
6. The product molecules have the functional groups formed by the condensation reactions interspersed regularly along the backbone of the polymer molecule:

$$\text{–C–C–Y–C–C–Y–}$$

Next let us consider a few specific examples of these classes of polymers. The addition polymerization of a vinyl monomer CH_2=CHX involves three distinctly different steps. First, the reactive center must be initiated by a suitable reaction to produce a free radical, anionic or cationic reaction site. Next, this reactive entity adds consecutive monomer units to propagate the polymer chain. Finally, the active site is capped off, terminating the polymer formation. If one assumes that the polymer produced is truly a high molecular weight substance, the lack of uniformity at the two ends of the chain – arising in one case from the initiation, and in the other from the termination – can be neglected. Accordingly, the overall reaction can be written

$$N\ CH_2{=}CHX \rightarrow (CH_2{-}CHX)_N \qquad (1.A)$$

Again we emphasize that end effects are ignored in writing reaction (1.A). These effects as well as the conditions of the reaction and other pertinent information will be discussed when these reactions are considered in Chapters 3 and 4. Table 1.1 lists several important addition polymers, showing the monomer and polymer structure in the manner of reaction (1.A). Also included in Table 1.1 are the molecular weights of the repeat units and the common names of the polymers. The former will prove helpful in many of the problems in this book; the latter will be discussed in the next section. Poly(ethylene oxide) and poly(ε-caprolactam) have been included in this list as examples of the hazards associated with classification schemes. They resemble addition polymers because the molecular weight of the repeat unit and that of the monomer are the same; they resemble condensation polymers because of the heteroatom chain backbone. The reaction mechanism, which might serve as arbiter in this case, can be either of the chain or the step type, depending on the reaction conditions! These last reactions are examples of *ring-opening polymerizations,* yet another possible category of classification.

Monomer	**M_o, g/mol**	**Repeat Unit**	**Name(s)**
$CH_2 = CH_2$	28.0	$-(-CH_2 - CH_2-)_N-$	Polyethylene
	104		Polystyrene
$CH_2 = CHCl$	62.5	$-(-CH_2 - CHCl-)_N-$	Poly(vinyl chloride), “vinyl”
$CH_2 = CHCN$	53.9	$-(-CH_2 - CHCN-)_N-$	Polyacrylonitrile,

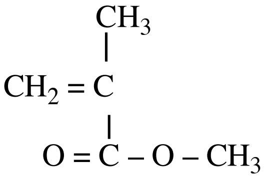
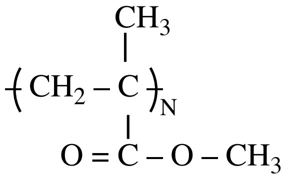
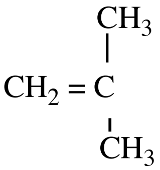
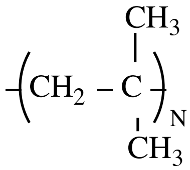
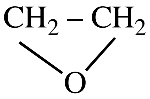
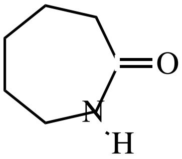
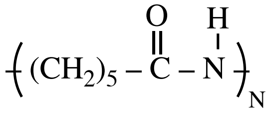
			"acrylic"
$CH_2 = CCl_2$	97.0	$-(-CH_2 - CCl_2-)_N-$	Poly(vinylidene chloride)
 $CH_2 = C(CH_3)(C(=O)-O-CH_3)$	100	 $-(CH_2 - C(CH_3)(C(=O)-O-CH_3))_N-$	Poly(methyl methacrylate), Plexiglas, Lucite
 $CH_2 = C(CH_3)_2$	56.0	 $-(CH_2 - C(CH_3)_2)_N-$	Polyisobutylene
$CF_2 = CF_2$	100	$-(-CF_2 - CF_2-)_N-$	Polytetrafluoroethylene, Teflon
	44.0	$-(-CH_2 - CH_2 - O-)_N-$	Poly(ethylene oxide), poly(ethylene glycol)
	113	 $-((CH_2)_5 - C(=O) - N(H))_N-$	Poly(ε-caprolactam), nylon-6

Table 1.1

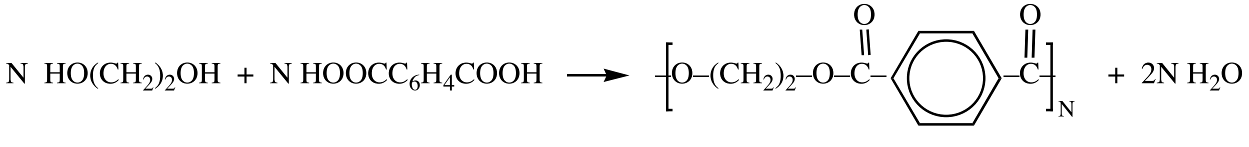
Reactions by which several important addition polymers can be produced

The requirements for formation of condensation polymers are twofold: the monomers must possess functional groups capable of reacting to form the linkage, and they ordinarily require more than one reactive group to generate a chain structure. The functional groups can be distributed such that two difunctional monomers with different functional groups react or a single monomer reacts which is difunctional with one group of each kind. In the latter case especially, but also with condensation polymerization in general, the tendency to form cyclic products from intramolecular reactions may compete with the formation of polymer.

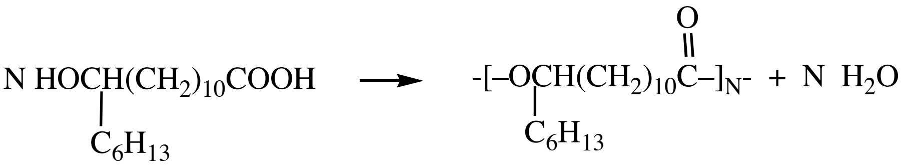
Condensation polymerizations are especially sensitive to impurities. The presence of monofunctional reagents introduces the possibility of a reaction product forming which would not be capable of further growth. If the functionality is greater than 2, on the other hand, branching becomes possible. Both of these modifications dramatically alter the product compared to a high molecular weight linear product. When reagents of functionality less than or greater than 2 are added in carefully measured and controlled amounts, the size and geometry of product molecules can be manipulated. When such reactants enter as impurities, the undesired results can be disastrous! Marvel has remarked that more money has been wasted in polymer research by the use of impure monomers than in any other manner [6].

Table 1.2 lists several examples of condensation reactions and products. Since the reacting monomers can contain different numbers of carbon atoms between functional groups, there are quite a lot of variations possible among these basic reactions types. The inclusion of poly(dimethyl siloxane) in Table 1.2 serves as a reminder that polymers need not be organic compounds. The physical properties of inorganic polymers follow from the chain structure of these molecules, and the concepts developed in this volume apply to them and to organic polymers equally well. For example, poly(dimethyl siloxane) shows a very low viscosity compared to other polymers of comparable degree of polymerization. We shall not examine explicitly the classes and preparations of the various types of inorganic polymers in this text.

1. Polyester



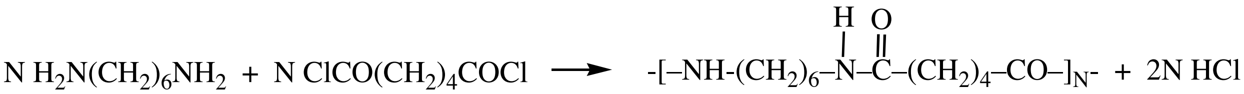
poly(ethylene terephthalate), Terylene, Dacron, Mylar



$$N\,HO\underset{C_6H_{13}}{\underset{|}{C}}H(CH_2)_{10}COOH \longrightarrow -[-O\underset{C_6H_{13}}{\underset{|}{C}}H(CH_2)_{10}\overset{O}{\overset{\|}{C}}-]_N- + N\ H_2O$$

poly(12-hydroxystearic acid)

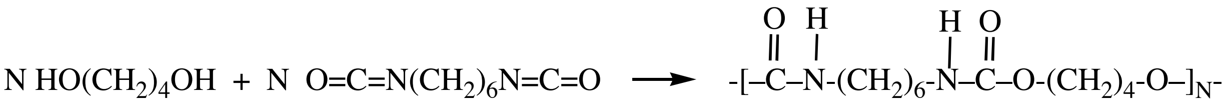
2. Polyamide



$$N\,H_2N(CH_2)_6NH_2 + N\,ClCO(CH_2)_4COCl \longrightarrow -[-NH-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-CO-]_N- + 2N\,HCl$$

poly(hexamethylene adipamide), nylon 6,6

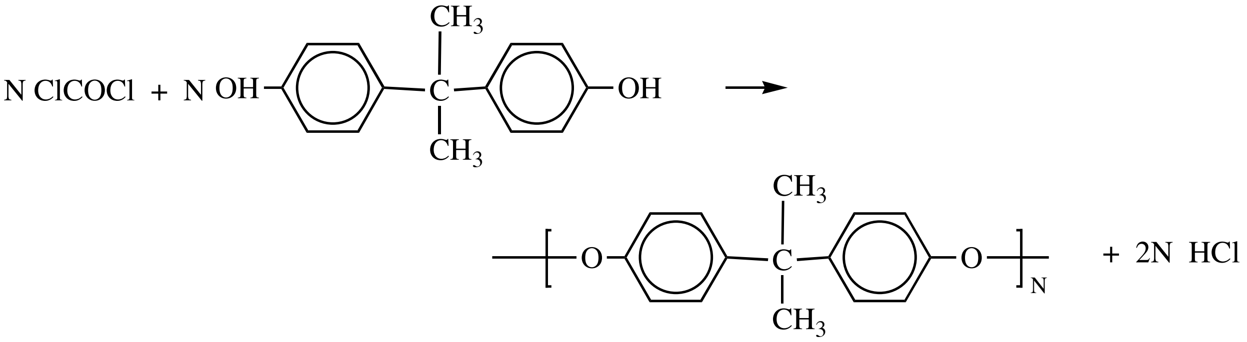
3. Polyurethane



$$N\,HO(CH_2)_4OH + N\;O{=}C{=}N(CH_2)_6N{=}C{=}O \longrightarrow -[-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O-]_N-$$

poly(tetramethylene hexamethylene urethane), Spandex, Perlon

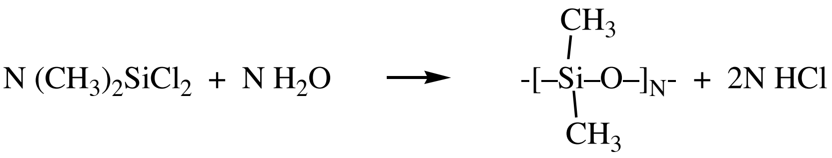
4. Polycarbonate



poly(4,4-isopropylidene diphenylene carbonate)

bisphenol A polycarbonate, Lexan

5. Inorganic



$$N\,(CH_3)_2SiCl_2 + N\,H_2O \longrightarrow -[-\underset{CH_3}{\overset{CH_3}{Si}}-O-]_N- + 2N\,HCl$$

polydimethyl siloxane

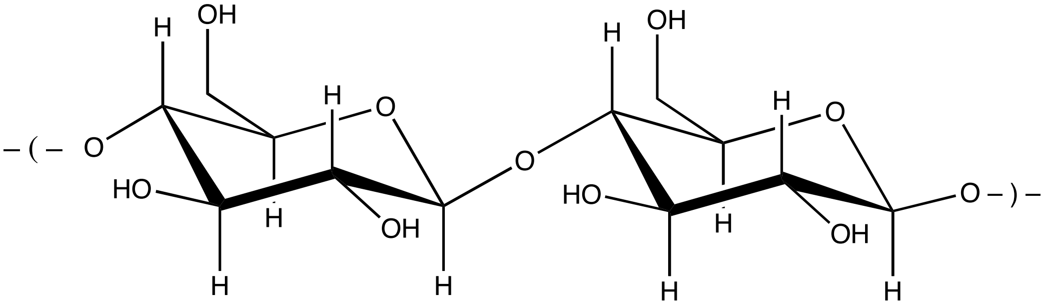
Table 1.2

Reactions by which several important condensation polymers can be produced

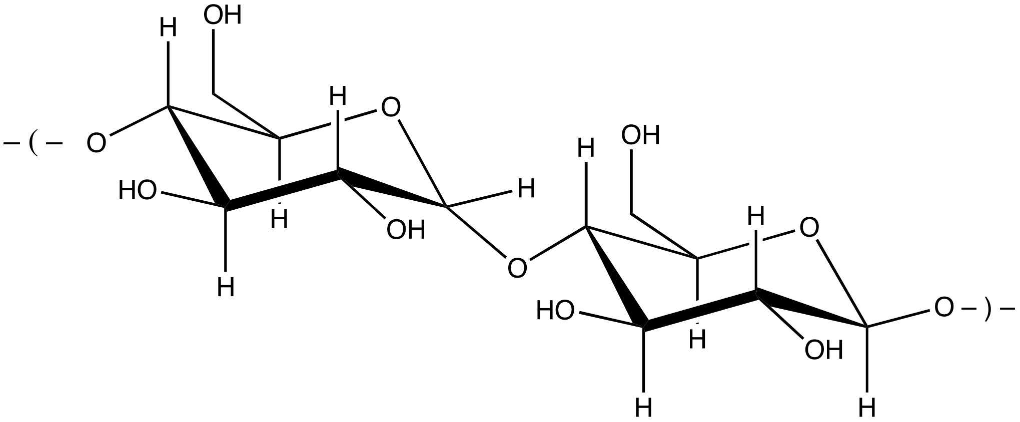
1.4B Natural polymers

We conclude this section with a short discussion of naturally occurring polymers. Since these are of biological origin, they are also called biopolymers. Although our attention in this volume is primarily directed toward synthetic polymers, it should be recognized that biopolymers, like inorganic polymers, have physical properties which follow directly from the chain structure of their molecules. For example, the denaturation of a protein involves an overall conformation change from a "native" state, often a globule, to a random coil. As another example, the elasticity and integrity of a cell membrane is often the result of an underlying network of fibrillar proteins, with the origin of the elasticity residing in the same conformational entropy as in a rubber band. Consequently, although we will not discuss the synthesis by, and contribution to the function of, living organisms by such biopolymers, many of the principles we will develop in detail apply equally well to natural polymers.

As examples of natural polymers, we consider *polysaccharides*, *proteins*, *and nucleic acids*. Another important natural polymer, polyisoprene, will be considered in Section 1.6. Polysaccharides are macromolecules which make up a large part of the bulk of the vegetable kingdom. *Cellulose* and *starch* are, respectively, the first and second most abundant organic compounds in plants. The former is present in leaves and grasses; the latter in fruits, stems, and roots. Because of their abundance in nature and because of contemporary interest in renewable resources, there is a great deal of interest in these compounds. Both cellulose and starch are hydrolyzed by acids to D-glucose, the repeat unit in both polymer chains. The configuration of the glucoside linkage is different in the two, however. Structures [I] and [II], respectively, illustrate that the linkage is a β-acetal – hydrolyzable to an equitorial hydroxide – in cellulose, and an α-acetal – hydrolyzable to an axial hydroxide – in amylose, a starch:



[I]

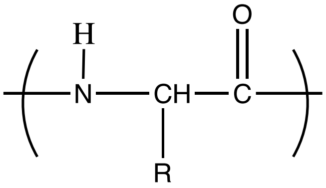


[II]

Amylopectin and glycogen are saccharides similar to amylose, except with branched chains.

The cellulose repeat unit contains three hydroxyl groups which can react and leave the chain backbone intact. These alcohol groups can be esterified with acetic anhydride to form cellulose acetate; this polymer is spun into the fiber acetate rayon. Similarly, the alcohol groups in cellulose react with CS_2 in the presence of strong base to produce cellulose xanthates. When extruded into fibers, this material is called viscose rayon, and when extruded into sheets, cellophane. In both the acetate and xanthate formation, some chain degradation also occurs, so the resulting polymer chains are shorter than those in the starting cellulose. The hydroxyl groups are also commonly methylated, ethylated, and hydroxypropylated for a variety of aqueous applications, including food products. A closely related polysaccharide is chitin, the second most abundant polysaccharide in nature, which is found for example in the shells of crabs and beetles. One of the hydroxyls on each repeat unit of cellulose is replaced with an –NHCO-CH_2 amide group. This is converted to a primary amine –NH_2 in chitosan, a derivative of chitin finding increasing applications in a variety of fields.

As noted above, proteins are polyamides in which α-amino acids make up the repeat units, as shown by structure [III]:



$$-\left(NH-CHR-C(=O)\right)-$$

[III]

These molecules are also called *polypeptides*, especially when $M \leq 10{,}000$. The various amino acids differ in their R groups. The nature of R, the name, and the abbreviation used to represent some of the more common amino acids are listed in Table 1.3. In proline (Pro) and hydroxyproline (Hyp), the nitrogen and the α-carbon are part of a five-atom pyrrolidine ring. Since some of the amino acids carry substituent carboxyl or amino groups, protein molecules are charged in aqueous solutions, and hence can migrate in electric fields. This is the basis of electrophoresis as a means of separating and identifying proteins.

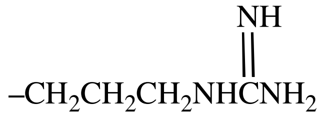
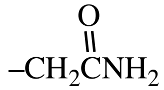
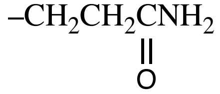
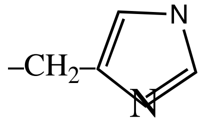
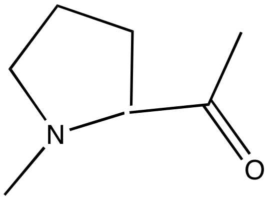
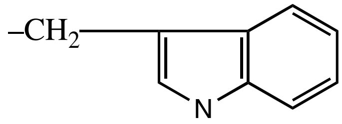
Name	Abbreviation	Letter Code	R group
Alanine	Ala	A	$-CH_3$
Arginine	Arg	R	 $-CH_2CH_2CH_2NH\overset{\overset{NH}{\Vert}}{C}NH_2$
Asparagine	Asn	N	 $-CH_2\overset{\overset{O}{\Vert}}{C}NH_2$
Aspartic acid	Asp	D	$-CH_2COOH$
Cysteine	Cys	C	$-CH_2SH$
Glutamic acid	Glu	E	$-CH_2CH_2OH$
Glutamine	Gln	O	 $-CH_2CH_2\underset{\underset{O}{\Vert}}{C}NH_2$
Glycine	Gly	G	$-H$
Histidine	His	H	
Isoleucine	Ile	I	$-CH(CH_3)CH_2CH_3$
Leucine	Leu	L	$-CH_2CH(CH_3)_2$
Lysine	Lys	K	$-CH_2CH_2CH_2CH_2NH_2$
Methionine	Met	M	$-CH_2CH_2SCH_3$
Phenylalanine	Phe	F	$-CH_2-\phi$
Proline	Pro	P	
Serine	Ser	S	$-CH_2OH$
Threonine	Thr	T	$-CH(OH)CH_3$
Tryptophan	Trp	W	
Tyrosine	Tyr	Y	$-CH_2-\phi-OH$
Valine	Val	V	$-CH(CH_3)_2$

Table 1.3
Name, abbreviations, and R group for common amino acids.

It is conventional to speak of three levels of structure in protein molecules:

1. *Primary structure* refers to the sequence of amino acids in the polyamide chain.
2. *Secondary structure* refers to the regions of the molecule that have particular spatial arrangements. Examples in proteins include the α-helix and the β-sheet.
3. *Tertiary structure* refers to the overall shape of the molecule, for example a globule perhaps stabilized by disulfide bridges formed by the oxidation of cysteine mercapto groups. By extension the full tertiary structure implies knowledge of the relative spatial positions of all the residues.

Hydrogen bonding stabilizes some protein molecules in helical forms, and disulfide cross-links stabilize some protein molecules in globular forms. Both secondary and tertiary levels of structure are also influenced by the distribution of polar and nonpolar amino acid molecules relative to the aqueous environment of the protein molecules. In some cases individual proteins associate in particular aggregates, which are referred to as quaternary structures.

Examples of the effects and modifications of the higher-order levels of structures in proteins are found in the following systems:

1. *Collagen* is the protein of connective tissues and skin. In living organisms, the molecules are wound around one another to form a three-strand helix stabilized by hydrogen bonding. When boiled in water, the collagen dissolves and forms gelatin, thereby establishing a new hydrogen bond equilibrium with the solvent. This last solution sets up to form the familiar gel when cooled, a result of shifting the hydrogen bond equilibrium.
2. *Keratin* is the protein of hair and wool. These proteins are insoluble because of the disulfide cross-linking between cysteine units. Permanent waving of hair involves the rupture of these bonds, reshaping of the hair fibers, and the reformation of cross-links which hold the chains in the new positions relative to each other. We shall see in Chapter

10 how such cross-linked networks are restored to their original shape when subjected to distorting forces.

3. The globular proteins *albumin* in eggs and *fibrinogen* in blood are converted to insoluble forms by modification of their higher-order structure. The process is called denaturation and occurs, in the systems mentioned, with the cooking of eggs and the clotting of blood.

4. *Actin* is a fascinating protein that exists in two forms: G-actin (globular) and F-actin (fibrillar). The globular form can polymerize (reversibly) into very long filaments, under the influence of various triggers. These filaments play a crucial role in the cytoskeleton, i.e. in allowing cells to maintain their shape. In addition, the uniaxial sliding of actin filaments relative to filaments of a related protein, myosin, is responsible for the working of muscles.

Ribonucleic acid (RNA) and *deoxyribonucleic acid* (DNA) are polymers in which the repeat units are substituted esters. The esters are formed between the hydrogens of phosphoric acid and the hydroxyl groups of a sugar, D-ribose in the case of RNA and D-2-deoxyribose in the case of DNA. The sugar rings in DNA carry four different kinds of substituents: adenine (A) and guanine (G), which are purines, and thymine (T) and cytosine (C), which are pyramidines. The familiar double-helix structure of the DNA molecule is stabilized by hydrogen bonding between pairs of substituent base groups: G – C and A – T. In RNA thymine is usually replaced by uracil (U). The replication of these molecules, the template model of their functioning, and their role in protein synthesis and the genetic code make the study of these polymers among the most exciting and actively researched areas in all science. As with the biological function of proteins, we will not discuss these phenomena in this book. However, as indicated previously, DNA plays a very important role as a prototypical semiflexible polymer, as it is now readily obtainable in pure molecular fractions of varying lengths, and because it is readily dissolved in aqueous solution. It is also a charged polymer, or *polyelectrolyte*, and thus serves as a model system in this arena as well.

1.5 Polymer Nomenclature

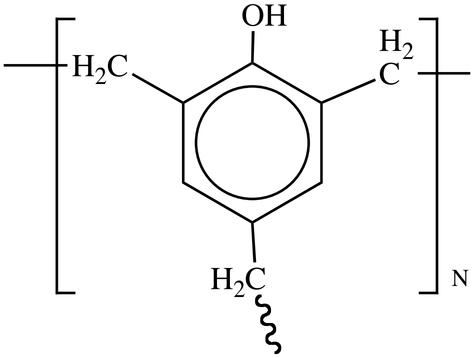
Considering that a simple compound like C_2H_5OH is variously known as ethanol, ethyl alcohol, grain alcohol, or simply alcohol, it is not too surprising that the vastly more complicated polymer molecules are also often known by a variety of different names. The International Union of Pure and Applied Chemistry (IUPAC) has recommended a system of nomenclature based on the structure of the monomer or repeat unit [7]. A semisystematic set of trivial names is also in widespread usage; these latter names seem even more resistant to replacement than is the case with low molecular weight compounds. Synthetic polymers of commercial importance are often widely known by trade names that have more to do with marketing considerations than with scientific communication. Polymers of biological origin are often described in terms of some aspect of their function, preparation or characterization.

If a polymer is formed from a single monomer, as in addition and ring-opening polymerizations, it is named by attaching the prefix *poly* to the name of the monomer. In the IUPAC system, the monomer is named according to the IUPAC recommendations for organic chemistry, and the name of the monomer is set off from the prefix by enclosing the former in parentheses. Variations of this basic system often substitute a common name for the IUPAC name in designating the monomer. Whether or not parentheses are used in the latter case is influenced by the complexity of the monomer name; they become more important as the number of words in the monomer name increases. Thus the polymer $(CH_2\text{–}CHC1)_N$ is called poly(1-chloroethylene) according to the IUPAC system; it is more commonly called poly(vinyl chloride) or polyvinyl chloride. Acronyms are not particularly helpful but are an almost irresistible aspect of polymer terminology, as evidenced by the initials PVC, which are widely used to describe the polymer just named. The trio of names poly(1-hydroxyethylene), poly(vinyl alcohol), and polyvinyl alcohol emphasizes that the polymer need not actually be formed from the reaction of the monomer named; this polymer is actually prepared by the hydrolysis of poly(1-

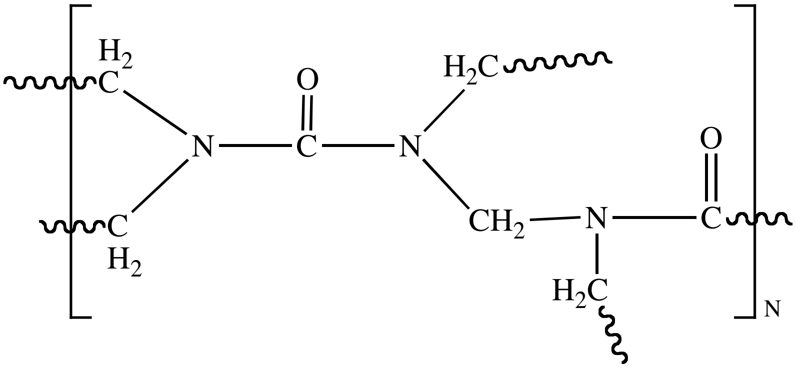
acetoxyethylene), otherwise known as poly(vinyl acetate). These same alternatives are used in naming polymers formed by ring-opening reactions; for example, poly(6-aminohexanoic acid), poly(6-aminocaproic acid), and poly(ε-caprolactam) are all more or less acceptable names for the same polymer.

Those polymers which are the condensation product of two different monomers are named by applying the preceding rules to the repeat unit. For example, the polyester formed by the condensation of ethylene glycol and terephthalic acid is called poly(oxyethylene oxyterphthaloyl) according to the IUPAC system, but is more commonly referred to as poly(ethylene terephthalate) or polyethylene terephthalate. The polyamides poly(hexamethylene sebacamide) and poly(hexamethylene adipamide) are also widely known as nylon-6,10 and nylon-6,6, respectively. The numbers following the word nylon indicate the number of carbon atoms in the diamine and dicarboxylic acid, in that order. On the basis of this system, poly(ε-caprolactam) is also known as nylon-6.

Many of the polymers in Tables 1.1 and 1.2 are listed with more than one name. Also listed are some of the patented trade names by which these substances – or materials which are mostly of the indicated structure – are sold commercially. Some commercially important cross-linked polymers go virtually without names. These are heavily and randomly cross-linked polymers which are insoluble and infusible and therefore widely used in the manufacture of such molded items as automobile and household appliance parts. These materials are called resins and, at best, are named by specifying the monomers which go into their production. Often even this information is sketchy. Examples of this situation are provided by phenol-formaldehyde and urea-formaldehyde resins, for which typical structures are given by structures [IV] and [V], respectively:



[IV]



[V]

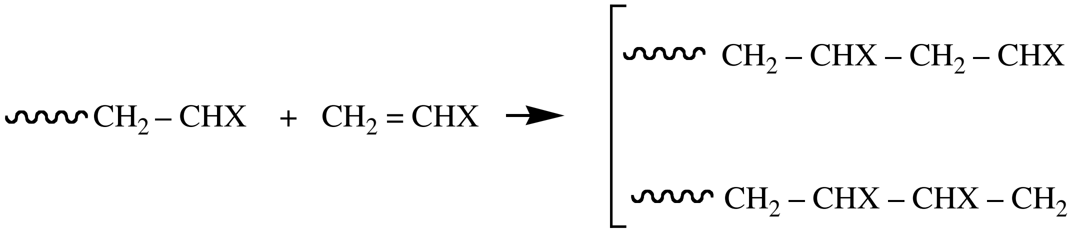
1.6 Structural isomerism

In this section we shall consider three types of isomerism which are encountered in polymers. These are positional isomerism, stereo isomerism, and geometrical isomerism. We shall focus attention on synthetic polymers and shall, for the most part, be concerned with these types of isomerism occurring singly, rather than in combinations. Some synthetic and analytical aspects of stereo isomerism will be considered in Chapter 5. Our present concern is merely to introduce the possibilities of these isomers and some of the associated vocabulary.

1.6A Positional isomerization

Positional isomerism is conveniently illustrated by considering the polymerization of a vinyl monomer. In such a reaction, the adding monomer may become attached to the growing chain in either of two orientations:

[VI]



$$\sim\!\sim CH_2-CHX + CH_2=CHX \rightarrow \left[\begin{array}{l} \sim\!\sim CH_2-CHX-CH_2-CHX \\ \\ \sim\!\sim CH_2-CHX-CHX-CH_2 \end{array}\right. \tag{1.B}$$

[VII]

Structures [VI] and [VII], respectively, are said to arise from *head-to-tail* or *head-to-head* orientations. In this terminology, the substituted carbon is defined to be the head molecule, and the methylene is the tail. Tail-to-tail linking is also possible.

For most vinyl polymers, head-to-tail addition is the dominant mode of addition. Variations from this generalization become more common for polymerizations which are carried out at higher temperatures. Head-to-head addition is also somewhat more abundant in the case of halogenated monomers such as vinyl chloride. The preponderance of head-to-tail additions is understood to arise from a combination of resonance and steric effects. In many cases the ionic or free-radical reaction center occurs at the substituted carbon due to the possibility of resonance stabilization or electron delocalization through the substituent group. Head-to-tail attachment is also sterically favored, since the substituent groups on successive repeat units are separated by a methylene carbon. At higher polymerization temperatures, larger amounts of available thermal energy make the less-favored states more accessible. In vinyl fluoride, no resonance stabilization is possible and steric effects are minimal. This monomer adds primarily in the head-to-tail orientation at low temperatures and tends towards a random combination of both at higher temperatures. The styrene radical, by contrast, enjoys a large amount of resonance stabilization in the bulky phenyl group and polymerizes almost exclusively in the head-to-tail mode. The following example illustrates how chemical methods can be used to measure the relative amounts of the two positional isomers in a polymer sample.

Example 1.3

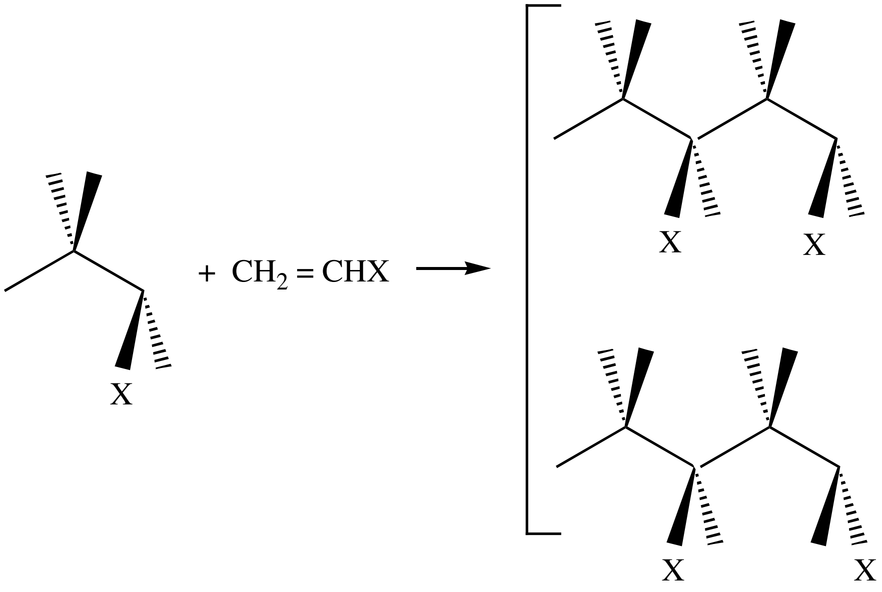
1,2-Glycol bonds are cleaved by reaction with periodate; hence poly(vinyl alcohol) chains are broken at the site of head-to-tail links in the polymer. The fraction of head-to-head linkages in poly(vinyl alcohol) may be determined by measuring the molecular weight before (subscript b) and after (subscript a) cleavage with periodate according to the following formula: Fraction = $44(1/M_a - 1/M_b)$. Derive this expression and calculate the value for the fraction in the case of $M_b = 10^5$ and $M_a = 10^3$.

Solution

Begin by recognizing that a molecule containing x of the head-to-head links will be cleaved into x + 1 molecules upon reaction. Hence if n is the number of polymer molecules in a sample of mass w, the following relations apply before and after cleavage: $n_a = (x+1)n_b$ or $w/M_a = (x+1)(w/M_b)$. Solving for x and dividing the latter by the total number of linkages in the original polymer gives the desired ratio. The total number of links in the mass w of polymer is w/n_bM_o. Therefore the ratio is $x/n_b = M_o\left(1/M_a - 1/M_b\right)$. For polyvinyl alcohol M_o is 44, so the desired formula has been obtained. For the specific data given, $x/n_b = 44\left(10^{-3} - 10^{-5}\right) = 0.044$, or about 4% of the additions are in the less favorable orientation. We shall see presently that the molecular weight of a polymer is an average which is different, depending on the method used for its determination. The present example used molecular weights as a means for counting the number of molecules present. Hence the sort of average molecular weight used should also be one which is based on counting.

1.6A Stereo isomerization

The second type of isomerism we discuss in this section is *stereo isomerism.* Again we consider the number of ways a singly substituted vinyl monomer can add to a growing polymer chain:



[VIII]

[IX]

(1.C)

Structures [VIII] and [IX] are not equivalent; they would not superimpose if the extended chains were overlaid. The difference has to do with the stereo-chemical configuration at the asymmetric carbon atoms. Note that the asymmetry is more accurately described as pseudoasymmetry, since two sections of chain are bonded to these centers. Except near chain ends, which we ignore for high polymers, these chains provide local symmetry in the neighborhood of the carbon under consideration. The designations of D and L or R and S are used to distinguish these structures, even though true asymmetry is absent.

We use the word *configuration* to describe the way the two isomers produced by reaction (1.C) differ. It is only by breaking bonds, moving substituents, and reforming new bonds that the two structures can be interconverted. This state of affairs is most readily seen when the molecules are drawn as fully extended chains in one plane, and then examining the side of the chain on which substituents lie. The configurations are not altered if rotation is allowed to occur around the various bonds of the backbone to change the shape of the molecule to a jumbled coil. We shall use the term *conformation* to describe the latter possibilities for different molecular shapes. The configuration is not influenced by conformational changes, but the stability of different conformations may be affected by differences in configuration. We shall return to these effects in Chapter 6.

In the absence of any external influence such as a catalyst which is biased in favor of one configuration over the other, we might expect structures [VIII] and [IX] to occur at random with equal probability as if the configuration at each successive addition were determined by the toss of a coin. Such, indeed, is the ordinary case. However, in the early 1950s, stereospecific catalysts were discovered; Ziegler and Natta received the Nobel Prize for this discovery in 1963. Following the advent of these catalysts, polymers with a remarkable degree of stereoregularity have been formed. These have such a striking impact on polymer science that a substantial part of Chapter 5 is devoted to a discussion of their preparation and characterization. For now, only the terminology involved in their description concerns us. Three different situations can be distinguished along a chain containing pseudoasymmetric carbons:

1. *Isotactic*. All substituents lie on the same side of the extended chain. Alternatively, the stereoconfiguration at the asymmetric centers is the same, say: –DDDDDDDDD–.

2. *Syndiotactic.* Substituents on the fully extended chain lie on alternating sides of the backbone. This alternation of configuration can be represented as –DLDLDLDLDLDL–.

3. *Atactic.* Substituents are distributed at random along the chain, for example, DDLDLLLDLDLL–.

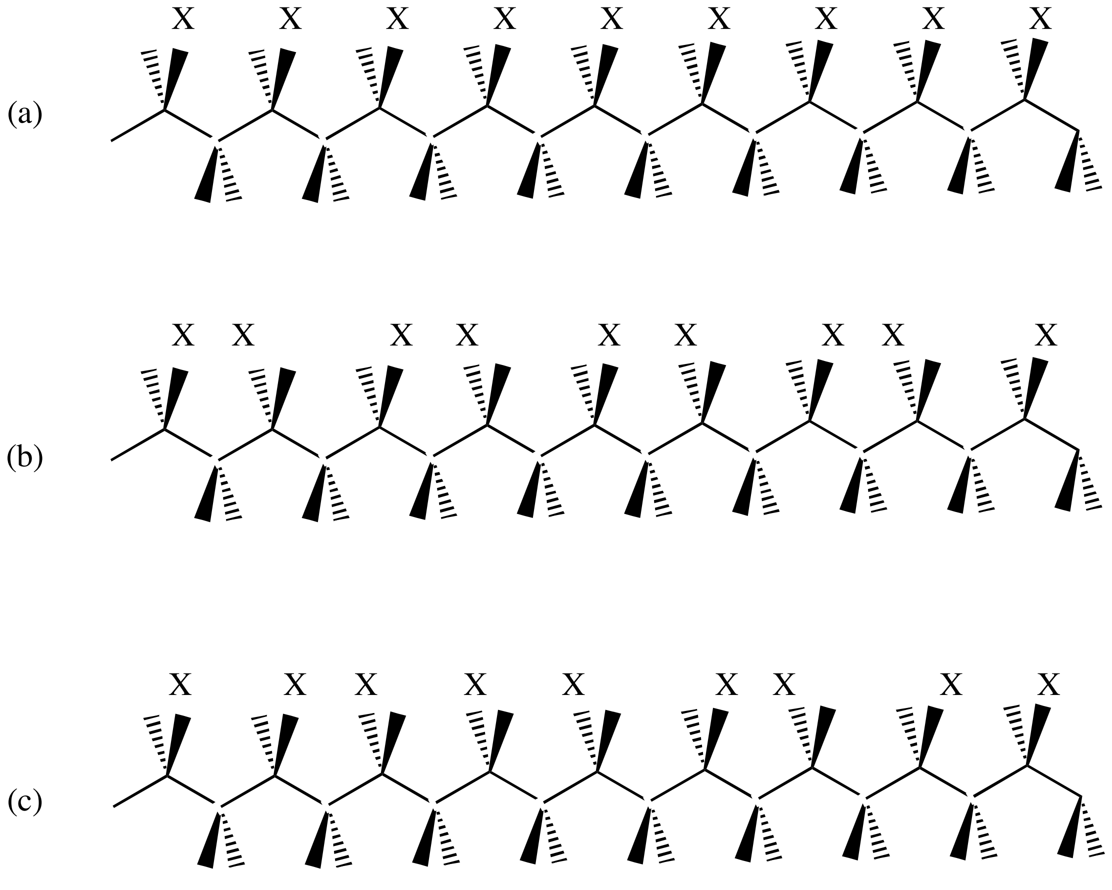


Figure 1.3
Sections of "polyvinylX" chains of differing tacticity: (a) isotactic, (b) syndiotactic, and (c) atactic.

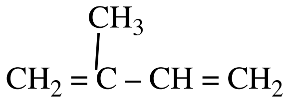
Figure 1.3 shows sections of polymer chains of these three types; the substituent X equals phenyl for polystyrene and methyl for polypropylene. The general term for this stereoregularity is *tacticity*, a term derived the Greek work meaning "to put in order". Polymers of different tacticity have quite different properties, especially in the solid state. As we will see in Chapter 13, one of the requirements for polymer crystallinity is high degree of microstructural regularity to enable the chains to pack in an orderly manner. Thus atactic polypropylene is a soft, tacky substance, whereas both isotactic and syndiotactic polypropylene are highly crystalline.

1.6C Geometric isomerization

The final type of isomerism we take up in this section is nicely illustrated by the various possible structures that result from the polymerization of 1,3-dienes. Three important monomers of this type are 1,3-butadiene, 1,3-isoprene, and 1,3-chloroprene, structures [X] - [XII], respectively:

$CH_2 = CH - CH = CH_2$

[X]



$CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2$

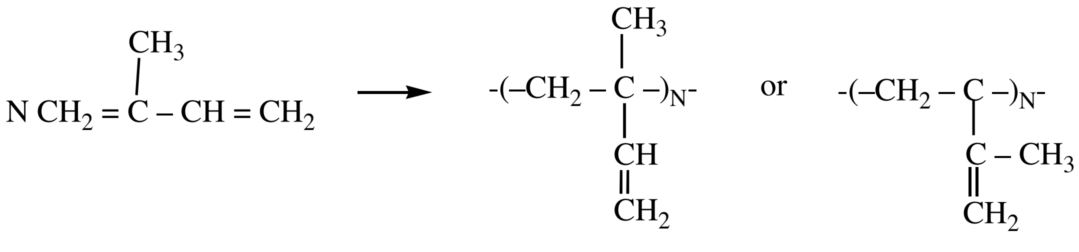
[XI]

$CH_2 = CCl - CH = CH_2$

[XII]

To illustrate the possible modes of polymerization of these compounds, consider the following reactions of isoprene:

1. 1,2- and 3,4-Polymerizations. As far as the polymer chain backbone is concerned, these compounds could just as well be mono-olefins, since the second double bond is relegated to the status of a substituent group. Because of the reactivity of the latter, however, it might become involved in cross-linking reactions. For isoprene, 1,2- and 3,4-polymerizations yield different products:

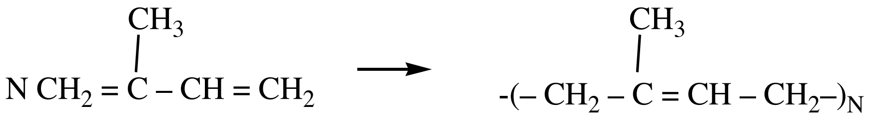


$$N\,CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2 \longrightarrow -(-CH_2 - \underset{\underset{\underset{CH_2}{\|}}{CH}}{\overset{\overset{CH_3}{|}}{C}} -)_N- \quad \text{or} \quad -(-CH_2 - \underset{\underset{\underset{CH_2}{\|}}{C - CH_3}}{\underset{|}{C}} -)_N- \qquad (1.D)$$

[XIII] [XIV]

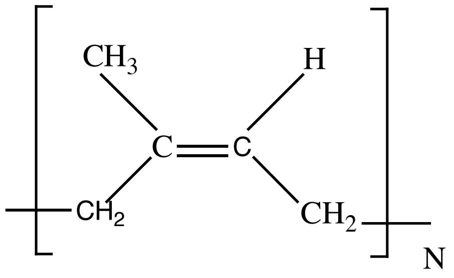
These differences do not arise from 1,2- or 3,4-polymerization of butadiene. Structures [XIII] and [XIV] can each exhibit the three different types of tacticity, so a total of six structures can result from this monomer when only one of the olefin groups is involved in the backbone formation.

2. 1,4-Polymerization. This mode of polymerization gives a molecule with double bonds along the backbone of the chain. Again using isoprene as the example,

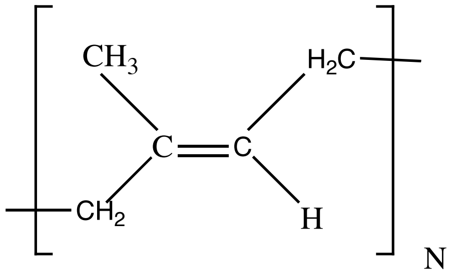


$$N\,CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2 \longrightarrow -(-\,CH_2 - \overset{\overset{CH_3}{|}}{C} = CH - CH_2-)_N \qquad (1.E)$$

As in all double-bond situations, the adjacent chain sections can be either cis or trans – structures [XV] and [XVI], respectively – with respect to the double bond, producing the following geometrical isomers:



[XV]



[XVI]

Figure 1.4 shows several repeat units of cis-1,4-polyisoprene and trans-1,4-polyisoprene. *Natural rubber* is the cis isomer of 1,4-polyisoprene, and *gutta-percha* is the trans isomer.

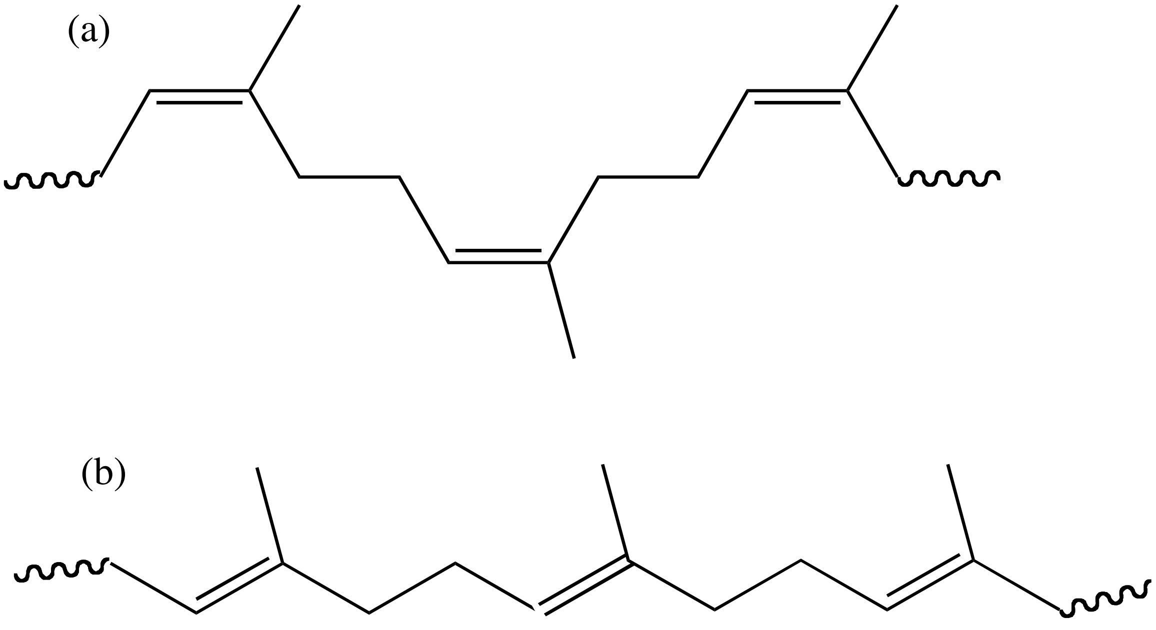


Figure 1.4
1,4-polyisoprene (a) all-cis isomer (natural rubber) and (b) all-trans isomer (gutta-percha).

3. Polymers of chloroprene (structure [XII]) are called neoprene and copolymers of butadiene and styrene are called SBR, an acronym for styrene-butadiene rubber. Both are used for many of the same applications as natural rubber. Chloroprene displays the same assortment of possible isomers as isoprene; the extra combinations afforded by copolymer composition and structure in SBR offsets the fact that structures [XIII] and [XIV] are identical for butadiene.

4. Although the conditions of the polymerization reactions may be chosen to optimize the formation of one specific isomer, it is typical in these systems to have at least some contribution of all possible isomers in the polymeric product, except in the case of polymers of biological origin, like natural rubber and gutta-percha.

Example 1.4

Suppose you have just ordered a tank car of polybutadiene from your friendly rubber company. By some miracle, all the polymers in the sample have M = 54,000. The question we would like to consider is this: what are the chances that any two molecules is this sample have exactly the same chemical structure?

Solution

We will not attempt to provide a precise answer to such an artificial question; what we really want to know is whether the probability is high (approximately 1), vanishing (approximately 0), or finite.

From the discussion above we recognize three geometrical isomers: trans-1,4, cis-1,4, and 1,2. We will ignore the stereochemical possibilities associated with the 1,2 linkages. Assuming all three isomers occur with equal probability, the total number of possible structures is 3x3x3...x3 = 3^N, where N is the degree of polymerization. (Recall that the combined probability of a sequence of events is equal to the products of the individual probabilities). In this case N = 54,000/54 = 1000, and thus there are about $3^{1000} \approx 10^{500}$ possible structures. Now we need to count how many molecules we have. Assuming for simplicity that the tank car is 3.3 m x 3.3 m x 10 m = 100 m = 10^8 cm^3, and that the density of the polymer is 1 g/cm^3 (it is actually closer to 0.89 g/cm^3), we have 10^8 g of polymer. As M = 54,000 g/mol, we have about 2000 moles, or 2000 x 6 x $10^{23} \approx 10^{27}$ molecules. Clearly, therefore, there is essentially no chance that any two molecules have the identical structure, even without taking the molecular weight distribution into account!

This example, as simplistic as it is, actually underscores two important points. First, polymer chemists have to get used to the idea that while all carbon atoms are identical, and all butadiene molecules are identical, polybutadiene actually refers to an effectively infinite number of distinct chemical structures. Second, almost all synthetic polymers are heterogeneous in more than one variable: molecular weight, certainly; isomer and tacticity distribution, probably;

composition and sequence distribution, for copolymers; and branching structure, when applicable.

1.7 Molecular weights and molecular weight averages

Almost every synthetic polymer sample contains molecules of various degrees of polymerization. We describe this state of affairs by saying that the polymer shows *polydispersity* with respect to molecular weight or degree of polymerization. To see how this comes about, we only need to think of the reactions between monomers that lead to the formation of polymers in the first place. Random encounters between reactive species are responsible for chain growth, so statistical descriptions are appropriate for the resulting product. The situation is reminiscent of the distribution of molecular velocities in a sample of gas. In that case, also, random collisions impart extra energy to some molecules while reducing the energy of others. Therefore, when we talk about the molecular weight of a polymer, we mean some characteristic *average* molecular weight. It turns out there are several distinct averages that may be defined, and that may be measured experimentally; it is therefore appropriate to spend some time on this topic. Furthermore, one might well encounter two samples of a particular polymer that were equivalent in terms of one kind of average, but different in terms of another; this, in turn, can lead to the situation where the two polymers behave identically in terms of some important properties, but differently in terms of others.

In Chapters 2, 3 and 4 we shall examine the expected distribution of molecular weights for condensation and addition polymerizations in some detail. For the present, our only concern is how such a distribution of molecular weights is described. We will define the most commonly encountered averages, and how they relate to the distribution as a whole. We will also relate them to the standard parameters used for characterizing a distribution: the mean and standard deviation. Although these are well-known quantities, many students are familiar with them only as results provided by a calculator, and so we will describe them in some detail.

1.7A Number-, weight-, and z-average molecular weights

Suppose we have a polymer sample containing many molecules with a variety of degrees of polymerization. We will call a molecule with degree of polymerization i an "i-mer", and the associated molecular weight $M_i = iM_o$, where M_o is the molecular weight of the repeat unit. (Conversion between a discussion couched in terms of i or in terms of M_i is therefore striaghtforward, and we will switch back and forth when convenient). The number of i-mers we will denote as n_i (we could also refer to n_i as the number of moles of i-mer, but again this just involves a factor of Avogadro's number). The first question we ask is this: if we choose a molecule at random from our sample, what is the probability of obtaining an i-mer? The answer is straightforward. The total number of molecules is $\sum_i n_i$, and thus this probability is give by

$$x_i = \frac{n_i}{\sum_i n_i} \tag{1.7.1}$$

The probability x_i is the number fraction or *mole fraction* of i-mer. We can use this quantity to define a particular average molecular weight, called the *number-average molecular weight*, M_n. We do this by multiplying the probability of finding an i-mer with its associated molecular weight, x_iM_i, and adding these all up:

$$M_n = \sum_i x_i M_i = \frac{\sum_i n_i M_i}{\sum_i n_i} = M_o \frac{\sum_i i\, n_i}{\sum_i n_i} \tag{1.7.2}$$

The other expressions on the right hand side of eq 1.7.2 are equivalent, and will prove useful subsequently. You should convince yourself that this particular average is the one you are familiar with in everyday life: take the value of the property of interest, M_i in this case, add it up for all the (n_i) objects that possess a value of the property, and divide by the total number of objects.

So far, so good. We return for a moment to our hypothetical sample, but instead of choosing a molecule at random, we choose a repeat unit or monomer at random, and ask about the molecular weight of the molecule to which it belongs. We will get a different answer, as a simple argument illustrates. Suppose we had two molecules, one a 10-mer and one a 20-mer. If we choose *molecules* at random, we would choose each one 50% of the time. However, if we choose *monomers* at random, 2/3 of the monomers are in the 20-mer, so we would pick the larger molecule twice as often as the smaller. The total number of monomers in a sample is $\sum_i i n_i$, and the chance of picking a particular i-mer will be determined by the product in_i. The resulting ratio is, in fact, the *weight fraction* or *mass fraction* of i-mer in the sample, w_i:

$$w_i = \frac{in_i}{\sum_i in_i} \tag{1.7.3}$$

Accordingly, we define the *weight-average molecular weight* of the sample, M_w, by:

$$M_w = \sum_i w_i M_i = \frac{\sum_i in_i M_i}{\sum_i in_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = M_o \frac{\sum_i i^2 n_i}{\sum_i in_i} \tag{1.7.4}$$

Of course, *mass-average* would be the preferred descriptor, but it is not in common usage. Qualitatively, we can say that M_n is the characteristic average molecular weight of the sample when the number of molecules is the crucial factor, whereas M_w is the characteristic molecular weight when the size of each molecule is the important feature. Although knowledge of M_w and

M_n is not sufficient to provide all the information about a polydisperse system, these two averages are by far the most important and most commonly encountered, as we shall see throughout the book.

Comparison of the last expressions in eqs 1.7.2 and 1.7.4 suggests a trend; we can define a new average by multiplying the summation terms in the numerator and denominator by i. The so-called *z-average molecular weight* M_z is constructed in just such a way:

$$M_z = M_o \frac{\sum_i i^3 n_i}{\sum_i i^2 n_i} \tag{1.7.5}$$

Although M_z is not directly related to a simple fraction like x_i or w_i, it does have some experimental relevance. We could continue this process indefinitely, just by incrementing the power of i by one in both numerator and denominator of eq 1.7.5, but it will turn out that there is no real need to do so. However, there is a direct relationship between this process and something well-known in statistical probability, namely the moments of a distribution, as we will see in the next section.

1.7B Polydispersity index and standard deviation

Although the values M_w or M_n tell us something useful about a polymer sample, individually they do not provide information about the breadth of the distribution. However, the ratio of the two turns out to be extremely useful in this regard, and it is a given a special name: the *polydispersity index* ("PDI") or just the *polydispersity*:

$$\mathrm{PDI} = \frac{M_w}{M_n} \tag{1.7.6}$$

The PDI is always greater than 1, unless the sample consists of exactly one value of M, in which case the PDI = 1; such a sample is said to be *monodisperse*. We will see in Chapters 2 and 3 that typical polymerization schemes are expected to give PDIs near 2, at least in the absence of various side reactions; in industrial practice, such side reactions often lead to PDIs as large as 10 or more. In Chapter 4, in contrast, so-called living polymerizations give rise to PDIs of 1.1 or smaller. Thus, distributions for which the PDI < 1.5 are said to be "narrow", whereas PDIs > 2 are said to be "broad"; of course, such designations are highly subjective. As a very simple example, the two-molecule example given in the previous section consisting of a 10-mer and a 20-mer has a number-average degree of polymerization of 15 and a weight average of 16.7; thus its PDI = 1.11, which in polymer terms would be considered "narrow". This trivial example actually underscores an important point to bear in mind: polymer samples with "narrow" distributions will still contain molecules that are quite different in size (see Problem 1.8 for another instance).

In most fields of science distributions are generally characterized by a *mean* and a *standard deviation*. We will now develop the relationships between these quantities and M_w and M_n, and in so doing justify the assertion that the PDI is a useful measure of the breadth of a distribution. The mean of any distribution of a variable i, <i>, is defined as

$$< i > \; = \frac{\sum_i i n_i}{\sum_i n_i} = \sum_i i x_i \approx \int_0^\infty i P(i) di \qquad (1.7.7)$$

where both discrete (x_i) and continuous (P(i)) versions are considered. From this definition, and eq 1.7.2, we can see that <i> is nothing more than the number-average degree of polymerization, and thus M_n is just the mean molecular weight.

The standard deviation σ quantifies the width of the distribution. It is defined as

$$\sigma \equiv \left(\frac{\sum_i n_i(i - <i>)^2}{\sum_i n_i}\right)^{1/2} = \left(\sum_i x_i(i - <i>)^2\right)^{1/2} \qquad (1.7.8)$$

Note that σ^2 has the significance of being the mean value of the square of the deviations of individual values from the mean. Accordingly, σ is sometimes called the root mean square (rms) deviation.

From a computational point of view, the standard deviation may be written in a more convenient form by carrying out the following operations. First both sides of eq 1.7.8 are squared, and then the difference i – <i> is squared to give

$$\sigma^2 = \frac{\sum_i n_i i^2}{\sum_i n_i} - 2 <i> \frac{\sum_i n_i i}{\sum_i n_i} + <i>^2 \qquad (1.7.9)$$

Recalling the definition of the mean, we recognize the first term on the right-hand side of eq 1.7.9 to be the mean value of i^2 and write

$$\sigma^2 = <i^2> - 2<i>^2 + <i>^2 = <i^2> - <i>^2 \qquad (1.7.10)$$

It is, of course, important to realize that $<i^2> \neq <i>^2$. An alternative to eq 1.7.8 as a definition of standard deviation is, therefore,

$$\sigma = \left(< i^2 > - < i >^2 \right)^{1/2} \qquad (1.7.11)$$

Similarly, the standard deviation can be written

$$\sigma = \left[\sum_i x_i (M_i - M_n)^2 \right]^{1/2} \qquad (1.7.12)$$

where in this case the standard deviation will have the units of molecular weight. If we expand eq 1.7.12 we find

$$\sigma = \left[\sum_i x_i \left(M_i{}^2 - 2 M_i M_n + M_n{}^2 \right) \right]^{1/2} = \left[(\sum_i x_i M_i{}^2) - M_n{}^2 \right]^{1/2} \qquad (1.7.13)$$

We can factor out $M_n = \sum_i x_i M_i$ to obtain

$$\sigma = M_n \left[\frac{\sum_i x_i M_i{}^2}{(\sum_i x_i M_i)^2} - 1 \right]^{1/2} \qquad (1.7.14)$$

and finally, by recognizing from eq 1.7.4 that

$$M_w = \frac{\sum_i n_i M_i{}^2}{\sum_i n_i M_i} = \frac{\sum_i x_i M_i{}^2}{\sum_i x_i M_i} \qquad (1.7.15)$$

we reach

$$\sigma \;=\; M_n\left[\frac{M_w}{M_n}-1\right]^{1/2} \tag{1.7.16}$$

This result shows that the square root of the amount by which the ratio M_w/M_n exceeds unity equals the standard deviation of the distribution relative to the number average molecular weight. Thus if a distribution is characterized by M_n =10000 and $\sigma = 3000$, then M_w/M_n = 1.09. Alternatively, if M_w/M_n = 1.50, then the standard deviation is 71% of the value of M_n. This shows that reporting the mean and standard deviation of a distribution or the values of M_n and M_w/M_n gives equivalent information.

We can define the quantities known as *moments of a distribution*, again either in the discrete or continuous forms. The kth moment μ_k is given by

$$\mu_k \;=\; \sum_i x_i i^k \text{ or } \int_0^\infty i^k P(i)di \tag{1.7.17}$$

In this definition both x_i and P(i) are *normalized* distributions, which means that $\sum_i x_i = 1$ and $\int_0 P(i)di = 1$. From eq 1.7.17 we can also see that the mean is equivalent to the first moment. From eqs 1.7.4 and 1.7.5 it is apparent that M_w and M_z are proportional to the ratio of the second to the first moment and the third to the second, respectively. More generally, moments can be referred to a particular value, such as the kth moment about the mean, ν_k:

$$\nu_k \;=\; \sum_i x_i(i-<i>)^k \tag{1.7.18}$$

From this expression we see that σ^2 is the second moment about the mean.

1.7C Examples of distributions

First, consider the following numerical example in which we apply some of the equations of this section to hypothetical data.

Example 1.5

The first and second columns of Table 1.4 give the number of moles of polymer in six different molecular weight fractions. Calculate M_w/M_n for this polymer and evaluate σ using both eqs 1.7.12 and 1.7.16.

Solution

Evaluate the product n_iM_i for each class; this is required for the calculation of both M_n and M_w. Values of this quantity are listed in the third column of Table 1.4. From $\sum_i n_iM_i$ and $\sum_i n_i, M_n = 734/0.049 = 15{,}000$. (The matter of significant figures will not be strictly adhered to in this example. As a general rule, one has to work pretty hard to obtain more than 2 significant figures in an experimental determination of M).

The products m_iM_i are mass-weighted contributions and are listed in the fourth column of Table 1.4. From $\sum_i m_i$ and $\sum_i n_iM_i, M_w = 113 \times 10^5/734 = 15{,}400$.

The ratio M_w/M_n is found to be 15,400/15,000 = 1.026 for these data. Using eq 1.7.16, we have $\sigma/M_n = (1.026 - 1)^{1/2} = 0.162$ or $\sigma = 0.162(15{,}000) = 2430$.

To evaluate σ via eq 1.7.12, differences between M_i and M_n must be considered. The fifth and sixth columns in Table 1.4 list $(M_i - M_n)^2$ and $n_i(M_i - M_n)^2$ for each class of data. From $\sum_i n_i$ and $\sum_i n_i(M_i - M_n)^2$, $\sigma^2 = 28.1 \times 10^4/0.049 = 5.73 \times 10^6$, and $\sigma = 2390$.

The discrepancy between the two values of σ is not meaningful in terms of significant figures; the standard deviation is 2400.

We shall see that, as polymers go, this is a very narrow molecular weight distribution.

n_i mol	**M_i** g/mol	**m_i** g	**$m_iM_i x10^{-6}$** g^2/mol	**$(M_i-M_n)^2$** x10^{-6} g^2/mol^2	**$n_i(M_i-M_n)^2$** x10^{-6} g^2/mol
0.003	10,000	30	3.0	25	7.50
0.008	12,000	96	11.5	9	7.20
0.011	14,000	154	21.6	1	1.10
0.017	16,000	272	43.5	1	1.70
0.009	18,000	162	29.2	9	8.10
0.001	20,000	20	4.0	25	2.50
Σ = 0.049		Σ = 734	Σ = 113	Σ = 70	Σ = 28.10

Table 1.4
Some molecular weight data for a hypothetical polymer used in Example 1.5

When we consider particular polymerization schemes in Chapters 2, 3, and 4, we will derive explicit expressions for the expected distributions x_i and w_i. For now, however, let us consider a particular mathematical function known as the *Schulz-Zimm distribution*. It has the virtue that by varying a single parameter, z, it is possible to obtain reasonable descriptions for typical narrow or moderately broad samples. We will use it to illustrate graphically how the distribution might appear for a given polydispersity. The Schulz-Zimm distribution can be expressed as

$$P(M_i) = \frac{z^{z+1}}{\Gamma(z+1)} \frac{M_i^{z-1}}{M_n^{z}} \exp\left(-\frac{zM_i}{M_n}\right) \qquad (1.7.19)$$

where Γ(z=1) is the so-called gamma function (which is tabulated in many mathematical references). For integer values of z, Γ(z+1) = z!, where z! (z factorial) = z x (z-1) x (z-2) ... x 1. From eqs 1.7.2 and 1.7.3 we can see that $w_i = x_i M_i / M_n$, and thus

$$w_i = \frac{z^{z+1}}{\Gamma(z+1)} \frac{M_i{}^z}{M_n{}^{z+1}} \exp\left(-\frac{zM_i}{M_n}\right) \tag{1.7.20}$$

The utility of this distribution arises in part because of a very simple relationship between the parameter z and the polydispersity:

$$\frac{M_w}{M_n} = \frac{z+1}{z} \tag{1.7.21}$$

The proof of eq 1.7.21 is left to problem 1.9 at the end of the chapter. Now we can use eqs 1.7.19 and 1.7.20 to generate distributions for specified values of M_n and M_w/M_n.

Figure 1.5a shows the mole fraction and weight fraction as a function of M, with the particular choice of M_n = 10,000, M_o = 100, and z = 1. Thus, according to eq 1.7.21, the PDI = 2 and M_w = 20,000. Both M_w and M_n are indicated by vertical lines on the plot. There are several remarkable features to point out. First, x_i is a continuously decreasing function of M (and therefore i). We shall see in Chapter 2 that this is to be expected in step-growth polymerizations. It means, for example, that there are more unreacted monomers (i = 1) than any other particular i-mer. The weight fraction, however, has a distinct but broad maximum. Notice also how many different values of M are present in significant amounts. For example, there is certainly a significant mass of the sample that is five times smaller than M_w, or 5 times larger than M_n.

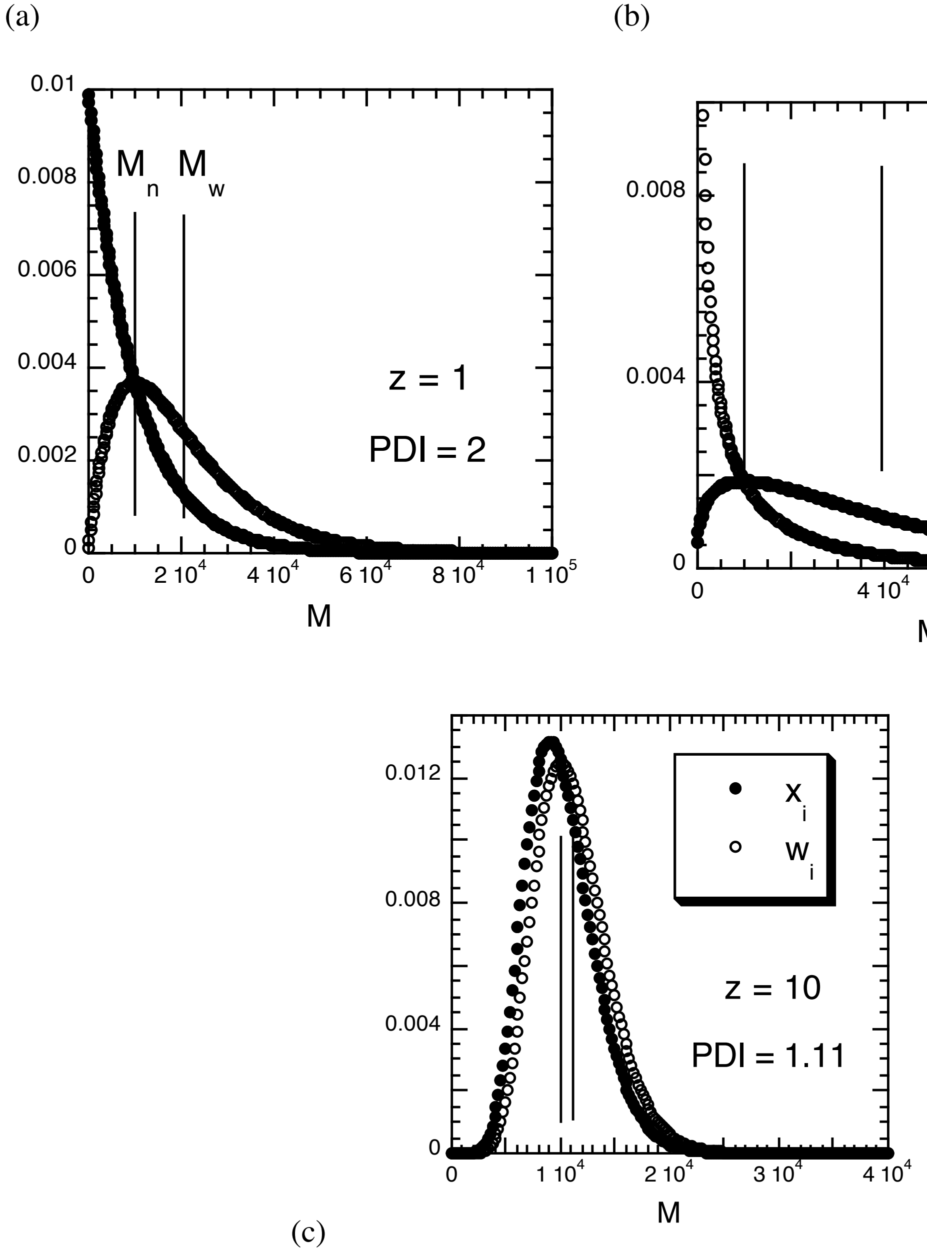


Figure 1.5

Number and weight distributions for the Schulz-Zimm distribution with the indicated polydispersities, and M_n = 10,000.

Figure 1.5.b shows the analogous curves, but now with PDI = 4 and z = 0.333. Although the mole fraction looks superficially similar to the previous case, the mass distribution is exceedingly broad, with a long tail on the high M side of M_n. (Note that the coincidence

between M_n and the peak in w_i is a feature of this distribution, but not a general result in polymers; see Problem 1.10). Figure 1.5.c shows the opposite extreme, or a narrow distribution with z = 10 and PDI = 1.11. Here both x_i and w_i are much narrower, and have distinct maxima that are also close to M_n and M_w, respectively. (Note also that the ordinate scale has been truncated). Even though this is a narrow distribution by polymer standards, there are still significant numbers of molecules that are 50% larger and 50% smaller than the mean.

1.8 Measurement of molecular weight

1.8A General considerations

The measurement of molecular weight is clearly the most important step in characterizing a polymer sample, although the previous sections have introduced many other aspects of polymer structure necessary for a full analysis. A rich variety of experimental techniques have been developed and employed for this purpose, and the major ones are listed in Table 1.5. As indicated in the rightmost column, we will describe endgroup analysis and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry in this section, while deferring treatment of size exclusion chromatography (SEC), osmotic pressure, light scattering, and intrinsic viscometry to subsequent chapters. Other techniques, such as those involving sedimentation, we will omit entirely. Before considering any technique in detail, some general comments about the entries in Table 1.5 are in order.

The first two techniques listed, SEC and MALDI, can provide information on the entire distribution of molecular weights. To the extent that either one can do this reliably, accurately, and conveniently, there is a diminished need for any other approach. Over the past 30 years SEC has emerged as the dominant method, without question. Automated analysis of a few milligrams of sample dissolved in a good solvent can be achieved in half an hour. It is hard to imagine any serious polymer lab that does not have SEC capability. Nevertheless, as will be discussed in

Chapter 9, SEC has some serious limitations; one of these is a lack of *resolution*. Resolution in this context refers to the difference in M values that can be determined; SEC would struggle to help you decide whether your sample was narrowly distributed with M_n = 50,000, or was bimodal with peak molecular weights at 40,000 and 60,000. In contrast, resolution is the real strength of MALDI, as we will see below. MALDI is a relative newcomer among the techniques listed in Table 1.5, but it will undoubtedly grow in importance as its scope expands.

The next group of techniques provide measurements of M_n. They do so by being sensitive to the *number* of solute molecules in solution, as is inherent in the so-called *colligative properties* (osmotic pressure, freezing point depression, boiling point elevation, etc.). Of these the osmotic pressure is the most commonly employed. It has the virtue (shared with light scattering) of being a technique based on equilibrium thermodynamics, that can provide an absolute measurement without resorting to calibration against other polymer samples. Endgroup analysis, to be discussed below, includes any of a number of analytical tools that can be used to quantify the presence of the unique structure of the polymer chain ends. For a linear chain, with two and only two ends, counting the number of ends is equivalent to counting the number of molecules.

Light scattering is sufficiently important that it merits a full chapter; determination of M_w is only one facet of the information that can be obtained. Sedimentation experiments will not be discussed further in this text, although they play a crucial role for biopolymer analysis in general, and proteins in particular. Similarly, gel electrophoresis (not listed in Table 1.5 or discussed further here) is an analytical method of central importance in biological sciences, and especially for the separation and sequencing of DNA in the Human Genome Project.

Information	Definition	Methods	Sections
Full distribution	x_i, w_i	Size exclusion chromatography	9.8
		MALDI mass spectrometry	1.8
M_n	$\frac{\sum_i n_i M_i}{\sum_i n_i}$	Osmotic pressure	7.4
		Other colligative properties	–
		End group analysis	1.8
M_w	$\frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$	Light scattering	8
		Sedimentation velocity	–
M_z	$\frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2}$	Sedimentation equilibrium	–
M_v	$\left(\frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i}\right)^{1/a}$	Intrinsic viscosity	9.3

Table 1.5
Summary of the molecular weight averages most widely encountered in polymer chemistry.

The intrinsic viscosity approach holds a place of particular historical importance; in the days before routine use of SEC (up to about 1970) it was by far the easiest way to obtain molecular weight information. The viscosity average molecular weight defined in Table 1.5 is not a simple moment of the distribution, but involves the *Mark-Houwink exponent* a, which needs to be known based on other information. As $0.5 \leq a \leq 0.8$ for most flexible polymers in solution, $M_n \leq M_v \leq M_w$. The relation between the viscosity of a dilute polymer solution and the molecular weight of the polymer actually rests on some rather subtle hydrodynamics, as we will explore in Chapter 9.

1.8B End group analysis

As indicated previously, the end groups of polymers are inherently different in chemical structure from the repeat units of the chain, and thus provide a possible means of counting the number of molecules in a sample. Any analytical technique that can reliably quantify the concentration of end groups can potentially be used in this manner, and over the years many have been so employed. It should be apparent from the discussion in the previous section that this approach will yield a measure of the number average molecular weight, M_n. The experiment will involve preparing a known mass of sample, probably in solution, which given M_o corresponds to a certain number of repeat units. The number of end groups is directly proportional to the number of polymers, and the ratio of the number of polymers to the number of repeat units is the number average degree of polymerization.

Several general principles apply to end group analysis:

1. The chemical structure of the end group must be sufficiently different from that of the repeat unit for the chosen analytical technique to resolve the two clearly.

2. There must be a well-defined number of end groups per polymer, at least on average. For a linear polymer, there will be two and only two end groups per molecule, which may or may not be distinct from each other. For branched polymers, the relation of the number of end groups to the number of polymers is ambiguous, unless the total number of branching points is also known.

3. The technique is limited to relatively low molecular weights, as the end groups become more and more dilute as N increases. This is an obvious corollary of the fact that we can ignore end groups in considering the structure of high molecular weight chains. How low is low in this context? The answer will depend on the particular system and analytical technique, but as a rule of thumb end groups present at the 1% level (corresponding to degrees of polymerization of 100 for a single end group, 200 for both end groups) can be reliably determined; those at the 0.1% level cannot.

As an example, consider polycondensation polymers such as polyesters and polyamides. They are especially well suited to this molecular weight determination, because they tend to have lower molecular weights than addition polymers, and because they naturally have unreacted functional groups at each end. Using polyamides as an example, we can readily account for the following possibilities:

1. A linear molecule has a carboxyl group at one end and an amino group at the other, such as poly(ε-caprolactam):

   $$HOOC\text{–}(CH_2)_5\text{ –[–}NHCO\ (CH_2)_5\text{–]}_N\text{–}NH_2$$

   In this case there is one functional group of each kind per molecule, and could be detected for example by titration with a strong base (for –COOH) or strong acid (for $-NH_2$).

2. If a polyamide is prepared in the presence of a large excess of diamine, the average chain will be capped by an amino group at each end:

$H_2N–R'–(–NHCO–R''–CONH–R'–)_N–NH_2$

In this case only the amine can be titrated, and two ends are counted per molecule.

3. Similarly, if a polyamide is prepared in the presence of a large excess of dicarboxylic acid, then the average chain will have a carboxyl group at each end:

   $HOOC–R''–(–CONH–R'–NHCO–)_N–R'–COOH$

   In this case the acid group can be titrated, and again two ends should be counted per molecule.

The preceding discussion illustrated how classical acid/base titration could be used for molecular weight determination. In current practice, nuclear magnetic resonance (NMR) spectroscopy is probably the most commonly used analytical method for end group analysis, especially proton (^1H) NMR. An additional advantage of this approach is the possibility of obtaining further information about the polymer structure from the same measurement, as illustrated in the following example.

Example 1.6

The ^1H NMR spectrum in Figure 1.6 corresponds to a sample of polyisoprene containing a *sec*-butyl initiating group and a hydroxyl terminating end-group. The relative peak integrations are (a) 26.9, (b) 5.22, (c) 2.00, and (d) 5.95. What is M_n for this polymer? What is the relative percentage of 1,4 and 3,4 addition?

Solution

Peak (c) corresponds to the methylene protons adjacent to the hydroxyl end-group; there are two such protons per polymer. Peak (a) reflects the single olefinic proton per 1,4 repeat unit, whereas peak (b) shows the two vinyl protons per 3,4 repeat unit. If we represent the integration of peak i as I_i, then the degree of polymerization is proportional to $(I_a + I_b/2) = 26.9 + 2.61 = 29.5$. The number of polymers is proportional to $I_c/2 = 1$. Thus the number average degree of polymerization is 29.5, which gives an $M_n = 29.5 \times 68 = 20{,}000$. Peak (d) indicates the six methyl protons on the initiator fragment. The peak integration $I_d = 5.95$ should be $3\ I_c$, which it is within experimental error. For this particular molecular structure, therefore, either endgroup could be used. An additional conclusion is that essentially 100% of the polymers were terminated with a hydroxyl group.

The percent 1,4 addition can be computed as follows

$$\%1{,}4 \quad = \quad \frac{I_a}{I_a + (I_b/2)} \times 100 \quad = \quad \frac{26.9}{29.5} \times 100 \quad = \quad 91.2\%.$$

This is a typical composition for polyisoprene prepared by anionic polymerization in a non-polar solvent (see Chapter 4).

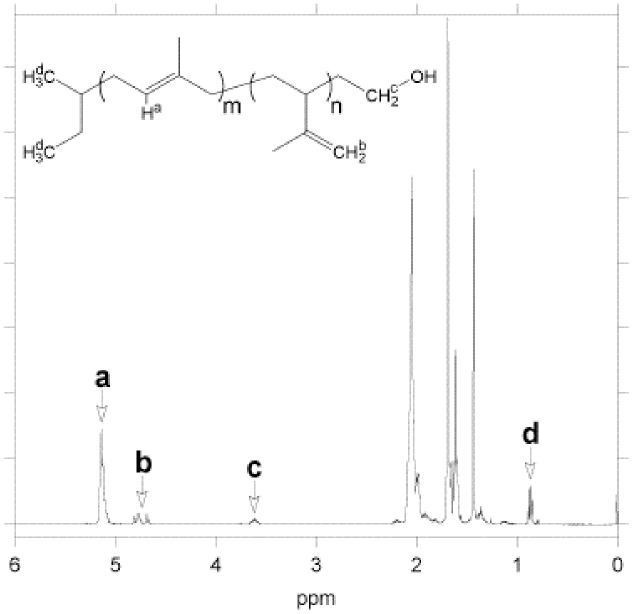


Figure 1.6
^{1}H NMR spectrum of a polyisoprene sample, discussed in Example 1.6. Data courtesy of N. Lynd and M. A. Hillmyer.

1.8C MALDI mass spectrometry

Mass spectrometry offers unprecedented resolution in the analysis of gas phase ions, and is a workhorse of chemical analysis. Its application to synthetic polymers has been limited until rather recently, due primarily to the difficulty of transferring high molecular weight species into the gas phase without degradation. However, progress in recent years has been quite rapid, with two general approaches being particularly productive. In one, electrospray ionization, a polymer solution is ejected through a small orifice into a vacuum environment; an electrode at the exit deposits a charge onto each drop of solution. The solvent then evaporates, leaving behind a charged macromolecule in the gas phase. In the other, the polymer sample is dispersed in a particular matrix on a solid substrate. An intense laser pulse is absorbed by the matrix, and the resulting energy transfer vaporizes both polymer and matrix. For uncharged synthetic polymers, the necessary charge is usually complexed with the polymer in the gas phase, after a suitable salt has been co-dissolved in the matrix. This technique*, matrix assisted laser desorption/ionization mass spectrometry*, or MALDI for short, is already a standard approach in the biopolymer arena, and is making substantial inroads for synthetic polymers as well.

It is worth recalling the basic ingredients of a mass spectrometric experiment. A sample molecule of mass m is first introduced into the gas phase in a high vacuum, and at some point in the process it must acquire a net charge z. The resulting ion is accelerated along a particular direction by suitably placed electrodes, and ultimately collected and counted by a suitable analyzer. The ion acquires kinetic energy in the applied field, which depends on the net charge z and the applied voltage. This energy will result in a mass-dependent velocity v, as the kinetic energy = $mv^2/2$. This allows for the discrimination of different masses, by a variety of possible schemes. For example, if the ions experience an orthogonal magnetic field B, their trajectories will be curved to different extents, and it is possible to tune the magnitude of B to allow a particular mass to pass through an aperture before the detector. For polymers it turns out to be more effective to use time-of-flight (TOF) analysis. For a given applied field and flight path to the detector, larger masses will take longer to reach the detector. As long as all the molecules are introduced into the gas phase at the same instant in time, the time of arrival can be converted directly into a value of m/z.

The preceding discussion may give the misleading impression that MALDI is rather a straightforward technique. This is not, in fact, the case, especially for synthetic polymers. A great deal remains to be learned about both the desorption and ionization processes, and standard practice is to follow particular recipes (matrix and salt) that have been found to be successful for a given polymer. For example, polystyrene samples are most often dispersed in dithranol (1,8,9-anthracenetriol) with a silver salt such as silver trifluoroacetate. This mixture is co-dissolved in a volatile common good solvent such as tetrahydrofuran, to ensure homogeneity; after depositing a drop on a sample plate, the solvent is then allowed to evaporate. An intense pulse from a nitrogen laser (λ = 337 nm) desorbs some portion of the sample, and some fraction of the resulting gas-phase polystyrene molecules are complexed with a single silver cation.

Two examples of MALDI spectra on narrow distribution polystyrene samples are shown in Figures 1.7a and b. In the former, the average molecular weight is in the neighborhood of 5000, and different i-mers are clearly resolved. Each peak is separated by 104 g/mol, which is the repeat unit molecular weight. The absolute molecular weight of each peak should correspond to the following sum: $(104i + 108 + 1 + 57) = 104i + 166$, where 108, 1, and 57 are the contributions of the silver ion, terminal proton, and *sec*-butyl initiator fragment, respectively. Using the formulae given in eqs 1.7.2 and 1.7.4, M_n and M_w can be calculated as 4620 and 4971, respectively, and the polydispersity is 1.076. This sample, which was prepared by living anionic polymerization as described in Chapter 4, is thus quite narrow. Nevertheless, the plot shows distinctly how many different i-mers are present, and in what relative proportion. The assumption is made that the height of each peak is proportional to its number concentration in the sample, and thus the y-axis corresponds to an unnormalized form of mole fraction x_i. This image, perhaps more than any other, underscores the point we have already made several times:

even the best of polymer samples is quite heterogeneous. Recalling Example 1.4 and the tank car of polybutadiene, it is worth pointing out that each peak in Figure 1.7a corresponds to many structurally different molecules, in terms of the stereo chemical sequence along the backbone.

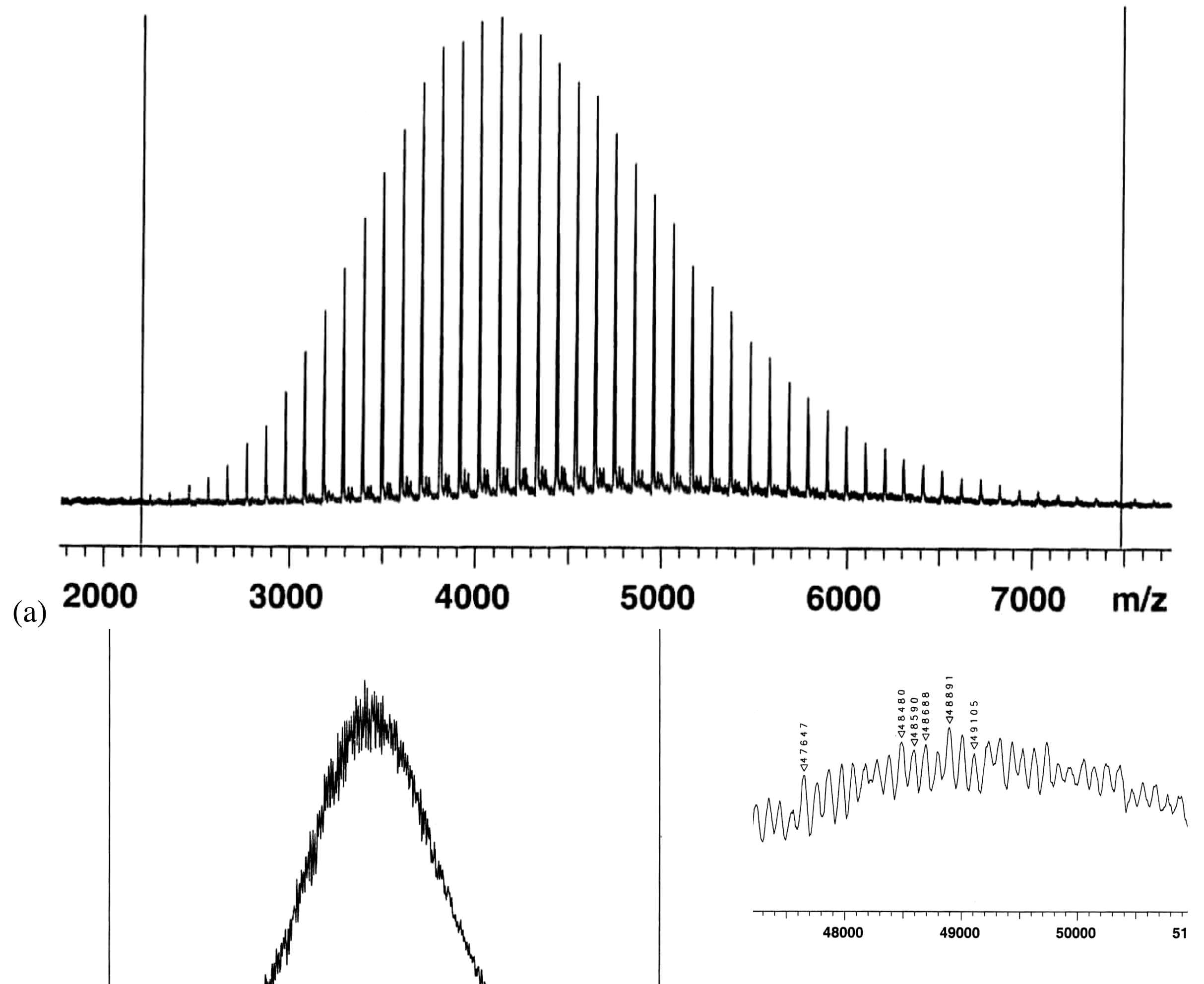


Figure 1.7

MALDI spectra for anionically prepared polystyrenes with (a) M_w = 4971, M_n = 4620, PDI = 1.076, and (b) M_w = 49306, M_n = 48916, PDI = 1.008. Inset shows that even in (b) there is some resolution of the different i-mers. Data from K. Fagerquist, T. Chang, and T. P. Lodge.

The MALDI spectrum in Figure 1.7b corresponds to a sample about 10 times higher in molecular weight. At this point it is not possible to see any structure between different i-mers, although the expanded version in the insert shows that there is still a hint of resolution of distinct molecular weights. This serves to point out one limitation with MALDI, namely that its main attribute, high resolution, is diminished as M increases. Not apparent from this plot, but even more troublesome, is the fact that the absolute amplitude of the signal is greatly reduced compared to Figure 1.7a. It is simply much harder to get higher molecular weight molecules into the gas phase. Nevertheless, the data in Figure 1.7b give $M_n = 48916$, $M_w = 49306$ and a polydispersity of 1.008. This turns out to be nearly as narrow as the theoretical limit for this class of polymerizations (see Chapter 4) yet it is still obviously quite heterogeneous.

We conclude this section with some further general observations about MALDI.

1. Generally, the more polar a polymer, the easier it is to analyze by MALDI. Thus polyethylene oxide is relatively easy; poly(methyl methacrylate) is easier than polystyrene; polyethylene is almost impossible.
2. An important, unresolved issue is relating the amplitude of the signal of a particular peak to the relative abundance of that molecule in the sample. For example, are all molecular weights desorbed to the same extent within a given laser pulse (unlikely), and are all molecular weights equally likely to be ionized once in the gas phase (no)? Consequently, it can be dangerous to extract M_w and M_n as we did for the samples in Figures 1.7a and b, because the signals have an unknown sensitivity to molecular weight. (In this instance this problem is mitigated because the samples are quite narrow). In general, lower molecular weights have a much higher yield.
3. Multiply-charged ions can present a problem, because one cannot distinguish between a molecule with a charge of 1 and a molecule of twice the molecular weight but with a charge of 2. In fact, if the technique were called “mass-to-charge ratio spectrometry” it

would be a mouthful, but it would serve as a constant reminder of this important complication.

4. It is difficult to compare the amplitudes of peaks from one laser pulse to another, and from one sample drop to another. This presumably reflects the microscopic details of the spot on the sample that is actually at the focus of the laser beam. As a consequence any quantitative interpretation should be restricted to a given spectrum.

1.9 Preview of things to come

The contents of this book may be considered to comprise three sections, each containing four separate chapters. The first section, including Chapters 2-5, addresses the synthesis of polymers, the various reaction mechanisms and kinetics, the resulting molecular weight distributions, and some aspects of molecular characterization. In particular, Chapter 2 concerns step-growth (condensation) polymerization and Chapter 3 chain-growth (free radical) polymerization. Chapter 4 describes a family of particular polymerization schemes that permit a much higher degree of control over molecular weight, molecular weight distribution, and molecular architecture than those in the preceding two chapters. Chapter 5 addresses some of the factors that control the structural details within polymers, especially copolymers and stereoregular polymers, and aspects of their characterization.

The second section takes up the behavior of polymers dissolved in solution. The conformations of polymers, and especially random coils, are treated in Chapter 6. Solution thermodynamics are the subject of Chapter 7, including the concepts of solvent quality, osmotic pressure, and phase behavior. The technique of light scattering, which provides direct information about molecular weight, solvent quality, and chain conformations, is covered in detail in Chapter 8. Chapter 9 explores the various hydrodynamic properties of polymers in solution, and especially as they impact viscosity, diffusivity, and size exclusion chromatography.

The concluding section addresses the properties of polymers in the bulk, with a particular emphasis on the various solid states: rubber, glass, and crystal. Thus Chapter 10 considers polymer networks, and their characteristic and remarkable elasticity. Chapter 11 treats the unusual viscoelastic behavior of polymer liquids, in a way that combines central concepts from both Chapters 9 and 10. Chapter 12 introduces the phenomenon of the glass transition, which is central to all polymer materials yet relatively unimportant in most atomic or small molecule-based materials. Finally, the rich crystallization properties of polymers are taken up in Chapter 13. The text concludes with an Appendix that reviews some of the mathematical manipulations encountered throughout the book.

CHAPTER SUMMARY

In this chapter we have introduced the central concept of chain molecules, and identified various ways in which polymers may be classified. The importance of molecular weight and its distribution was emphasized, and associated averages defined. Examples were given of the many possible structural variations that commonly occur in synthetic polymers.

1. The most important feature of a polymer is its degree of polymerization or molecular weight. For example, even though polyethylene has the same chemical formula as the n-alkanes, it has remarkably different physical properties from its small molecule analogs.

2. The statistical nature of polymerization schemes inevitably leads to a distribution of molecular weights. These can be characterized via specific averages, such as the number-average and weight-average molecular weights, or by the full distribution, which can be determined by size exclusion chromatography or MALDI mass spectrometry.

3. Polymers can exhibit many different architectures, such as linear, randomly branched, or regularly branched chains, and networks. Homopolymers contain only one type of repeat unit, whereas copolymers contain two or more.

4. There are many possible variations in local structure along a polymer chain, which we have classified as positional, stereo chemical, or geometric isomers. Given these possibilities, and those identified in the previous point, it is unlikely that any two polymer molecules within a particular sample have exactly the same chemical structure, even without considering differences in molecular weight.

5. Natural polymers such as polysaccharides, proteins, and nucleic acids, share many of the attributes of their synthetic analogs, and as such are an important part of the subject of this book. On the other had, the specific biological functions of these macromolecules, especially proteins and nucleic acids, fall outside our scope.

Bibliography

[1] *Chemical & Engineering News*, 58, 29 (1980).

[2] *The Graduate*, directed by Mike Nichols, Embassy Pictures Coroporation, 1967.

[3] No enterprise as rich as polymer science has only one "father". Herman Mark is one of those to whom the title could readily be applied. An interesting interview with Professor Mark appears in the *Journal of Chemical Education*, 56, 38 (1979).

[4] H. Morawetz, *Polymers: The Origins and Growth of a Science*, Wiley, New York, NY, 1985.

[5] R. B. Seymour, History of Polymer Science and Technology, Marcel Dekker, New York, NY, 1982.

[6] Carl S. Marvel, another pioneer in polymer chemistry, reminisced about the early days of polymer chemistry in the United States in the *Journal of Chemical Education*, 58, 535 (1981).

[7]. see IUPAC Macromolecular Nomenclature Commission, *Macromolecules* 6, 149 (1973).

Suggestions for further reading on introductory material:

Allcock, H. R., Lampe, F. W., and J. E. Mark, *Contemporary Polymer Chemistry*, 3rd Edition, Prentice Hall, Englewood Cliffs, NJ, 2003.

Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953.

Grosberg, A. Y. and Khokhlov, A. R., *Giant Molecules, Here, There and Everywhere*, Academic Press, San Diego, CA, 1997.

Lehninger, A. L. *Biochemistry*, 2nd Edition, Worth Publishers, New York, NY 1975.

Munk, P. and Aminabhavi, T. M., *Introduction to Macromolecular Science*, 2nd Edition, Wiley Interscience, New York, NYm 2002.

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

Painter, P. C. and Coleman, M. M., *Fundamentals of Polymer Science*, Technomic, Lancaster, PA, 1994.

Seymour, R. B. and Carraher, C. E., Jr. *Polymer Chemistry: An Introduction*, Marcel Dekker, New York, NY, 1981.

Sperling, L. H. *Introduction to Physical Polymer Science*, Wiley Interscience, New York, NY 1986.

Young, R. J., and Lovell, P. A., *Introduction to Polymers*, 2nd Edition, Chapman and Hall, London (1991).

Problems

To a significant extent the problems in this book are based on data from the original literature. In many instances the values given have been estimated from graphs, transformed from other functional representation, or changed in units. Therefore these quantities do not necessarily reflect the accuracy of the original work, nor is the given number of significant figures always justified. Finally, the data may used for purposes other than were intended in the original study.

1. R.E. Cohen and A. R. Ramos (*Macromolecules* 12, 131 (1979)) describe phase equilibrium studies of block copolymers of butadiene (B) and isoprene (I). One such polymer is described as having a 2:1 molar ratio of B to I with the following microstructure:

   B – 45% cis-1,4; 45% trans-1,4; 10% vinyl.

   I – over 92% cis-1,4.

   Draw the structure of a portion of this polymer consisting of about 15 repeat units, and having approximately the composition of this polymer.

2. Hydrogenation of polybutadiene converts both cis and trans isomers to the same linear structure, and vinyl groups to ethyl branches. A polybutadiene sample of molecular weight 168,000 was found by infrared spectroscopy to contain double bonds consisting of 47.2% cis, 44.9% trans, and 7.9% vinyl. (W. E. Rochefort, G. G. Smith, H. Rachapudy, V. R. Raju, and W. W. Graessley, *J. Polym. Sci., Polym. Phys.* 17, 1197 (1979)). After hydrogenation, what is the average number of backbone carbon atoms between ethyl side chains?

3. Landel used a commercial material called Vulcollan 18/40 to study the rubber-to-glass transition of a polyurethane. (R. F. Landel, *J. Colloid Sci.* 12, 308 (1957)). This material is described as being “prepared from a low molecular weight polyester which is extended and crosslinked…by reacting it with naphthalane-1,4,-diisocyanate and 1,4-butanediol. The polyester … is prepared from adipic acid and a mixture of ethylene and propylene glycols”. Draw the structural formula of a portion of the cross-linked polymer which includes the various possible linkages that this description includes. Remember that isocyanates react with active hydrogens; use this fact to account for the cross-linking.

4. Some polymers are listed below using either IUPAC (I) names or acceptable trivial (T) names. Draw structural formulas for the repeat units in these polymers, and propose an alternative name in the system other than the one given.

   Polymethylene (I)

   Polyformaldehyde (T)

   Poly(phenylene oxide) (T)

   Poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene] (I)

   Poly(1-acetoxyethylene) (I).

   Poly(methyl acrylate) (T).

5. Star polymers are branched molecules with a controlled number of linear arms anchored to one central molecular unit acting as a branch point. Schaefgen and Flory *(J. Am. Chem. Soc.* 70, 2709 (1948)) prepared poly(ε-caprolactam) 4- and 8-arm stars using cyclohexanone tetrapropionic acid and dicyclohexanone octapropionic acid as branch points. The authors present the following stoichiometric definitions/relations to relate the molecular weight of the polymer to the concentration of unreacted acid groups in the product. Provide the information required for each of the following steps:

   (a) The product has the formula $\text{R-}\{\text{–CO[–NH(CH}_2)_5\text{CO–]}_y\text{–OH}\}_b$. What is the significance of R, y, and b?

   (b) If Q is the number of equivalents of multifunctional reactant which reacts per mole of monomer and L represents the number of equivalents of unreacted (end) groups per mole of monomer, then $\langle y \rangle = (1–L)/(Q+L)$. Justify this relationship, assuming all functional groups are equal in reactivity.

   (c) If M_o is the molecular weight of the repeat unit and M_b is the molecular weight of the original branch molecule divided by b, then the number average molecular weight of the star polymer is

$$M_n = b\left\{M_o \frac{1-L}{Q+L} + M_b\right\}$$

   Justify this result and evaluate M_o and M_b for the b = 4 and b = 8 stars.

   (d) Evaluate M_n for the following molecules:

b	**Q**	**L**
4	0.2169	0.0018
8	0.134	0.00093

6. Batzer reported the following data for a fractionated polyester made from sebacic acid and 1,6-hexaediol (*Makromol. Chem.* 5, 5 (1950)); evaluate M_n, M_w, and M_z.

Fraction	1	2	3	4	5	6	7	8	9
Mass(g)	1.15	0.73	0.415	0.35	0.51	0.34	1.78	0.10	0.94
$M \times 10^{-4}$	1.25	2.05	2.40	3.20	3.90	4.50	6.35	4.10	9.40

7. The Mark-Houwink exponent a for poly(methyl methacrylate) at 25 °C has the value 0.69 in acetone and 0.80 in chloroform. Calculate (retaining more significant figures than strictly warranted) the value of M_v that would be obtained for a sample with the following molecular weight distribution if the sample were studied by viscometry in each of these solvents (S. N. Chinai, J. D. Matlock, A. L. Resnick, and R. J. Samuels, *J. Polym. Sci.* 17, 391 (1955)). Compare the values of M_v with M_n and M_w.

$n_i \times 10^3$ (mol)	1.2	2.7	4.9	3.1	0.9
$M_i \times 10^5$ (g/mol)	2.0	4.0	6.0	8.0	10.0

8. Consider a set consisting of 4 – 8 family members, friends, neighbors, etc.; try to select a variety of ages, genders, and other attributes. Take the mass of each individual (a rough estimate is probably wiser than asking directly) and calculate the number- and weight-average masses for this set. Does the resulting polydispersity index indicate a rather "narrow" distribution? If you picture this group in your mind, do you imagine them all to be roughly the same size, as the polydispersity index probably suggests?

9. Prove that the polydispersity of the Schulz-Zimm distribution is given by eq 1.7.21. You may want to look up the general solution for integrals of the type $\int x^a e^{-bx} dx$.

10. In Figures 1.5a-c it appears that the maximum in w_i corresponds closely to M_n. Differentiate eq 1.7.20 with respect to M_i to show why this is the case.

11. The MALDI spectrum in Figure 1.7b resembles a Gaussian or normal distribution. One property of a Gaussian distribution is that the half-width at half-height of the peak is approximately equal to 1.2 σ. Use this relation to estimate σ from the trace, and compare it to the value you would get from eq 1.7.16.