

CHAPTER 1

INTRODUCTION

Although relatively new to the scene of materials science, polymers have become ubiquitous over the past century. In fact, since the Second World War, polymeric materials represent the fastest growing segment of the U.S.' chemical industry. It has been estimated that more than a third of the chemical research dollar is spent on polymers, with a correspondingly large proportion of technical personnel working in the area. From the beginning, the study of polymers was an interdisciplinary science, with chemists, chemical engineers, mechanical engineers, and materials scientists working to understand the chemical structure and synthesis of polymers, develop methods to scale up and process polymers, and evaluate the wide range of mechanical properties existing within the realm of polymeric materials. The molecular structure of polymers is far more complex than the molecules you may have studied in a general chemistry course: just compare the molecular weights, H_2O is 18, NaCl is about 58, but polymers have molecular weights from 10,000 to tens of millions (or possibly much higher for cross-linked polymers). Many of the structures you might have seen in a general cell biology course are made of polymers—proteins, polysaccharides, and DNA are all notable biological polymers. In a material science course, you may have studied crystal structures in metals to understand the mechanical behavior of different alloys (polymers can form crystals, too, but imagine the difficulty of trying to line up a huge polymer molecule into a crystal structure). Polymers are a unique class of materials having wide ranging applications.

A modern automobile contains over 300 lb (150 kg) of plastics, and this does not include paints, the rubber in tires, or the fibers in tires and upholstery. Newer aircraft incorporate increasing amounts of polymers and polymer-based composites. With the need to save fuel and therefore weight, polymers will continue to replace traditional materials in the automotive and aircraft industries. Similarly, the applications of polymers in the building construction industry (piping, resilient flooring, siding, thermal and electrical insulation, paints, decorative laminates) are already impressive and will become even more so in the

future. A trip through your local supercenter will quickly convince anyone of the importance of polymers in the packaging (bottles, films, trays), clothing (even cotton is a polymer), and electronics industries. Many other examples from pharmaceutical coatings to playground equipment could be cited, but to make a long story short, the use of polymers now outstrips that of metals not just on a volume basis but also on a *mass* basis.

People have objected to synthetic polymers because they are not “natural.” Well, botulism is natural, but it is not particularly desirable. Seriously, if all the polyester and nylon fibers in use today were to be replaced by cotton and wool, their closest natural counterparts, calculations show that there would not be enough arable land left to feed the populace, and we would be overrun by sheep. The fact is that there simply are no practical natural substitutes for many of the synthetic polymers used in modern society.

Since most modern polymers have their origins in petroleum, it has been argued that this increased reliance on polymers constitutes an unnecessary drain on energy resources. However, the raw materials for polymers account for less than 2% of total petroleum and natural gas consumption, so even the total elimination of synthetic polymers would not contribute significantly to the conservation of hydrocarbon resources. Furthermore, when *total* energy costs (raw materials plus energy to manufacture and ship) are compared, the polymeric item often comes out well ahead of its traditional counterpart, for example, glass versus plastic beverage bottles. In addition, the manufacturing processes used to produce polymers often generate considerably less environmental pollution than the processes used to produce the traditional counterparts, for example, polyethylene film versus brown kraft paper for packaging.

Ironically, one of the most valuable properties of polymers, their chemical inertness, causes problems because polymers do not normally degrade in the environment. As a result, they increasingly contribute to litter and the consumption of scarce landfill space. One of the challenges in using polymers in materials is developing suitable methods for recycle or effective methods to improve the degradation of disposable items.

Environmentally degradable polymers are being developed, although this is basically a wasteful approach and we are not yet sure of the impact of the degradation products. Burning polymer waste for its fuel value makes more sense, because the polymers retain essentially the same heating value as the raw hydrocarbons from which they were made. Still, the polymers must be collected and this approach wastes the value added in manufacturing the polymers.

This ultimate solution is recycling. If waste polymers are to be recycled, they must first be collected. Unfortunately, there are literally dozens (maybe hundreds) of different polymers in the waste mix, and mixed polymers have mechanical properties similar to Cheddar cheese. Thus, for anything but the least-demanding applications (e.g., parking bumpers, flower pots), the waste mix must be separated prior to recycling. To this end, several automobile manufacturers have standardized plastics used in cars that can be easily removed, remolded, and reused in newer models. Another identifier helpful in recycling plastics is obvious if you have ever looked at the bottom of a plastic soda bottle; there are molded-in numbers on most of the large volume commodity plastics, allowing hand sorting of different materials.

Processes have been developed to separate the mixed plastics in the waste. The simplest of these is a sink–float scheme that takes advantage of density differences among various plastics. Unfortunately, many plastic items are foamed, plated, or filled (mixed with nonpolymer components), which complicates density-based separations. Other separation processes are based on solubility differences between various polymers. An intermediate approach chemically degrades the waste polymer to the starting materials from which new

polymer can be made. Other efforts related to polymeric waste have focused on reducing the seemingly infinite lifetime of many plastics in the environment by developing biodegradable commodity polymers.

There are five major areas of application for polymers: (1) plastics, (2) rubbers or elastomers, (3) fibers, (4) surface finishes and protective coatings, and (5) adhesives. Despite the fact that all five applications are based on polymers, and in many cases the same polymer is used in two or more, the industries pretty much grew up separately. It was only after Dr. Hermann Staudinger [1,2] proposed the “macromolecular hypothesis” in the 1920s explaining the common molecular makeup of these materials (for which he won the 1953 Nobel Prize in chemistry in belated recognition of the importance of his work) that polymer science began to evolve from the independent technologies. Thus, a sound fundamental basis was established for continued technological advances. The history of polymer science is treated in detail elsewhere [3,4].

Economic considerations alone would be sufficient to justify the impressive scientific and technological efforts expended on polymers in the past several decades. In addition, however, this class of materials possesses many interesting and useful properties completely different from those of the more traditional engineering materials and that cannot be explained or handled in design situations by the traditional approaches. A description of three simple experiments should make this obvious.

1. Silly putty, a silicone polymer, bounces like rubber when rolled into a ball and dropped. On the other hand, if the ball is placed on a table, it will gradually spread to a puddle. The material behaves as an elastic solid under certain conditions and as a viscous liquid under others.
2. If a weight is suspended from a rubber band, and the band is then heated (taking care not to burn it), the rubber band will contract appreciably. All materials other than polymers will undergo thermal expansion upon heating (assuming that no phase transformation has occurred over the temperature range).
3. When a rotating rod is immersed in a molten polymer or a fairly concentrated polymer solution, the liquid will actually climb up the rod. This phenomenon, the Weissenberg effect, is contrary to what is observed in nonpolymer liquids, which develop a curved surface profile with a lowest point at the rod, as the material is flung outward by centrifugal force.

Although such behavior is unusual in terms of the more familiar materials, it is a perfectly logical consequence of the *molecular structure* of polymers. This molecular structure is the key to an understanding of the science and technology of polymers and will underlie the chapters to follow.

Figure 1.1 illustrates the followings questions to be considered:

1. How is the desired molecular structure obtained?
2. How do the polymer's processing (i.e., formability) properties depend on its molecular structure?
3. How do its material properties (mechanical, chemical, optical, etc.) depend on molecular structure?
4. How do material properties depend on a polymer's processing history?
5. How do its applications depend on its material properties?

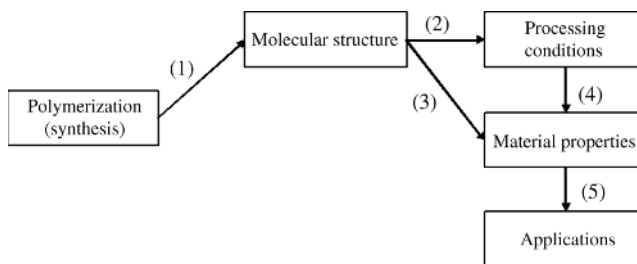
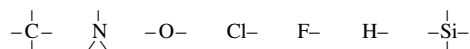


FIGURE 1.1 The key role of molecular structure in polymer science and technology.

The word polymer comes from the Greek word meaning “many- membered.” Strictly speaking, it could be applied to any large molecule formed from a relatively large number of smaller units or “mers,” for example, a sodium chloride crystal, but it is most commonly (and exclusively, here) restricted to materials in which the mers are held together by covalent bonding, that is, shared electrons. For our purposes, only a few bond valences need be remembered:



It is always a good idea to “count the bonds” in any structure written to make sure they conform to the above.

Example 1.1 Carbon is the most common element in polymers. Why?

Solution. To make a polymer, the atoms that make up the repeat units must be capable of forming at least two bonds, so H, F, and Cl would terminate a polymer, and can be only on the ends or in functional groups on the sides of the polymer. Two bonds are enough for bonding to occur to continue a polymer structure, but using only oxygen (O—O—O...) would not provide any functionality. C and Si both can make four bonds, and since most polymers are derived from petroleum sources, carbon is found in the vast majority of polymers. The four bonds allow two to be used to form the backbone (C—C—C...), but the remaining two can be used to include different functional groups, which give polymers their unique characteristics.

The basic structure of a polymer consists of a backbone and pendant (or side) groups (Figure 1.2). Atoms that are covalently linked and stretch from one end of a polymer to the other make up the polymer backbone (which is often not only carbon, but can also contain other atoms such as N, O, or Si). All other atoms are part of the side groups (H is the simplest, methyl (—CH₃) or alcohol (—OH) groups are among many possibilities, making for a wide variety of structures that make up polymers). Polymers are named based on the repeat unit since that can describe a rather lengthy molecule in a succinct way.

Because carbon is so versatile and can form the backbone of a polymer while being covalently attached to two other side groups, some basic organic chemistry will help to understand the molecular structure of polymers. While organic chemistry is not a prerequisite for learning about polymers, some basic terminology related to organic functional groups will help in understanding molecular structures and polymerization reactions.

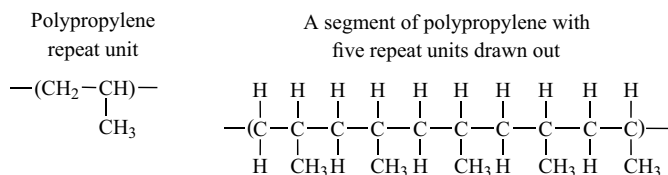
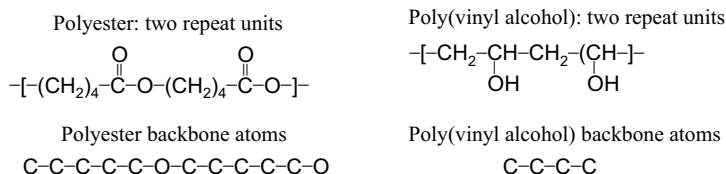


FIGURE 1.2 Structure of a typical polymer polypropylene is shown here, with an all-carbon backbone and side groups of -H or -CH_3 . Note that fixed bond angles make the three-dimensional structure more complex than shown here.

Organic chemicals can be categorized based on common functional groups (types of bonds) that are found within a structure (Figure 1.3). These functionalities are helpful in determining if a molecule might be reactive, whether it is likely to be hydrophilic (or hydrophobic), and how (or if) a molecule can participate in a polymerization reaction. Alcohols ($-\text{OH}$) are perhaps one of the more familiar functional groups, and they can be reacted with carboxylic acids ($-\text{COOH}$) to form an ester bond. As long as each molecule has at least two reactive functional groups (e.g., a dialcohol (more commonly referred to as a diol) and a dicarboxylic acid (a diacid) can react to form a continuous polymer molecule with multiple ester linkages along the polymer backbone, yielding a polyester!). Alcohols can also be found in the side groups of polymers, as in poly(vinyl alcohol), where the $-\text{OH}$ group stays intact after the reaction.



Note that the hydrogens written alongside carbons are not part of the backbone of a polymer molecule. They can bond only to one other atom (the carbon), so a more accurate drawing would show the hydrogens off to the side of the backbone, just as the —OH group is in the poly(vinyl alcohol).

Some of the organic functional groups that are reactive to form polymers include alcohols, amines, carboxylic acids, and alkenes. Although alkanes (C–C bonds) are common in polymers, both in the backbone and in the side groups, they are not reactive. Other bonds commonly found in polymers include amides (for nylons), esters, carbonates, imides, and urethanes. Of this last set, even those who have had organic chemistry probably have not run across the last three, as they are more common in polymers than in traditional organic chemistry. Further reviews of organic chemistry functional groups are also available, and many others can be found online [5,6].

While there is no simple rule about the structures found in a polymer, the most common polymers have only a few organic functional groups, that repeat over and over to make the macromolecules. Of the groups shown in Figure 1.3, alkanes, esters, urethanes, carbonates, aryls, silanes, amides, and imides are commonly found in the backbone of polymers. Alcohols, carboxylic acids, and amines are either reactive parts of monomers or can be found in polymer side groups.

6 INTRODUCTION

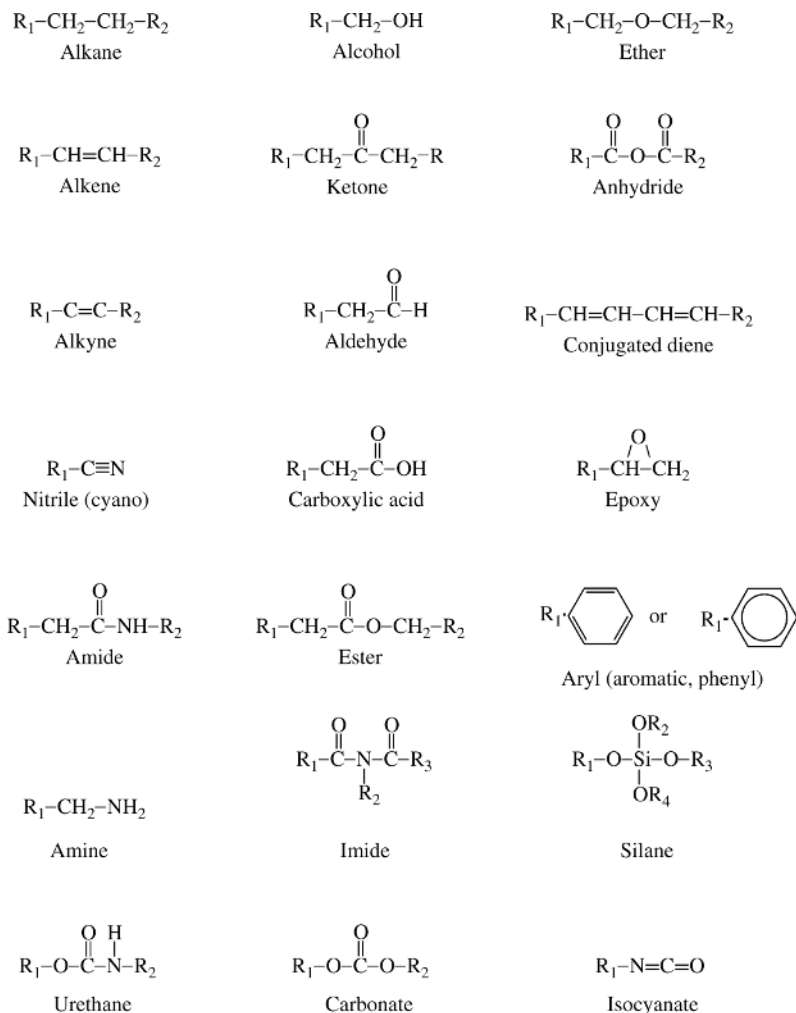


FIGURE 1.3 Common organic functional groups (note: R_1 and R_2 stand for general organic molecules that continue the molecule away from the functional group).

Also keep in mind that when the covalently bound atoms differ in electronegativity, the electrons are not shared evenly between them. In gaseous HCl, for example, the electrons cluster around the electronegative chlorine atom, giving rise to a molecular dipole:



Electrostatic forces between such dipoles can play an important role in determining polymer properties, as can be imagined for polymers containing the electronegative oxygen, nitrogen, chlorine, or fluorine atoms (which are generally δ^-). These atoms pull the electrons away from other atoms they are covalently attached to (often carbons), making the carbon atom somewhat positive (δ^+).

The most important constituents of living organisms, cellulose and proteins, are naturally occurring polymers (as is DNA), but most commercially important polymers are synthetic or modified natural polymers.

PROBLEMS

- 1 Consider the room you are in while doing your homework (dorm room, library, cafeteria, pub., and so on).
 - (a) Identify five items in it that are made of polymers.
 - (b) What would you make those items of if there were no polymers?
 - (c) Why do you suppose polymers were chosen over competing materials (if any) for each particular application?
- 2 Consider the plastic used in the construction of an automobile. List four different parts of a car that may be made of a polymer (consider the exterior, under the hood, and interior of the car—there are many more than four!). For each part, list two physical or chemical properties important for that part. For example, for plastic cup holders, the polymer must be moldable to form into correct shape and should not turn rubbery when heated to $\sim 150^{\circ}\text{F}$ (if exposed to the sun or a hot cup of coffee).
- 3 You wish to develop a polymer to replace glass in window glazing. What properties must a polymer have for that application?
- 4 Vinyl chloride is the monomer from which the commercially important polymer poly(vinyl chloride), PVC, is made. It has the chemical formula $\text{C}_2\text{H}_3\text{Cl}$. Show the structure of vinyl chloride and identify any dipoles present.
- 5 Acrylonitrile monomer, $\text{C}_3\text{H}_3\text{N}$, is an important constituent of acrylic fibers and nitrile rubber. It does not have a cyclic structure and it has only one double bond.
 - (a) Show the structure of acrylonitrile and identify any dipoles present.
 - (b) Draw the repeating structure of polyacrylonitrile, ignore end groups.
- 6 Poly(octyl cyanoacrylate) is an important adhesive. With the help of the Internet, draw the repeating structure for this polymer, show any dipoles present, and find one trademarked product made from poly(octyl cyanoacrylate).
- 7 Propylene (C_3H_6) is the monomer from which the fastest growing plastic, polypropylene, is made. It contains one double bond. Show its structure and identify any dipoles present.

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