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The World of Plastics and Polymers

E

Dustin Hoffman as "The Graduate," probably pondering his future in plastics.



Ben, "The Graduate," played by a young Dustin Hoffman, has just returned home from college, picking up his luggage to "The Sounds of Silence," sung by Simon and Garfunkel. Now a party in his honor is underway. His parents' upper middle class home is filled with their upper middle class friends, all fawning over Ben's academic and extracurricular accomplishments. Suddenly Mr. McGuire appears, looking appropriately earnest in his dark blue suit, and calls Ben out for a serious conversation:

McG: Ben, come with me for a minute. I want to talk to you. I just want to say one word to you. Just one word.

Ben: Yes, sir.

McG: Are you listening?

Ben: Yes, I am.

McG: Plastics!

Ben: Exactly how do you mean?

McG: There's a great future in plastics. Think about it. Will you think about it?

Ben: Yes, I will.

With the prophetic word, "plastics," ringing in our ears, we leave Ben to the seductive wiles of Mrs. Robinson and cut to another, even more imaginary scene. You and Dustin Hoffman are sitting in a kitchen. Suddenly, all of the plastic in the room disappears. As a result, you and Hoffman find yourselves in your underwear. (We have assumed it to be made of cotton. Nylon underwear would earn the film an X rating.) Around you, various liquids and solids pour out of the cabinets as their containers disappear. Foodstuffs flow from the refrigerator because, being mostly plastic, it has largely vanished. Countertops, floor coverings, and the paint on the walls and woodwork have all disappeared. At this point, a fire breaks out. The plastic insulation on the electrical wiring has vanished and the wires have shorted out.

10.1 Consider This

Using your imagination, continue the above scenario and describe other events that could occur if all plastics were to suddenly disappear.

Table 3.1 Chronological Development of Commercial Polymers

Date	Material (Brand/Trade Name and/or Inventor)	Typical Application
Before 1800	Cotton, flax, wool and silk fibers; bitumen caulking materials; glass and hydraulic cements, leather, cellulose sheet (paper); balata, shellac, gutta-percha, <i>Hevea brasiliensis</i> .	
1839	<u>Vulcanization of rubber (Charles Goodyear)</u>	<u>Tires</u>
1846	Nitration of cellulose (Schönbein)	Coatings
1851	Ebonite (hard rubber; Nelson Goodyear)	Electrical insulation
1860	Molding of shellac and gutta-percha	Electrical insulation
1868	Celluloid (CN: Hyatt)	Combs, mirror, frames
1889	Regenerated cellulosic fibers (Chardonnet)	Fabric
	Cellulose nitrate photographic films (Reichenbach)	Pictures
1890	Cuprammonia rayon fibers (Despeisses)	Fabric
1892	Viscose rayon fibers (Cross, Bevan, and Beadle)	Fabric
1893	Cellulose recognized as a polymer (E. Fischer)	
1907	Phenol-formaldehyde resins (PF: Bakelite; Baekeland)	Electrical
→ 1908	Cellulose acetate photographic films (CA)	
1912	Regenerated cellulose sheet (<u>cellophane</u>)	<u>Sheets, wrappings</u>
1923	Cellulose nitrate automobile lacquers (Duco)	Coatings
1924	Cellulose acetate fibers	
	Concept of macromolecules (H. Staudinger)	
1926	Alkyd polyesters (Kienle)	Electrical insulators
1927	<u>Polyvinyl chloride (PVC; Semon; Koroseal)</u>	Wall covering
1927	Cellulose acetate sheet and rods	Packaging Films
1929	Polysulfide synthetic elastomer (Thiokol; Patrick)	Solvent-resistant rubber
1929	Urea-formaldehyde resins (UF)	Electrical switches and parts
* → 1931	Polymethyl methacrylate plastics (PMMA; <u>Plexiglas</u> ; Rohm)	Display signs
1931	Polychloroprene elastomer (<u>Neoprene</u> ; Carothers)	Wire coatings
* → 1933	<u>Polyethylene (LDPE; Fawcett and Gibson)</u>	Cable coating, packaging, squeeze bottles
1935	Ethylcellulose	Moldings
1936	Polyvinyl acetate (PVAc)	Adhesives
1936	Polyvinyl butyral (PVB)	Safety glass
→ 1937	<u>Polystyrene (PS)</u>	Kitchenware, toys, foam STYROFOAM
1937	<u>Styrene-butadiene (Buna-S; SBR), acrylonitrile (Buna-N), copolymer elastomers (NBR)</u>	Tire treads
* → 1938	<u>Nylon 6,6 fibers (Carothers)</u>	Fibers NYLON stockings
* → 1938	<u>Fluorocarbon polymers (Teflon; Plunkett)</u>	Gaskets, grease-repellent coatings
1939	Melamine-formaldehyde resins (MF)	Tableware
1938	Copolymers of vinyl chloride and vinylidene chloride (Pliovic)	Films, coatings
1939	Polyvinylidene chloride (PVDC; <u>Saran</u>)	Films, coatings

↳ **SARAN**
↳ **WRAP** (DOW Chemical)

Table 3.1 (Continued)

Date	Material (Brand/Trade Name and/or Investor)	Typical Application
WW II 1940	Isobutylene-isoprene elastomer (butyl rubber; Thomas and Sparks)	Adhesives, coatings, caulkings
→ 1941	Polyester fibers (PET; Whinfield and Dickson)	Fabric
1942	Unsaturated polyesters (Foster and Ellis)	Boat hulls
* → 1942	Acrylic fibers (Orlon; Acrylan)	Fabrics
→ 1943	Silicones (Rochow)	Gaskets, caulkings
* → 1943	Polyurethanes (Baeyer)	Foams, elastomers
1944	Styrene-acrylonitrile-maleic anhydride, engineering plastic (Cadon)	Moldings, extrusions
1947	Epoxy resins (Schlack)	Coatings
1948	Copolymers of acrylonitrile butadiene and styrene (ABS) → Telephones	Luggage, electrical devices
* → 1955	Polyethylene (HDPE; Hogan, Banks, and Ziegler)	Bottles, film
1956	Polyoxymethylenes (acetals)	Moldings
1956	Polypropylene Oxide (Hay; Noryl)	Moldings
* → 1957	Polypropylene (Hogan, Banks, and Natta)	Moldings, carpet fiber
→ 1957	Polycarbonate (Schnell and Fox) engineering plastic	Appliance parts
1959	cis-Polybutadiene and cis-polyisoprene elastomers	Rubber
1960	Ethylene-propylene copolymer elastomers (EPDM)	Sheets, gaskets
1962	Polyimide resins	High-temperature films and coatings
1965	Polybutene	Films, pipe
1965	Polyarylsulfones	High-temperature thermoplastics
1965	Poly-4-methyl-1-pentene (TPX)	Clear, low-density (0.83 g/l) moldings
1965	Styrene-butadiene block copolymers (Kraton)	Shoe soles
1970	Polybutylene terephthalate (PBT)	Engineering plastic
1970	Ethylene-tetrafluoroethylene copolymers	Wire insulation
1971	Polyphenylene sulfide (Ryton; Hill and Edmonds)	Engineering plastic
→ 1971	Hydrogels, hydroxyacrylates	Contact lenses
1972	Acrylonitrile barrier copolymers (BAREX)	Packaging
* → 1974	Aromatic nylons (Aramids; Kwolek and Morgan)	Tire cord; Bullet-proof vests
1980	Polyether ether ketone (PEEK; Rose)	High-temperature service
1982	Polyether imide (Ultem)	High-temperature service

As a result of Carothers' contributions and subsequent discoveries, polymerization, that is, the production of giant molecules from small molecules, has been recognized as one of the greatest discoveries of all time. As was true in the nineteenth century, the art usually preceded the science, but many developments in the mid-twentieth century were based on macromolecular concepts championed by Staudinger, Mark, and Carothers.

■ Chapter Overview

We begin the chapter by asking you to observe some of the properties of common plastics. This leads to a section of definition and description, and an introduction to the ways in which chemists can vary the properties of polymers by modifying their molecular structure. Because polyethylene is the simplest and most widely used plastic, it is subjected to a fairly detailed analysis. Its composition, structure, production, properties, modifications, and uses are all considered. This study leads to briefer treatments of the five other plastics that complete the "Big Six." In this context, both addition and condensation polymerization are described. A brief, but significant, aside addresses proteins, an important class of natural polymers, and nylon, a related synthetic polymer. As an example of the impact of plastics on modern life, we consider the many ways in which sports and recreation have been transformed by the introduction of synthetic materials.

The phenomenal success of plastics and their widespread distribution have not been without cost. Therefore, the final third of the chapter is devoted to the raw materials that go into the manufacture of plastics and the problems associated with the disposal of used plastics. Using the issue of plastics versus paper as a recurring case study, we examine disposal options including incineration, biodegradation, recycling, and source reduction. Not surprisingly, we find that there are no easy solutions to the problems posed by these useful and ubiquitous forms of matter.

■ Plastics and Properties

The best way to begin your study is by collecting various types of plastic and making some observations.

10.2 Consider This

Gather up a variety of plastic items from home or your dorm room—plastic bags, soda bottles, whatever happens to be at hand. Make a list of the objects and note the properties of the plastics. Include color, transparency, flexibility, elasticity, hardness, tensile strength, and other properties that could be used to classify and identify the plastics. Try to draw conclusions about which objects are made from the same material.

You have no doubt discovered from this activity (or from prior experience) that plastics exhibit a wide range of properties. We can illustrate this with a few objects that might well be found in your room. The ubiquitous Styrofoam cup is white, opaque, light, soft, and easily deformed and torn, but it is an excellent heat insulator. An audiocassette box is transparent and almost glass-like in its clarity, hard, and brittle. The tape in it is flexible and very strong; it is difficult to stretch or to tear it. The plastic that makes up most soft-drink bottles is transparent and has moderate hardness and flexibility. A typical plastic bag is light, transparent, and flexible. When a strip cut from a bag is pulled, the plastic stretches and often "necks down." This refers to the dramatic increase of the length of the plastic strip as the width and thickness decrease. The necking effect is not reversible, as is the stretching of a rubber band. A fairly strong pull is required to start the necking process, but once it begins, less force is needed to keep it going. A little shoulder forms on the wider part of the strip and the narrow neck almost seems to flow from it. Eventually, however, the plastic tears. Finally, in our brief survey, a plastic milk bottle is somewhat opaque or at least translucent and although it can be deformed, it is not as soft and flexible as many plastics.

Investigations of this sort yield useful information about the properties of plastics. Additional data can be obtained in the laboratory by quantitative determination of density, hardness, tensile strength, melting point, and so on. But it is sometimes difficult

to relate these properties unambiguously to the chemical composition of the plastics. If you were trying to sort the items described in the previous paragraph for recycling, you might find it hard to do so. In fact, it may be surprising that objects as different as the coffee cup and the cassette box are made of the same plastic—polystyrene. The audiotape and the soda bottle are compounded primarily of polyethylene terephthalate and the plastic bag and the milk bottle are both polyethylene.

It follows that the properties of a plastic must be a consequence of more than just its chemical composition—the ratio of the elements that make up the material. How the atoms of those elements are linked together is an important factor. Indeed, the great variety in the properties of plastics are all consequences of variations in molecular structure. Therefore, a major goal of this chapter is to correlate the molecular structures, properties, and uses of plastics. But first we ask an even more fundamental question: What is a plastic?

According to a standard dictionary definition, plastic is an adjective meaning “capable of being molded” or a noun referring to something that is capable of being molded. More specifically, the Merriam-Webster *Seventh New Collegiate Dictionary* mentions “any of numerous organic synthetic or processed materials that are molded, cast, extruded, drawn, or laminated into objects, films, or filaments.” Plastics come in a large variety of types, with different characteristics and applications. You are familiar with the common or brand names of dozens of examples—Teflon®, polyurethane, Saran®, Styrofoam®, Formica®, rayon, and nylon to list only a few. In this text we will reserve the term *plastics* for such synthetic substances—all creations of the chemist and all polymers. What they have in common is evident at the molecular level.

10.3

Consider This

Keep a journal to determine how much plastic you throw away in one week. Record every plastic item you discard during this time, including plastic-coated materials. In your journal, classify the plastic according to its various uses, such as food packaging, bottles, etc.

■ Polymers: The Long, Long Chain

All plastics are made up of long chains of atoms covalently bonded together. Like a linked strand of paper clips, the molecular chain in a plastic consists of subunits that are repeated many times. This subunit is called a monomer (from *mono* meaning “one” and *meros* meaning “unit”). Many monomers join together to form a long molecular strand called a polymer (*poly* means “many”). These polymer molecules can be very long indeed. Sometimes they involve thousands of atoms, and molecular masses can reach over a million. No wonder that polymers are sometimes referred to as macromolecules.

Although this chapter will focus primarily on synthetic polymers, it is important to note that many polymers occur in nature. Natural polymers are found in wood, wool, cotton, skin, hair, starch, and even some minerals, such as asbestos. Polymeric molecules give strength to an oak tree, delicacy to a spider’s web, softness to goose down, and flexibility to a blade of grass. Much of the motivation for the synthesis of plastics has been a desire to reproduce such properties in artificial materials. Indeed, many synthetic polymers were originally created as substitutes for expensive or rare naturally occurring materials or to improve on nature.

As a matter of fact, the first commercial plastic, celluloid, was developed in response to a \$10,000 prize offered for a synthetic substitute for ivory in billiard balls. In 1870, a printer named John Hyatt obtained a patent for a mixture of cellulose nitrate, alcohol, and camphor that was heated, molded, and allowed to harden. Cellulose nitrate, made by treating cotton with nitric and sulfuric acids, is better known as “gun

Macromolecule
Polymer
Plastic

cotton." It is highly flammable and, under some conditions, sufficiently explosive to be used in smokeless gunpowder. Such properties are somewhat less than desirable in billiard balls, though the story of exploding pool balls may be apocryphal. Back in 1870, the primary motivation for seeking substitutes for ivory was probably economic. Today, the motivation has changed. Elephant herds have been drastically depleted by poachers collecting tusks for the ivory trade. In response, the United States government has banned the import of ivory. New plastics provide the starting materials, not only for billiard balls, but for many art objects as well.

To some people, the word "plastic" may carry the connotation "cheap" or "tacky." But the fact remains that synthetic polymers have revolutionized modern life. Few advocates of natural materials would be willing to give up nylon stockings, synthetic rubber tires, "fake" furs that spare endangered species, and the dozens of other plastic objects that have become an accepted part of today's lifestyle. As chemists have developed new polymers, the variety of properties and uses have expanded dramatically. For example, plastics have become increasingly important in automobile manufacturing. Some new plastics are stronger than steel and much more resistant to corrosion. Hence, they can be substituted for steel and other metals and materials in various parts of a car. Because the plastic is considerably less dense than structural metals, such substitution has led to significant reductions in vehicle weight. As a result, new cars have generally become more fuel efficient because more plastics have been used in their manufacture.

strength
density

This is, of course, only one of many examples. Plastic packaging reduces weight, eliminates breakage, and helps to save fuel during shipping. Plastic construction materials have replaced wood in some applications, and plastic pipes substitute effectively for lead, iron, copper, and tile. And, as we will see later, recreation has been revolutionized by the introduction of synthetic polymers. All of this adds up to a formidable economic opportunity. Ben's friend gave him good advice. As Figure 10.1 indicates, from 1935 to 1985, production of plastics in the United States increased 500-fold. In 1988 alone, 57 billion pounds of plastics were produced in this country. Indeed, since 1976, the United States has manufactured a larger volume of synthetic polymers than the volume of steel, copper, and aluminum combined.

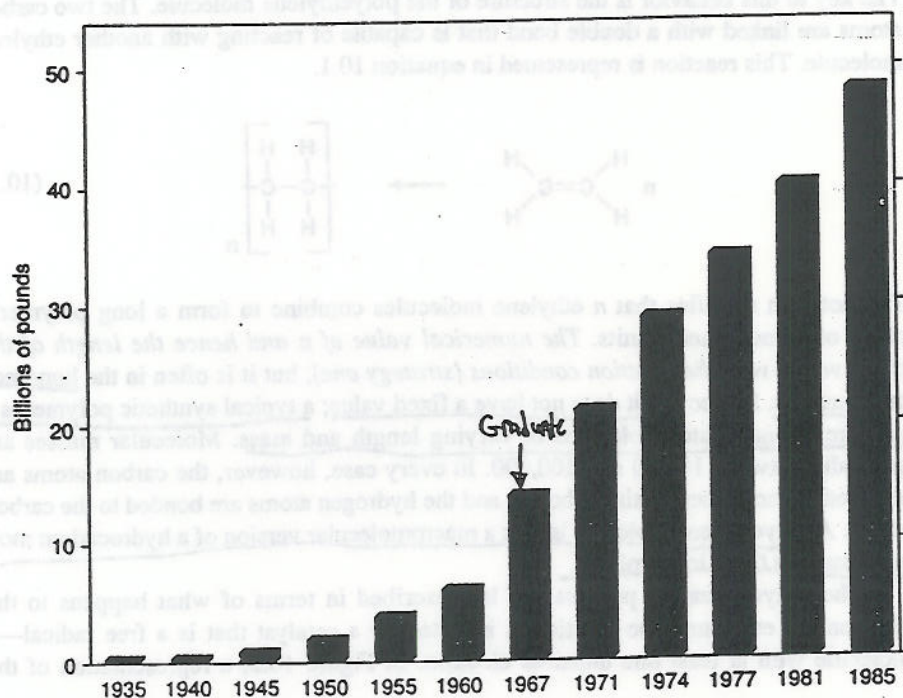


Figure 10.1

Annual United States production of plastics from 1935 to 1985, in pounds. (Data from Joseph Alper and Gordon L. Nelson. *Polymeric Materials: Chemistry for the Future*. Washington: American Chemical Society, 1989, p. 3.)

The widespread applicability of plastics is a consequence of the ability of chemists to modify the properties of plastics in particular ways by altering their molecular structures. Such activities provide meaningful and gainful employment to many of our colleagues. As a matter of fact, more chemists are employed in the polymer/plastics sector than in any other branch of the chemical industry. In a sense, these scientists "design" the desired properties of plastics into their constituent molecules. In doing so, they follow one or more of only six general strategies for modifying polymer chains—a remarkably small number when you consider the thousands of plastics known. Yet these six ways produce stunning results.

The strategies involve one or more alterations of the following molecular features of the polymer chain:

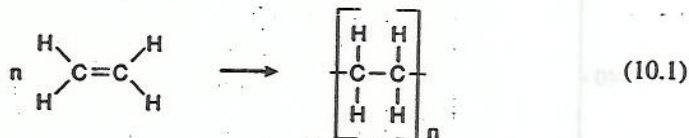
1. the length of the chain (the number of monomer units),
2. the three-dimensional arrangement of the chains in the solid,
3. the branching of the chain,
4. the chemical composition of the monomer units,
5. the bonding between chains, and
6. the orientation of monomer units within the chain.

All of these options will be illustrated in the pages that follow. We begin with the most common plastic of all.

■ Polyethylene: The Most Common Plastic

You probably encounter polyethylene (or polythene, if you are in the British Isles) every day of your life. Nearly 10 million tons of it are produced in the United States each year. It is found in grocery bags for fruits and vegetables, dry-cleaner garment bags, squeeze bottles, TV cabinets, toys, and hundreds of other objects. This wide variety of uses suggests a similarly wide range of properties for this single polymer. Yet all polyethylene is made from the same starting material—ethylene, C_2H_4 .

Ethylene is a compound obtained from petroleum. At ordinary temperatures and pressures it is a gas. However, it was discovered in the 1930s that, with the initiation of a catalyst, individual ethylene molecules will bond to each other to form a polymer. The key to this behavior is the structure of the polyethylene molecule. The two carbon atoms are linked with a double bond that is capable of reacting with another ethylene molecule. This reaction is represented in equation 10.1.



The notation signifies that n ethylene molecules combine to form a long polymeric chain of n monomeric units. *The numerical value of n and hence the length of the chain varies with the reaction conditions (strategy one), but it is often in the hundreds or thousands. Moreover, it does not have a fixed value; a typical synthetic polymer is a mixture of individual molecules of varying length and mass. Molecular masses are generally between 10,000 and 100,000. In every case, however, the carbon atoms are attached to each other by single bonds, and the hydrogen atoms are bonded to the carbon atoms. A polyethylene molecule is thus a macromolecular version of a hydrocarbon molecule such as those in petroleum.*

The polymerization process can be described in terms of what happens to the electrons in ethylene. The reaction is initiated by a catalyst that is a free radical—a molecule with at least one unpaired electron. In Figure 10.2, a representation of the

$n = \#$ repeat units
 $n = 100 - 1000$

Molecular size
distribution

10.4 Your Turn

The average molar mass of a sample of polyethylene is 84,500. What is the average value of n in the polymer? In other words, how many monomer units are present in an average polyethylene molecule? How many atoms?

Soln: The monomeric unit in polyethylene is CH_2CH_2 , with a molar mass of 28.0 g. Therefore, n , the number of monomer units, is obtained by an operation that is equivalent to dividing the molar mass of the polymer by the molar mass of the monomer.

$$n = 84,500 \text{ g/mole polymer} \times \frac{1 \text{ mole monomer}}{28.0 \text{ g}}$$

$$= 3000 \text{ mole monomer/mole polymer}$$

This means that there are 3000 monomer units in the average polymer molecule. To answer the second part of the question, you need to make use of the fact that there are six atoms in each CH_2CH_2 monomer.

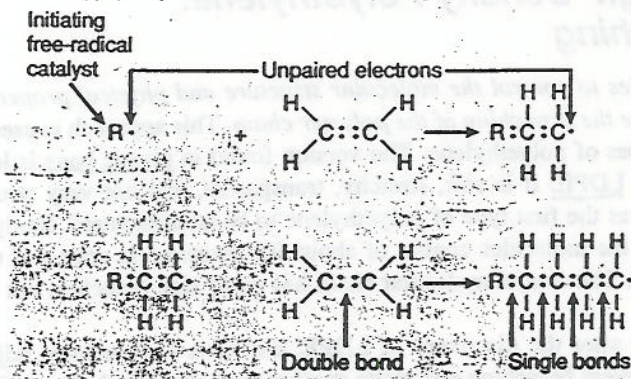


Figure 10.2

The polymerization of ethylene.

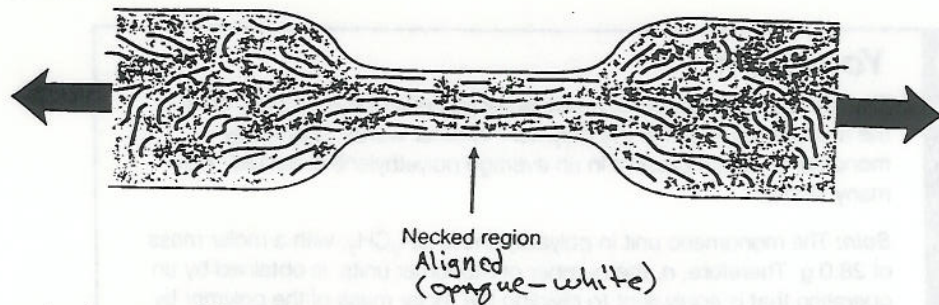
polymerization of polyethylene, the free radical is represented by "R·" (the dot indicates an unpaired electron). The radical reacts readily with a CH_2CH_2 molecule. One of the two bonds between the carbon atoms breaks, and one of the electrons from that bond pairs with the unpaired electron of the radical to form a covalent bond. The new molecule that is formed, $\text{RCH}_2\text{CH}_2\cdot$, is another free radical because it carries an unpaired electron left over from the broken carbon-carbon bond. It can therefore react with another ethylene molecule that bonds to the carbon atom at the reactive, growing end of the polymer. This process is repeated many times over in many chains at the same time. Occasionally, the active ends of two free radical polymers will interact to form a bond and stop the chain growth. The result of all this is that gaseous ethylene is converted to solid polyethylene.

Many of the properties of polyethylene are related to the presence of these long molecular chains. Relatively speaking, they are very long indeed. If a polyethylene molecule were as wide as a piece of spaghetti, the molecular chain could be as much as half a mile long. To continue the analogy, in the polyethylene used to make plastic bags these chains are arranged somewhat like spaghetti on a plate. The strands are jumbled up and not very well aligned, though there are quasi-crystalline regions where the molecular chains are parallel. Moreover, the polyethylene molecules, like spaghetti strands, are not bonded to each other. Now recall what happens when a polyethylene strip is stretched. As the strip narrows and necks down, the previously mixed-up

Spaghetti Analogy

Figure 10.3

Molecular rearrangement as polyethylene is stretched.



molecules move. They shift, slide, and become aligned parallel to each other and the direction of the pulling force (Figure 10.3). In some plastics, such stretching or “cold drawing” is carried out as part of the manufacturing process in order to obtain ordered polymer chains. This is an example of the general strategy of altering the three-dimensional arrangement of the chains (the second in our list of six). Of course, as the force and stretching continue, the polymer eventually reaches a point where the strands can no longer realign, and the plastic breaks. Paper, another polymeric material, tears when pulled because the strands (fibers) in paper are rigidly held in place and are not free to slip like the long molecules in polyethylene.

■ Low- and High-Density Polyethylene: Chain Branching

The third of the strategies to control the molecular structure and physical properties of polymers is to regulate the branching of the polymer chain. This approach is used to produce two general types of polyethylene. The version found in plastic bags is low-density polyethylene or LDPE. It is soft, stretchy, transparent, and not very strong. This low density form was the first type of polyethylene to be manufactured. Study of its structure reveals that the molecules consist of about 500 monomeric units and that they are highly branched. The central molecular chain has many side branches, not unlike a tree trunk.

About twenty years after the discovery of LDPE, chemists were able to adjust reaction conditions to prevent branching and make another form of polyethylene called high-density polyethylene (HDPE). In their Nobel Prize-winning research, Karl Ziegler and Giulio Natta developed new catalysts that enabled them to make linear polyethylene chains consisting of about 10,000 monomer units. Because these long chains are not impeded by side branches, they can be arranged parallel to one another. The structure of HDPE is thus more like a regular crystal than the amorphous tangle of the polymer chains in LDPE. The highly ordered structure of HDPE gives it greater density, rigidity, strength, and a higher melting point than LDPE. Furthermore, the high-density form is opaque and the low-density form tends to be transparent. Figure 10.4 provides a detailed view of molecular structure in linear and branched polyethylene. Figure 10.5 is a representation on a somewhat larger scale.

The differences in properties of high- and low-density polyethylene give rise to different applications. HDPE is used to make toys, gasoline tanks, radio and television cabinets, heavy-duty pipes, and the opaque grocery bags often used as a substitute for paper. One new use has been spurred by the AIDS epidemic. Surgeons who break their skin during an operation on an HIV-positive patient run the risk of acquiring the HIV virus through contact with the patient's blood. Allied-Signal has produced a linear polyethylene fiber called Spectra that can be fabricated into liners for surgical gloves. Spectra gloves are said to have 15 times the cut resistance of medium-weight leather work gloves, but they are so thin that a surgeon can retain a keen sense of touch. A sharp scalpel can be drawn across the glove with no damage to the fabric or the hand inside. Such strength is in marked contrast to the properties of the common plastic bag, which is made of low-density polyethylene. LDPE is also used for the covers of disposable diapers, squeeze bottles, cling wrap for foods, and plastic flowers.

Spectra
fiber

10.6 Consider This

Suppose you were transported back to the Middle Ages as a court magician. The only material you have brought from the twentieth century is a 500-foot roll of Saranwrap™. How would you use it to assure your status as the greatest sorcerer of the times?

■ The Big Six

In spite of polyethylene's range of properties and many uses, it cannot fill all the roles we assign to plastics. It melts at a low temperature, it is permeable to gases, it swells in the presence of oil or organic solvents, it is not very transparent, and it is very expensive to make polyethylene crystalline enough to be exceptionally rigid and strong. A serious limitation is the fact that polyethylene is the simplest of polymers, made up of carbon chains with attached hydrogen atoms. Because the ethylene monomer is so simple, the only options chemists have for changing the structure and properties of the polymer are to alter molecular branching and, within limits, the length of the molecular chain. These alterations can, in turn, result in changes in the three-dimensional arrangement of the chains in the solid. As we have just seen, this has been done brilliantly. *But to obtain greater variety in properties and greater control over them, chemists have made frequent use of one of the most important strategies of molecular manipulation—the use of different monomers to form different polymers (item four on our list).*







Today, more than 60,000 plastics are known. Most have been developed for special purposes ranging from fry pan coatings to resins for restoring antiques. Yet, the two types of polyethylene (LDPE and HDPE) and four other polymers make up the bulk of the plastics you regularly encounter. Approximately 20 million tons of these six polymers are made annually in the United States, and they account for about 63% of all plastics used in this country. In addition to polyethylene, the other four plastics are polypropylene, polystyrene, polyvinyl chloride (PVC), and polyethylene terephthalate (PET). All are ultimately based on petroleum.

Table 10.1 is a summary of information about "The Big Six." Six different monomers are involved. Ethylene, vinyl chloride, styrene, and propylene molecules are similar in that they each contain two carbon atoms connected by a double bond. In ethylene, two hydrogen atoms are attached to each of the doubly-bonded carbon atoms. But in vinyl chloride, styrene, and propylene molecules, one of the hydrogen atoms has been replaced with something else. In the case of vinyl chloride, the substituent is a chlorine atom. In styrene it is a phenyl group, $-C_6H_5$, consisting of six carbon atoms bonded in a ring with a hydrogen atom attached to five of them. The replacement in propylene is a methyl group, $-CH_3$. These "side chains" introduce variety into the monomers and the polymers formed from them. Moreover, the substituents give the chemist greater latitude in designing plastics for particular uses. Polyethylene terephthalate appears to be a special case, and we will return to it, but only after spending more time with the other members of this sextet.

Table 10.1 also lists some of the more important properties of these six polymers. They are all thermoplastic (in other words, they can be melted and shaped), and all tend to be flexible. Three of them, the two polyethylenes and polypropylene, have both crystalline and amorphous regions. The regions of structural regularity convey toughness and resistance to mechanical abrasion and make the polymers opaque. The amorphous regions promote flexibility. The other three polymers—polyethylene terephthalate, polystyrene, and polyvinyl chloride—are not crystalline. Their molecular chains are bonded together tightly but more or less randomly. This process, called

NO!

Table 10.1 The Big Six (This table also includes the code identifying the polymer.)

Polymer	Monomer	Properties of Polymer
Polyethylene (LDPE)  LDPE	Ethylene $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	Opaque, white, soft, flexible, impermeable to water vapor, unreactive toward acids and bases, absorbs oils and softens, melts at 100° – 125°C, does not become brittle until –100°C, oxidizes on exposure to sunlight, subject to cracking if stressed in presence of many polar compounds.
Polyethylene (HDPE)  HDPE	Ethylene $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	Similar to LDPE, more opaque, denser, mechanically tougher, more crystalline and rigid.
Polyvinyl chloride  V	Vinyl chloride $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{Cl} \end{array}$	Rigid, thermoplastic, impervious to oils and most organic materials, transparent, high impact strength.
Polystyrene  PS	Styrene $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{C}_6\text{H}_5 \end{array}$	Glassy, sparkling clarity, rigid, brittle, easily fabricated, upper temperature use 90°C, soluble in many organic materials.
Polypropylene  PP	Propylene $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{CH}_3 \end{array}$	Opaque, high melting point (160°–170°C), high tensile strength and rigidity, lowest density commercial plastic, impermeable to liquids and gases, smooth surface with high luster.
Polyethylene terephthalate  PETE	Ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$ Terephthalic acid $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$	Transparent, high impact strength, impervious to acid and atmospheric gases, not subject to stretching, most costly of the six.

10.7 Consider This

For each of the following uses, specify the desirable properties of a plastic and, using the information in Table 10.1, suggest the most suitable polymer or polymers.

- a bottle for salad oil
- a bottle for a carbonated beverage
- a gallon milk bottle
- a disposable coffee cup
- a dishwasher-safe coffee cup
- a tool box

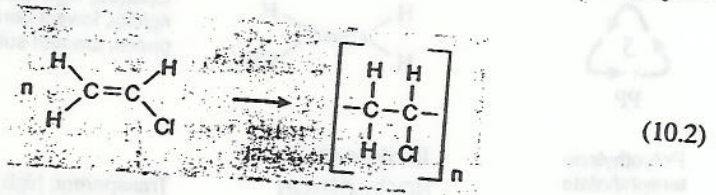
No!
This is NOT
crosslinking

cross-linking, was number five in the list of strategies identified for modifying polymer structure and properties. As a consequence of the cross-linking, the chains cannot move or slip. This linkage is somewhat like the arrangement of strands in a net, but there is a wide variety of randomly sized holes. The bonding between the chains means that the bulk plastic is rigid and hard to stretch. Another property of L-amorphous polymers is their transparency and clarity. This range of properties means that different polymers are differently suited for specific applications. Consider This 10.7 gives you an opportunity to match uses, properties, and polymers.

Whatever use is made of them, the six plastics also generally have small amounts of other materials added to them. Because all six are colorless, coloring agents are often introduced. Plasticizers, substances that improve the flexibility of the polymer, are commonly added, as are a variety of other substances that enhance the performance and durability of the plastic. Indeed, the smell associated with certain plastics (and new cars) is sometimes due to escaping plasticizers.

■ Addition Polymerization: Adding up the Monomers

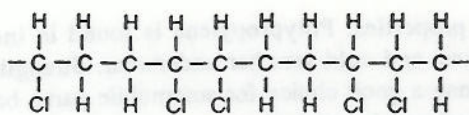
We have already noted that ethylene, vinyl chloride, and propylene molecules each contain a carbon-carbon double bond. All of these monomers polymerize by a process called **addition polymerization**. In every case, the reaction involves the unpairing and re-pairing of electrons described above for polyethylene. The monomers simply add to the growing polymer chain in such a way that the product contains all the atoms of the starting material. No other products are formed, and no atoms are eliminated. Thus, vinyl chloride molecules become bonded together to form polyvinyl chloride (PVC). In the process, the double bonds disappear, and the polymer contains only single bonds.



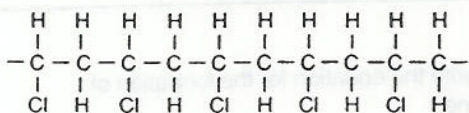
Ethylene and polyethylene are made up only of carbon and hydrogen atoms. But the fact that a vinyl chloride molecule contains a chlorine atom introduces an opportunity for variability in the structure of polyvinyl chloride. Let us arbitrarily think of the carbon atom bearing two hydrogens (CH_2) as the "head" of a vinyl chloride molecule and the chlorinated carbon atom (CHCl) as its "tail." (We could just as easily have made the reverse assignments.) The presence of the chlorine atom creates an asymmetry in the molecule. Because of this, when vinyl chloride molecules add to each other to form polyvinyl chloride, the molecules can be oriented in three possible arrangements: alternating head-to-head and tail-to-tail; repeating head-to-tail; and a random distribution of heads and tails. Figure 10.6 should help make this more obvious.

In a head-to-head/tail-to-tail arrangement of PVC, chlorine atoms are on adjacent carbons. In the head-to-tail structure, chlorine atoms are on alternate carbons. And in the random polymer, an irregular mixture of the previous two types occurs. In each case, the properties are somewhat different. You will recall that controlling monomer orientation within the chain was strategy number six in our list of methods to influence polymer properties. The head-to-tail arrangement is the usual product for polyvinyl chloride. Depending on its formulation, PVC can be stiff or flexible. The former finds use in phonograph records, pipes, house siding, toys, furniture, and various automobile parts. The flexible version is familiar in wall coverings, upholstery, shower curtains, garden hoses, insulation for electrical wiring, and packaging films.

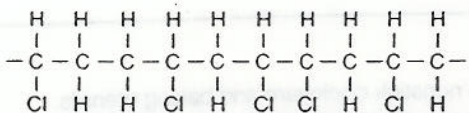
The familiar plastic foam hot beverage cup is the most common example of polystyrene. The styrene monomer, like vinyl chloride, has a substituent (here the



Head-to-head, Tail-to-tail



Head-to-tail-to-head



Random

Figure 10.6

Three possible arrangements of monomers in PVC.

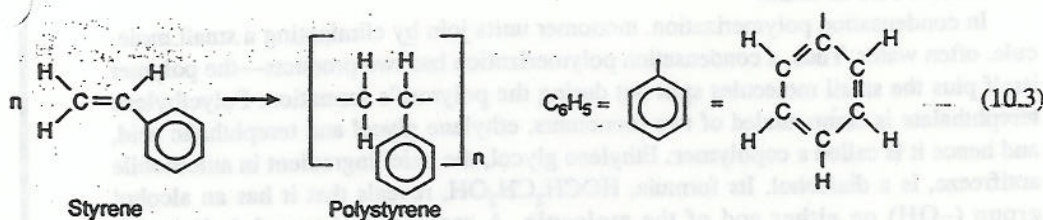
Typical monomer units

10.8 Your Turn

A molecule of polyvinyl chloride consists of 15,000 monomer units. Calculate the molar mass of this polymer.

Ans. 937,500 g

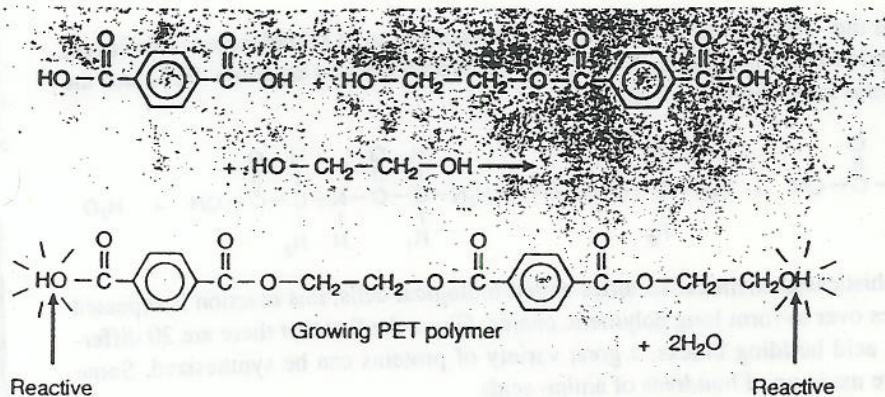
C_6H_5 ring) in place of a hydrogen atom on one of the doubly bonded carbons. Under appropriate catalytic conditions, styrene polymerizes to polystyrene, usually with the head-to-tail arrangement. The, by now, familiar type of addition equation applies; here $n = \text{about } 5000$.



We noted earlier that the hard, brittle, transparent audiocassette boxes are chemically almost identical to light, white, opaque foam coffee cups. Both are polystyrene. Styrofoam is made by expansion molding. Polystyrene beads containing 4–7% of a low-boiling liquid are placed in a mold and heated using steam or hot air. The heat causes the liquid to vaporize and the expansion of the gas also expands the polymer. The expanded particles are fused together into the shape determined by the mold. Because it contains so many bubbles, this plastic foam is not only light, but it is also an excellent thermal insulator. Until relatively recently, chlorofluorocarbons were used as foaming agents, but concern over the involvement of CFCs in the destruction of stratospheric ozone (Chapter 2) led to their replacement in 1990. Hydrocarbons are now frequently used for this purpose. The hard, transparent version of polystyrene is made by molding the melted polymer without the foaming agent. It is used to fabricate wall tile, window moldings, and radio and television cabinets.

Polypropylene, like PVC and polystyrene, is also formed by an addition reaction, in this case using propylene monomers. A particularly useful form of polypropylene has the monomeric units bonded in a head-to-tail fashion. This regularity imparts a high degree of crystallinity and makes the polymer strong, tough, and able to withstand high

Figure 10.7
A growing PET molecule.

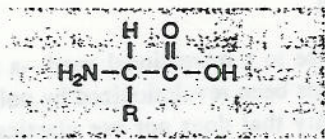


with an acid group of another molecule of terephthalic acid. This process, represented in Figure 10.7, occurs many times over to yield a long polymeric chain of polyethylene terephthalate.

PET is classified as a polyester because it contains many ester linkages. Since their introduction, polyester fibers have found many uses in fabrics and clothing. The polymer is perhaps most familiar under the trade name Dacron. This polyester is frequently mixed with cotton, wool, or other natural polymers, but it has many other uses. Indeed, over 5 million pounds of PET are produced annually in the United States. Narrow, thin-film ribbons of it (under the trade name Mylar) are coated with metal oxides and magnetized to make audio- and videotapes. Dacron tubing is used surgically to replace damaged blood vessels, and artificial hearts contain parts made of PET. The most common use for this plastic is in two-liter soft drink bottles (Figure 10.14), developed by the late Nathaniel Wyeth, a chemical engineer and the brother of the famous painter Andrew Wyeth. Both scientific and artistic creativity run in this remarkable American family.

▲ Polyamides: Natural and Nylon

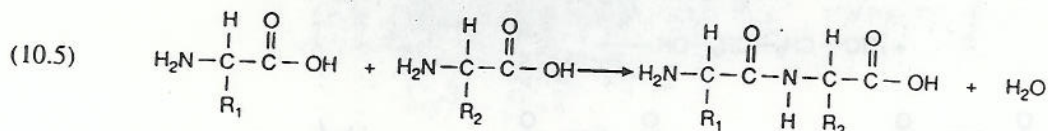
No discussion of condensation polymerization can be complete without including one of the most important classes of natural polymers and the synthetic substitute that brilliantly duplicates some of the properties of the natural material. The naturally occurring polymer is protein. Actually there are a wide variety of these biological macromolecules that make up our skin, hair, muscle, and enzymes. All proteins are polyamides, which are polymers of amino acids. As the name suggests, molecules of amino acids contain both amine groups ($-\text{NH}_2$) and acidic groups ($-\text{COOH}$). A general formula for an amino acid is given below. The amine and acid groups are both attached to the same carbon atom. In addition, a hydrogen atom and another group (represented by an R) are bonded to the same carbon.



The 20 amino acids found in most proteins differ in the identity of the R group. In some amino acids, R consists of carbon and hydrogen atoms, as in alanine, where R is a methyl group, $-\text{CH}_3$. In others, R also includes oxygen, nitrogen, or sulfur atoms. Some R groups are acidic and some are basic.

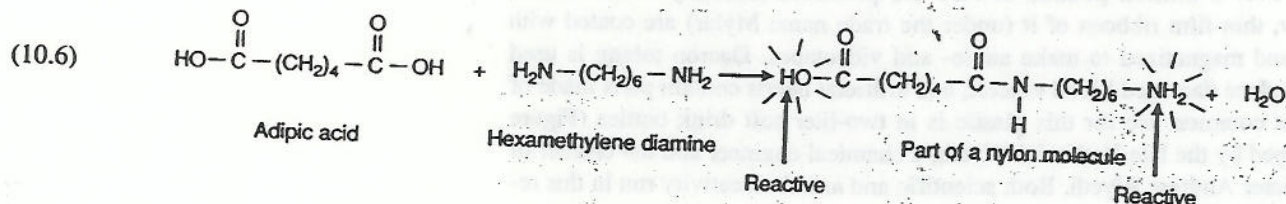
Chapter 12 includes a good deal of additional information about amino acids and proteins. At present we will focus on some fundamentals. The crucial point in the formation of the protein polymer is the fact that the $-\text{COOH}$ group of one amino acid can

react with the -NH_2 group of another. In this reaction, an H_2O molecule is eliminated and a peptide bond is formed. The reaction is represented by equation 10.5, and the peptide bond is enclosed in a box.



In the sophisticated chemical factories called biological cells, this reaction is repeated many times over to form long polymeric chains. Given the fact that there are 20 different amino acid building blocks, a great variety of proteins can be synthesized. Some proteins are made up of hundreds of amino acids.

Chemists are often well advised to attempt to replicate the chemistry of nature. In the 1930s, a brilliant chemist working for the DuPont Company set out to do just that. Wallace Carothers (1896–1937) was studying a variety of polymerization reactions, including the formation of peptide bonds. Instead of using amino acids, Carothers tried combining adipic acid, $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, and hexamethylene diamine, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$. Note that a molecule of adipic acid has an acidic group on both ends and the hexamethylene diamine molecule has a basic amine group on each end. As in the case of protein synthesis, the acid and amine groups reacted to eliminate water and form peptide bonds. But in this instance, the polymer consisted of alternating adipic acid and hexamethylene diamine monomers.



DuPont executives decided the new polymer had promise, especially after company scientists learned to draw it into thin filaments. These filaments were strong and smooth, and very much like the protein spun by silkworms. Therefore, it was as a substitute for silk that "Nylon" was first introduced to the world. The world greeted it with open arms and open pocketbooks. Four million pairs of nylon stockings were sold in New York City on May 15, 1940, the first day that they became available. But in spite of consumer passion for "nylons," the supply soon dried up, as the polymer was diverted from hosiery to parachutes, ropes, clothing, and hundreds of other wartime uses. By the time World War II ended in 1945, nylon had repeatedly demonstrated that it was superior to silk in strength, stability, and resistance to rot. Today this polymer, in its many modifications, continues to find wide applications in clothing, sportswear, camping equipment, the work room, the kitchen, and the laboratory.

■ *Plastics and Recreation*

The first plastic was developed in response to a recreational need—a substitute for ivory in billiard balls. Today, recreation has been revolutionized by polymers. There is hardly any sport or recreational activity that does not use plastics. Football is played on artificial turf by players wearing plastic helmets and padding and nylon pants. Tennis balls, tennis racket frames, and racket strings are all made from synthetic polymers. Ice skaters can skate without ice—on rinks of Teflon or high density polyethylene. Most modern canoes are made of polymers, not birchbark, wood, or aluminum. And an athletic shoe may contain as many as five different types of polymer: in the sole, the padding, the upper portion, the trim, the laces, and even the lace tips. Professional baseball, that bastion of conservatism, still clings to natural polymers in the form of wooden bats, leather gloves, and a ball made of horsehide covering woolen yarn and a cork center. But even here, double-knit polyester uniforms have replaced the hot scratchy wool worn by Babe Ruth and Joe DiMaggio.

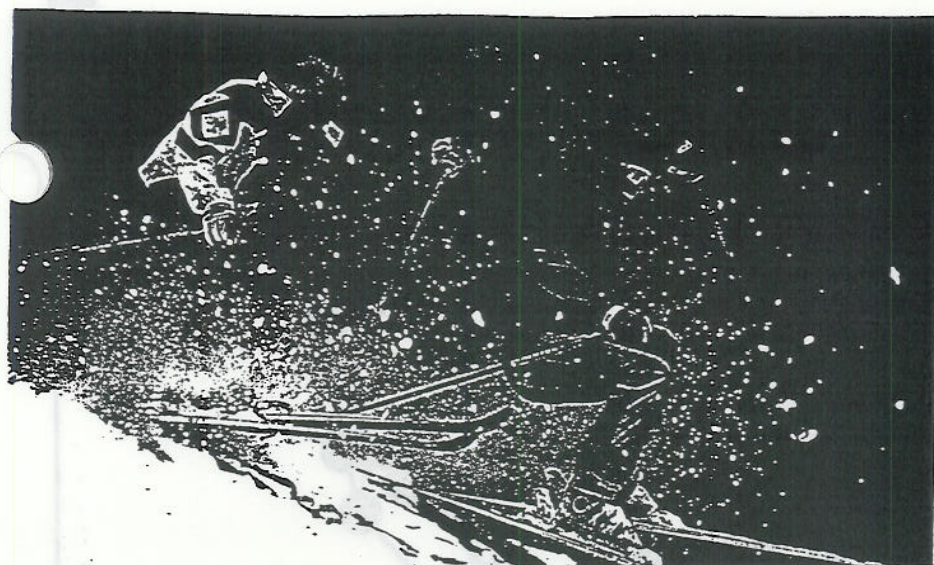


Figure 10.8

An example of polymers at play.

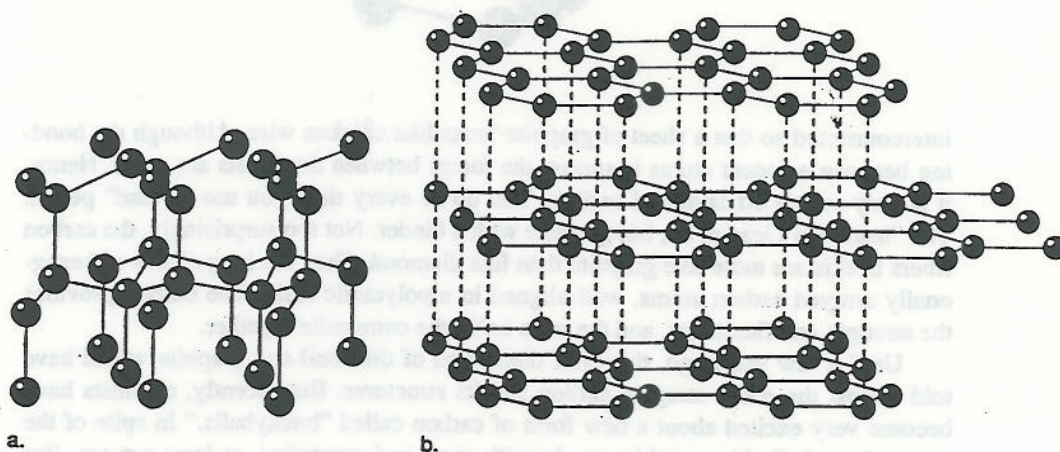


Figure 10.9

Structures of diamond (a) and graphite (b). The spheres represent the carbon atoms and the solid lines the covalent bonds between them. (Adapted, with permission, from *Chemistry* by J. W. Moore, W. G. Davies, and R. W. Collins, McGraw-Hill, 1978.)

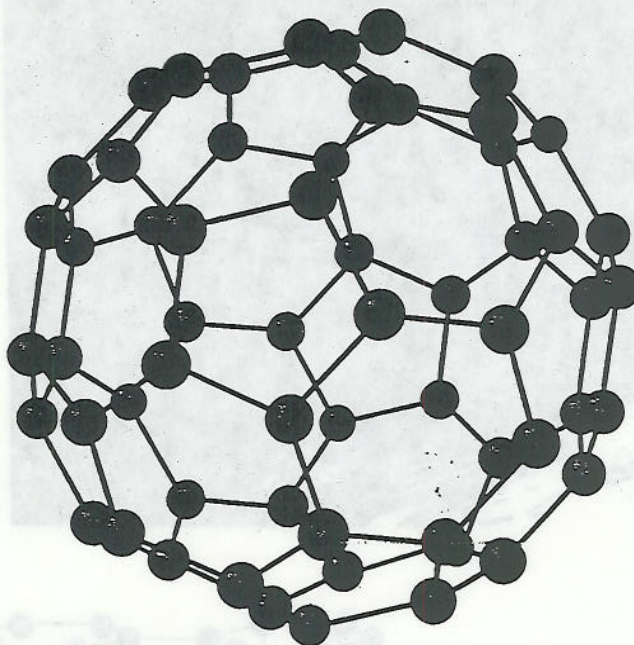
As a case in point, consider downhill (alpine) skiing, a recreational sport enjoyed by thousands worldwide (Figure 10.8). Not too many years ago, a skier would take to the slopes in woolen clothing, leather ski boots, and wooden skis. The wool got wet, the leather cracked or mildewed, and the skis broke. Now, skiers keep warm and dry with synthetic materials such as polypropylene, nylon, Thinsulate®, and Gore-Tex®. Their boots are preformed hardened plastic that easily withstand the repeated twisting and turning of downhill skiing while providing excellent ankle support and protection. And the skis themselves are made of plastic resins reinforced with carbon fibers.

Composite materials of this sort have found wide applications in other recreational gear—in tennis rackets, fishing rods, and golf-club shafts—where strength and flexibility are essential. Both the carbon fibers and the matrix in which they are embedded are polymers. All of the polymers we have studied exist because carbon atoms have a remarkable tendency to bond to each other. They combine in chains, in rings, in mesh-like networks, and in three-dimensional structures.

Even pure carbon possesses these characteristics, which are evident in its two allotropes—graphite and diamond. In diamond, the upscale allotrope, each of the carbon atoms is covalently bonded to four others as illustrated in Figure 10.9. The shared electron pairs are tightly held between adjacent atoms. In the low-priced form, graphite, the atoms are arranged at the corners of six-membered rings. These rings are

Figure 10.10

Structure of C_{60} , buckminsterfullerene. Again, the spheres indicate the carbon atoms and the lines the bonds.



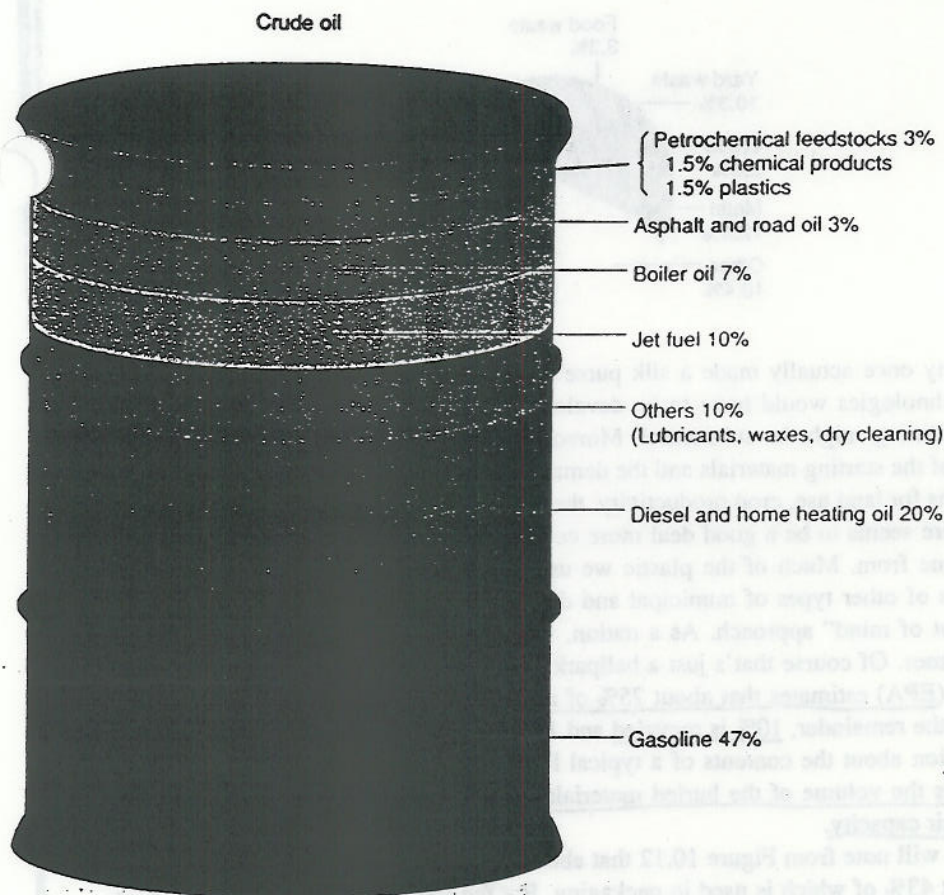
interconnected so that a sheet of graphite looks like chicken wire. Although the bonding between adjacent atoms is strong, the forces between the sheets are weak. Hence, it is easy to rub off layers of carbon. You do so every time you use a “lead” pencil. The “lead” isn’t lead at all, but graphite with a binder. Not too surprisingly, the carbon fibers in skis are more like graphite than like diamond. They are long chains of hexagonally arrayed carbon atoms, well aligned in a polymeric resin. The carbon provides the strength and flexibility, and the resin holds the composite together.

Until a few years ago, this brief discussion of diamond and graphite would have told almost the entire story of carbon and its structures. But recently, chemists have become very excited about a new form of carbon called “buckyballs.” In spite of the name, these balls have nothing to do with sport and recreation, at least not yet. But they have a good deal to do with the arrangement of atoms. Chemists have succeeded in forming and isolating carbon molecules composed of 60 atoms. The shape of one of these C_{60} molecules is beautiful to behold, (Figure 10.10). It looks like a soccer ball, with the carbon atoms bonded in 20 six-membered rings and 12 five-membered rings. This new form of carbon bears the fanciful name of buckminsterfullerene, after the late imaginative and visionary designer and thinker, Buckminster Fuller. Fuller was a pioneer in designing geodesic domes, rigid structures with the same three-dimensional geometry as his namesake molecules. Right now, fullerenes are mostly chemical curiosities, but chemists are already thinking of dozens of potential uses (see Chapter 13).

It may even be that buckyballs will someday find their way into athletics and recreation. In any case, there is no doubt that polymers will continue to play an ever important part in professional sports and leisure time activities. But as these and other uses of plastic proliferate, so do the plastics themselves. Therefore, it is essential that we consider the sources and the disposal of polymeric materials.

10.11 Consider This

Regardless of which leisure or recreational activity you enjoy, from photography to football, synthetic polymers have had an influence on your hobby or sport. Study the equipment used in your favorite activity and list the places where plastics appear. Also identify the properties of the polymers that make them especially suitable for the intended uses.

**Figure 10.11**

End-uses for products made from the refinement of one barrel of crude oil. (Source: Data from United States Energy Information Administration.)

Plastics: Where from and Where to?

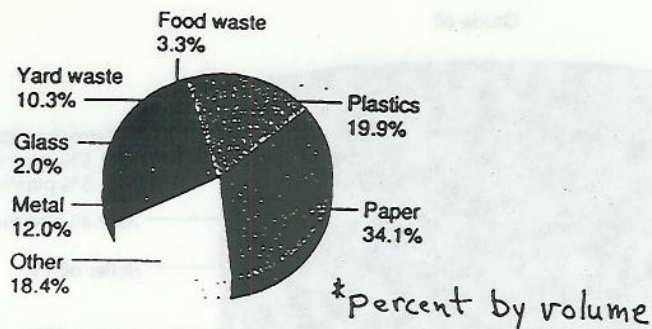
Given the constraints of the law of conservation of matter, it is obviously important that we pay close attention to the raw materials that are incorporated into plastics and the disposal or recycling of this matter after its use. You have already read that the source of most synthetic polymers is petroleum. Crude oil is, of course, a mixture of many compounds that is refined into various fractions on the basis of boiling point and molecular mass. Figure 10.11 graphically depicts those fractions and their primary uses. Not surprisingly, given our discussion in Chapter 4, the great majority of petroleum is burned as fuel. Only 3% is feedstock for manufacturing polymers and other chemicals.

This 3% is essential to current methods of manufacturing the polymers that have reshaped modern life. But the planet's supply of petroleum is limited and non-renewable, a fact that creates a serious dilemma. You already know from previous chapters that petroleum is not an ideal energy source. Its combustion releases carbon dioxide that can contribute to global warming, and unburned fragments and other compounds that give rise to smog and air pollution. But compared to coal, petroleum is quite clean and convenient. Therefore, we return to a question posed earlier: "To burn or not to burn?" What are the risks and benefits—the economic and social trade-offs—in using oil as a source of energy or a source of matter? Should at least some fraction of petroleum be reserved for use in the synthesis of materials that cannot now be made from any other source? If not, the age of plastics may prove very short.

It is important to note that chemistry may rescue society from this dilemma. In principle, at least, polymers can be made from any carbon-containing starting material. Crude oil is simply the most convenient and the most economical. But it might also prove possible to convert renewable biological materials such as wood, cotton fibers, straw, starch, and sugar into polymers. After all, chemists at the Arthur D. Little

Figure 10.12

What's in our garbage?
 (Source: Data from "Characterization of Municipal Solid Waste in the United States: 1990 Update, Executive Summary," June 1990, United States Environmental Protection Agency.)



Company once actually made a silk purse out of a sow's ear. But new methods and new technologies would have to be developed, and the cost of the research and the manufacturing might be substantial. Moreover, it would be essential to estimate the supply of the starting materials and the demand for the finished products. There are implications for land use, crop productivity, the environment, and no doubt much more.

There seems to be a good deal more concern about where plastics go than where they come from. Much of the plastic we use eventually ends up in a landfill, along with lots of other types of municipal and domestic solid wastes, in the usual "out of sight, out of mind" approach. As a nation, we daily discard enough trash to fill two Superdomes. Of course that's just a ballpark figure, but the Environmental Protection Agency (EPA) estimates that about 75% of all municipal solid waste is put into landfills. Of the remainder, 10% is recycled and 15% is incinerated. Figure 10.12 provides information about the contents of a typical landfill given in terms of percent by volume. It is the volume of the buried materials, not the weight, that causes landfills to reach their capacity.

You will note from Figure 10.12 that about 20% of municipal solid waste is plastic, about 43% of which is used in packaging. But the largest percentage of municipal solid waste (34.1%) is paper and paper products. This raises a question that has been much in the news: Which constitutes the lesser environmental burden, paper or plastic? The section that follows is a real-life glimpse into this controversy.

10.12 Consider This

Suppose that the federal government has decided that nonessential uses of plastic is more than a waste—it is a crime. Anyone found using or possessing nonessential plastics will be subject to a heavy fine. Your room is due to be inspected by the authorities in one hour. What will you dispose of what will you keep? Be prepared to defend your choices.

■ Paper or Plastic? The Battle Rages

The rather melodramatic title of this section appeared recently as a headline in the *Syracuse Herald-Journal*. It introduced a heated exchange of opinions, forcefully expressed by readers. At issue was whether grocery bags should be made of paper or plastic. The actual letters that follow are selected from many more, and reprinted here to illustrate this controversy in the context of a supermarket.

In these environmentally conscious times I am often appalled at the number of people who choose plastic bags over paper ones at the supermarket. They must be aware that plastic bags are neither biodegradable nor as easily recycled as the paper variety.

It's common knowledge that plastic bags are not biodegradable, and although some forms of plastic are recyclable, no recycling center in the local area takes plastic bags. What most consumers fail to realize is that the *production and processing of plastic involves a great amount of highly toxic chemicals.

Improper land disposal of hazardous wastes, emissions of toxic chemicals into the air, and discharges of toxic industrial effluents into waterways as a result of plastic production seriously threaten the public health and the environment.*

The local supermarket took the opposite position, and argued that by using plastic bags it was acting in an environmentally responsible manner. As evidence, it printed the following message on its grocery bags:

Thank you for using plastic bags. If all of the Wegmans shoppers using plastic bags last year had insisted on paper, they would have increased the amount of solid waste by over eight million pounds and taken up nearly seven times more space in landfills.

1000 plastic bags equal	1000 paper bags equal
17 lbs and 1219 cubic inches	122 lbs and 8085 cubic inches*

A second letter to the editor, based on information such as that given above, provides the perspective of a consumer and an employee.

As an employee of Wegmans Food markets you may determine that my opinion is biased and it certainly is. . . . Clearly the plastic bags take up less space than paper. . . . In our backroom of the store, an entire pallet of paper bags takes up as much space as the plastic, however, there are only approximately 10,000 paper bags on a pallet compared to approximately 30,000 plastic sacks. . . . (T)he cost certainly is a benefit. Plastic bags cost 1.5 cents whereas paper ones cost 3 cents. If all customers would insist on plastic bags, the savings would certainly be passed on to the consumer.

Finally, I would like to address the landfill issue. As mentioned on our plastic bags, the use of paper sacks fills landfills much faster than the use of plastic bags. Plastic bags take up considerably less space than paper. . . . While environmental groups claim that paper bags degrade at a rapid rate, they are simply misleading the public.*

There is much in these letters to engage the Sceptical Chymist, but we may not yet have enough information to pass critical judgment on the many complex issues involved. Indeed, we may not achieve such knowledge and wisdom within the limitations of this chapter. Nevertheless, in the next section we press on in our efforts to become better informed.

10.13 *The Sceptical Chymist*

Analyze these two letters with their opposing views. Pay particular attention to the initial assumptions, the evidence cited, the logic used, and the conclusions drawn. Which makes the more compelling case and why? On the basis of these two letters only, which position would you support?

* So does
Paper
MANUFACTURE



17 lbs
1219 in³



122 lbs
8085 in³

Figure 10.13

A scale representation of the volumes occupied by 1000 plastic bags and 1000 paper bags.

10.14

Consider This

Information and evidence should influence opinions. Do some additional reading concerning the paper/plastic controversy and reach a conclusion concerning the packaging material that you advocate for groceries. Defend your choice in a draft of a letter to the editor of the Herald-Journal.

Disposing of Plastics

Every year, about 60 billion pounds of plastic are produced in the United States—nearly 250 pounds for every man, woman, and child. Most of this ultimately finds its way into landfills. Given this huge quantity, there is little consolation in the fact that the landfills contain considerably more paper than plastic. The reduction of the amount of plastic going into landfills remains a high priority. Four strategies suggest themselves: incineration, biodegradation, recycling, and source reduction. In the paragraphs that follow, we will examine all of these approaches and attempt to weigh their relative merits.

Since "The Big Six" and most other polymers are primarily made of carbon and hydrogen, it would seem that incineration would be an excellent way to dispose of waste plastics. The chief products of their combustion are carbon dioxide, water, and energy. Although some plastics tend to burn incompletely in their usual form, they can be made to burn efficiently by shredding them and appropriately adjusting the combustion conditions such as the temperature and the oxygen supply. In some cases, fuel oil or other combustibles are mixed with the polymer waste. Because of their composition, plastics have a high fuel value. A sizable fraction of the energy obtained from the garbage-burning power plant described in Chapter 4 comes from polymers.

But incineration of plastics is not without some drawbacks. The repeated message of Chapters 1, 2, and 3, that burning does not destroy matter, applies here as well. Effluent gases may be "out of sight," but they had best not be "out of mind." Of special concern are chlorine-containing polymers such as polyvinyl chloride, which release hydrogen chloride during combustion. Because HCl dissolves in water to form hydrochloric acid, a strong and corrosive compound, the smokestack exhaust could make a serious contribution to acid rain. Moreover, some plastics are printed with inks containing heavy metals such as lead and cadmium. These toxic elements concentrate in the ash left after incineration and thus contribute to a secondary disposal problem. On balance, however, if carefully monitored and controlled, incineration can lead to a large reduction in plastic waste, generate much-needed energy, and have little negative impact on the environment.

Another potential strategy for disposing of plastic wastes is to enlist bacteria to do the job—in other words, to employ biodegradation. The problem is that bacteria and fungi do not find most plastics very appetizing. Because these microorganisms evolved in our natural environment, they possess enzymes to break down naturally occurring polymers into simpler molecules. Indeed, many strains of bacteria use cellulose from plants or proteins from plants and animals as their primary energy sources. You have already encountered several instances of such processes in this text. In Chapter 3 you read about the release of methane by belching cattle. Actually, the methane is produced when bacteria decompose cellulose in the cow's rumen. In the same chapter, we also mentioned that methane is generated by natural decomposition of organic material in landfills.

Ironically, the very properties of inertness and durability that make plastics so desirable as replacements for natural materials also create serious problems with their disposal. Thus, as in the case of the highly stable chlorofluorocarbons, a virtue becomes a liability. To be sure, synthetic polymers, like their natural counterparts, are based on carbon, hydrogen, oxygen, and nitrogen. Yet, subtle differences in the way in which these atoms are bonded to one another make most synthetic polymers nonbiodegradable.

Of late, scientists have been attempting to engineer biodegradability into artificial polymers. Certain bonds or groups are introduced into the molecules to make them susceptible to fungal or bacterial attack, or to decomposition by ultraviolet light. One strategy has been to incorporate starch, a naturally degradable biopolymer, into plastic formulations. Another example is the research project launched by the Procter & Gamble Company to evaluate the biodegradation of the absorbent filler used in disposable diapers. Although some progress is being made in achieving biodegradability in polymers, a recent EPA report raises cautions:

biodegradable?

Before the application of these technologies can be promoted, the uncertainties surrounding degradable plastics must be addressed. First, the effect of different environmental settings on the performance (e.g., degradation rate) of degradables is not well understood. Second, the environmental products or residues of degrading plastics and the environmental impact of degradables on plastic recycling is unclear.²

Part of the difficulty is that even natural polymers do not decompose as completely in landfills as was suggested earlier in this chapter. Modern waste disposal facilities are covered and lined to prevent leaching into the surrounding ground. This creates anaerobic (oxygen-free) conditions that impede bacterial and fungal action. As a result, many supposedly biodegradable substances decompose slowly or not at all. Recent excavations of old landfills have found 37-year-old newspapers that are still readable and five-year-old hot dogs that, while hardly edible, are at least recognizable.

Given the problems associated with land disposal of natural and synthetic polymers, attention has logically turned to recycling both. Although recycling does not literally dispose of plastics as does incineration or biodegradation, it helps to reduce the amount of new plastic entering the waste stream. Soft drink bottles are the most recycled plastic material, with about 20% of them being melted and reused. But less than 3% of plastic jugs made from high density polyethylene are recycled. Altogether, only about 1% of all plastics are recycled, compared to nearly 30% of aluminum.

*20% PET recycled
1% of plastics recycled
3% HDPE (milk jugs) recycled.*

10.15 Consider This
Find out what chemical and economic factors might account for the significant difference in the percentage of aluminum recycled compared to the percentage of plastic.

In spite of this low overall rate, increasing amounts of "post-consumer" plastics are being recycled. For example, national supermarket chains are now recycling their polyethylene grocery bags. In fact, if you read the labels on plastic materials, you will increasingly find them made of a mixture of virgin and recycled plastics. Recycling centers pay about 8 cents per pound of PET, and the cleaned, recycled PET sells for 38 cents per pound. This is roughly half the price of about 67 cents per pound for virgin PET. Of course, the laws of supply and demand work here as they do throughout the economy. During the Persian Gulf war, when petroleum prices rose significantly, virgin PET prices rose accordingly to about 80 cents per pound. At the same time, recycled PET suppliers raised their prices to 48 cents per pound in response to the market.

volatile market for recycled goods

Another major recycling initiative involves Styrofoam (polystyrene). More than 200 million pounds of polystyrene foam food and beverage containers were recycled in 1989. The 1995 goal of the National Polystyrene Recycling Company is to recycle 25% of the plastic foam used in the United States for food service and beverage packaging. This ambitious project, if successful, would recycle a quarter billion (250,000,000) pounds of polystyrene a year.

goal: 25% PS recycled

²PA Report to Congress "Methods to Manage and Control Plastic Wastes," February, 1990.

10.16 The Sceptical Chymist

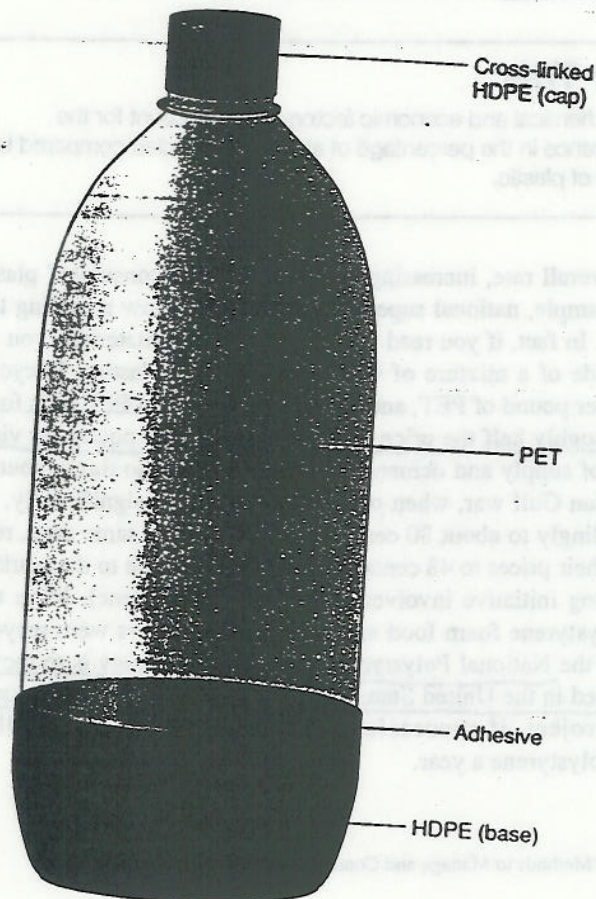
One of the major uses of polystyrene foam has been for "clamshell" fast food containers (though many chains have now discontinued their use). If each container weighs 10 grams and if they are assumed to be the only polystyrene source, how many of these containers would have to be recycled in a single year to achieve the goal of 250,000,000 pounds? Is this a reasonable and attainable goal?

Ans. 11×10^9 or 11 billion

For recycling to be economically self-sustaining, a number of factors must be coordinated. The first is supply. A relatively large volume of material must be consistently available at designated locations for reprocessing. This creates the rather formidable task of collection, along with the associated problem of separation of the plastics either before collection or before reuse. The codes that have started appearing on plastic objects (Table 10.1) are provided to help facilitate this sorting. Once the entropy and disorder have been overcome, the reprocessing is relatively simple. Almost any polymer that is not extensively cross-linked can be melted. If the supply of waste is homogenous, that is, if it contains only one type of plastic, it can be melted and used directly to fabricate new products. Alternatively, it can be solidified, pelletized, and stored for future use.

Many plastic objects, however, are intentionally constructed of several different polymers. A good example is the familiar two-liter soft drink bottle (Figure 10.14). The bottle itself is made of polyethylene terephthalate, with a high-density polyethylene bottom reinforcement and a cap of cross-linked HDPE. In addition, the cap liner and the adhesives for the bottom and the label may be still other polymers. When heterogeneous plastic objects such as these bottles are melted, the product tends to be

Figure 10.14
The anatomy of a two-liter soft drink bottle.



dark with varying properties, depending on the nature of the mixture. Although this reprocessed material does not have outstanding working properties, it is good enough for general lower grade uses such as parking lot bumpers, disposable plastic flower pots, and cheap plastic lumber.

The problems are more than simply technical. Uses for recycled plastics are obviously important because without a product and a market, recycling programs are doomed to fail. In fact, recycling laws in a number of cities have not been implemented and enforced because one of the links in this polymeric chain of supply, collection, sorting, processing, manufacturing, and marketing is missing. Without all of these, the system will not work, unless it is heavily subsidized, and municipalities have been unwilling to provide the necessary funds.

10.17 *Consider This*

A number of national supermarket chains ask customers to return their plastic grocery bags for recycling. If there is such a program in your area, find out what happens to the returned plastic after it leaves the supermarket site. How is the plastic used after reprocessing and recycling?

10.18 *Consider This*

Laws have been passed making recycling mandatory in several states and the District of Columbia. Because of these laws, the volume of material recycled has increased substantially. Yet in spite of legislative mandates, recycling has not yet proved financially self-sustaining. As a legislator attempting to rectify this situation, you decide to draft or redraft recycling laws so that they contain financial incentives, not legislative mandates. Describe the incentives you would create.

The remaining option, source reduction, appears to be simplest and most direct—simply decrease the quantity of plastics produced and consumed. However, even this seemingly innocuous option is far more complicated than it appears. The problem is that something else is generally used to replace the plastic, and this substitution can be fraught with hidden pitfalls. In making choices between alternative materials, the decisions must be informed by the source and nature of feedstocks, the method of manufacturing, waste products produced during manufacturing and their disposal, and many other factors. Energy costs as well as economic costs must be taken into account. How much energy must be expended in the entire life cycle of a product from raw material to final disposal?

Obviously, the identification and proper weighing of all of the possible variables is a complex and difficult task. But when the job is done properly, one sometimes discovers that attempts to reduce the amount of plastic waste by substitution may actually increase the overall amount of waste and the associated negative environmental impact. As an example, take the replacement of a plastic cup with one made of paper. Each occupies about the same volume in a landfill, where both will probably remain undecomposed for a long time. But it is likely that a larger quantity of potentially harmful emissions enters the air and water from the production of the paper than the plastic. Moreover, the net energy input required for the paper is higher than for plastic. This kind of cradle-to-grave evaluation is essential if we are to obtain a reliable test of which material is more environmentally sound. Popular opinion must be supported by fact.

10.19 Consider This

If you did 10.2 Consider This, examine your list of discarded plastic objects and suggest alternatives to plastics for each of these items.

Of course, the best method of source reduction is not to replace plastics, but to do without them whenever possible. One correspondent in the great plastic versus paper battle said it well:

There is a danger in this grocery bag controversy of losing sight of issues of greater importance. One of these is the matter of legitimate, responsible use of resources. Plastics are made from one of the most precious resources, one which cannot be renewed or replaced. In many respects we should regard it as more precious than gold or diamond. There are products essential to human health and well-being which can be made only from petroleum. There are also non-essential, wasteful uses of this priceless commodity. Where did we get the idea that it is our right to waste millions of barrels of oil each year exceeding the speed limit? Who said we're justified in manufacturing and using plastic items like shopping bags, burger boxes, and disposable diapers which are instant garbage? How did we get hooked on the consumer habits that are destroying not only a level of comfort we take for granted, but the very air and water we need to survive?*

■ Conclusion

Quite clearly, the letter that concludes the last section goes well beyond a choice of plastic or paper shopping bags. Once more we come to an issue of lifestyle. Over the past 50 years, chemists have created an amazing array of polymers and plastics—new materials that have made our lives more comfortable and more convenient. Many of these plastics represent a significant improvement over natural polymers. Furthermore, many of the products we take for granted today would be impossible without synthetic polymers and plastics. There would be no audio- and videotape, no compact discs, no kidney dialysis apparatus and no heart/lung machines. We have become dependent on plastics, and it would be difficult if not impossible to abandon their use.

Chemical industry has given consumers what they want. But there now appears to be rather more of it than we would like—mountains of soft drink bottles and miles of plastic bags. At times the world seems to be filling up with polystyrene peanuts. We must learn to cope with this glut of stuff while saving matter and energy for tomorrow. Mr. McGuire was right, there still is a great future in plastics. To create a new world of plastics and polymers will require the intelligence and efforts of policy planners, legislators, economists, manufacturers, consumers, and, above all, chemists. Perhaps Ben should go back to college, and this time major in chemistry.

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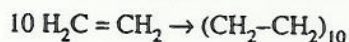
■ Experiments and Investigations

16. The Ubiquitous Styrofoam® Cup

17. Classification of Polymers

■ Exercises

1. Consider the polymerization of ten ethylene monomers to form a segment of polyethylene:



Use the bond energies of Table 4.1 to calculate the energy change during this reaction. Is the reaction endothermic or exothermic? Should heat be supplied or removed to promote this reaction?

2. Determine the number of CH_2CH_2 monomeric units in one molecule of polyethylene with a molar mass of 40,000 g.

*3. The current U.S. production of polyethylene is 10 million tons per year. Calculate the number of moles of ethylene necessary for this production. What volume would this C_2H_4 occupy at a pressure of one atmosphere and a temperature of 25°C if one mole occupies 24.5 liters?

4. Suggest why a free radical with an unpaired electron should be an effective catalyst for the polymerization of ethylene.

5. The text suggests that a polyethylene molecule as wide as a piece of spaghetti would be about half a mile in length. If the spaghetti is 1 millimeter in diameter, calculate the ratio of its length to its width.

6. Calculate the percentage by mass of each of the following.

- chlorine in polyvinyl chloride
- hydrogen in polystyrene
- oxygen in polyethylene terephthalate
- nitrogen in nylon

7. Describe briefly how each of the six strategies for modifying the molecular structure of polymers would be expected to change the properties of material produced.

8. Of the three orientations of polyvinyl chloride in Figure 10.6, which arrangement would you expect to be most likely to give rise to the flexible form of PVC and which would be most likely to give rise to the more rigid variety? Explain your answer.

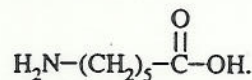
9. Calculate the molar mass of a polystyrene molecule consisting of 5000 monomer units.

*10. Of the "Big Six" polymers, which contains the highest percentage by mass of carbon? What is that percentage?

11. One limitation of the "Big Six" is the relatively low temperatures at which they melt, $90\text{--}170^\circ\text{C}$. Suggest ways to raise these temperature limits while maintaining the other desirable properties of these substances.

12. Butadiene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$, is polymerized to make buna rubber. Write an equation representing this process. Is this an example of addition or condensation polymerization?

13. Nylon 6 is made by the polymerization of



Write an equation for the polymerization of two such monomeric units. Is this an addition or a condensation polymerization?

14. What structural features must a monomer possess in order to undergo addition polymerization? What characteristics are necessary for condensation polymerization?
- *15. A tripeptide is made up of three amino acids. The identity and properties of a tripeptide depend on the amino acids present and their sequence. Assume three amino acids are available: alanine (Ala), glutamic acid (Glu), and lysine (Lys).
- Write down all the possible tripeptides that could be formed from these amino acids if each amino acid could be used only once per tripeptide, e.g., Ala-Lys-Glu.
 - Write down all the possible tripeptides that could be formed from these amino acids if each amino acid could be used more than once per tripeptide.
16. Insulin is a protein made up of 51 amino acids. Assuming an average amino acid to have a molar mass of 120 g, calculate the molar mass of insulin if the mass of H_2O eliminated is ignored. Repeat the calculation taking into consideration the mass of H_2O that is eliminated on polymerization.
17. Assuming the average amino acid to have a molar mass of 120 grams, and ignoring the mass of the water eliminated on polymerization, estimate the number of amino acids in the following proteins. Note the molar masses (MM) of the proteins.
- lipase (an enzyme found in milk) MM = 6700 g
 - crototoxin (rattlesnake venom) MM = 29,900 g
 - fibrinogen (involved in blood clotting) MM = 340,000 g
18. Natural polymers include cotton, rubber, silk, and wool. Consult other sources to identify the monomer unit in each of these polymers and specify which are addition and which are condensation polymers.
- *19. Assume that the average household discards 1.0 kg (2.2 lb) of plastics each week. Suppose a town of 5000 households and 100 linear miles of streets sets up a once-weekly plastics collection system. Estimate the weekly energy and monetary costs of this system. Consider the number of trucks required, the number of workers, the fuel consumed, and other relevant variables. Do not include processing costs. Specify the other assumptions and approximations you used to obtain your answers.
20. The text offers four strategies for addressing the problem of disposing of plastics: incineration, biodegradation, recycling, and source reduction. Which strategy do you favor and why?

Polymer Structure—Organic Aspects (Definitions)

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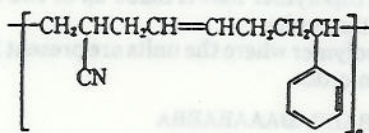
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In the following alphabetical listing, the definitions of key organic-based terms used in characterizing the structure of polymers are provided. Several of the common polymers, some of their uses, as well as their respective structure are also included in the table that follows. The reader should note that the name of the polymer often provides the key to its representative structure. There are, however, names such as polycarbonate that can represent a variety of polymeric materials. In either case, we will cite a representative structure for each.

acrylonitrile-butadiene-styrene terpolymer (ABS).

Automotive grills, instrument panels, and exterior decorative trim; power tool housings, business machines, television cabinets, molded parts, appliance housings—600,000 tons.¹



addition polymers. Typically formed through the reaction of similar (copolymers) or the same (homopolymers) monomers. Examples are polyethylene, polystyrene, poly(methyl methacrylate), poly(vinyl chloride).

alternating copolymer. An ordered copolymer where the units alternate.



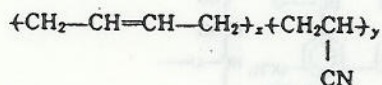
azeotropic copolymer. Polymer in which the composition (amount of each comonomer) of the polymer chain is the same as the amount of each comonomer in the reaction mixture.

biopolymer. Naturally occurring polymer such as proteins, enzymes, polysaccharides (starch, cellulose) and nucleic acids.

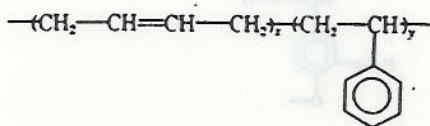
block copolymers. Copolymer consisting of long sequences, blocks, of one mer (polymer unit derived from one of the comonomers) followed by long sequences of the second mer.



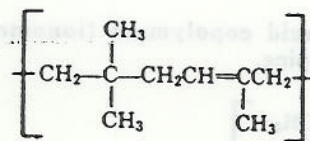
Buna-N. Elastomeric copolymer of butadiene and acrylonitrile.



Buna-S. Elastomeric copolymer of butadiene and styrene.

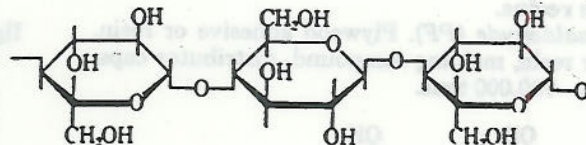


butyl rubber. Tire inner tubes, inflatable sporting goods (balls), inner liners of tubeless tires—150,000 tons.



cellophane. Regenerated cellulosic film; cellulose, such as derived from dissolving cotton, is precipitated or solvent is allowed to evaporate forming a film.

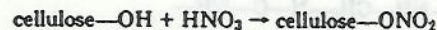
cellulose. Most abundant naturally occurring organic material; main structural material of higher plants; constitutes about one-third of the total mass of higher plants; polymer of D-glucopyranose units linked through β (1-4) bonds; largely linear; major component of paper and paper products; production of ropes; derivatives include cellulose acetates and nitrates, methyl- and ethylcelluloses, and carboxymethylcellulose.



cellulose acetate. The ester formed from reaction of cellulose with acetic acid or other acetylating agents. The cellulose may be acetylated to varying degrees. If the majority of OH groups are acetylated, the product is called cellulose triacetate. If an average of two of the three OH groups in each glucose repeating unit is acetylated, the product is called cellulose diacetate.



cellulose nitrate. The product obtained by the reaction of nitric acid and sulfuric acid with cellulose; erroneously called nitrocellulose. The product is classified as primary, secondary, or tertiary according to how many groups in each repeating anhydroglucose unit in cellulose are nitrated.



condensation polymers. Formed through the reaction of two different functional groups typically producing a by-product such as HCl. Examples are polyamides, polyesters, polyurethanes, proteins, nucleic acids.

copolymer. Polymer containing repeating units from two or more monomers.

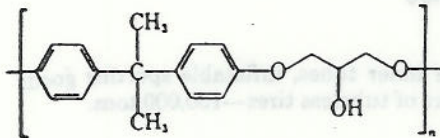


¹ Approximate U.S. annual productions in tons are cited throughout.

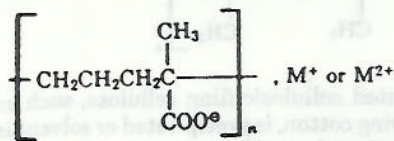
copolymer may be of a variety of compositions including alternating, block, graft, and branch copolymers.

ran. Extracellular polysaccharide consisting of branched chains of α (1-6) linked D-glucopyranose units; branches formed by the presence of 1-2, 1-3, or 1-4 links; used as a blood plasma volume extender, emulsion stabilizer in foodstuffs such as ice cream, gels for gel permeation chromatography.

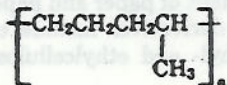
y resins. Coating for beverages and food, drum and tank liners, varnishes, printed circuit boards, binders for regrete in the surfacing of floors, adhesives—170,000 tons.



ene-methacrylic acid copolymers (ionomers). Used for soles, weather stripping.

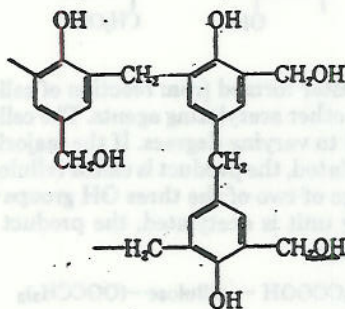


ene-propylene elastomers. Radiator and heater hose, body and chassis parts, car bumpers, mats, seals, weather stripping, wire and cable insulation, coated fabrics, impact modification, appliance parts—150,000 tons.

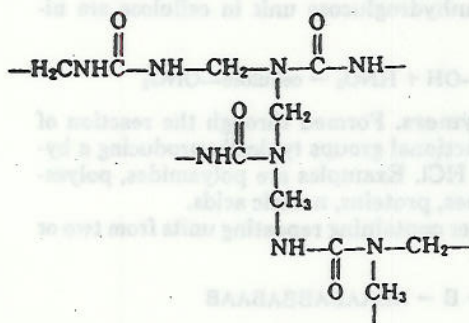


aldehyde resins.

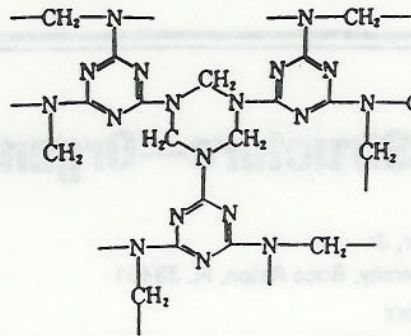
phenol formaldehyde (PF). Plywood adhesive or resin, glass fiber resin, molding compound, distributor caps, wire boxes—700,000 tons.



urea-formaldehyde (UF). Particle-board binder resin, molding compound, coating, paper and textile treatment—600,000 tons.

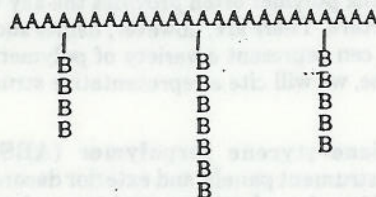


melamine-formaldehyde (MF). Dinnerware, coating, table tops (Formica)—100,000 tons.



glycogen. Main food-reserve polysaccharide of animals; has a multibranch structure with chain lengths of 10-14 glucose units common.

graft copolymer. Branched copolymer where the backbone and the branches consist of different building units, mers.

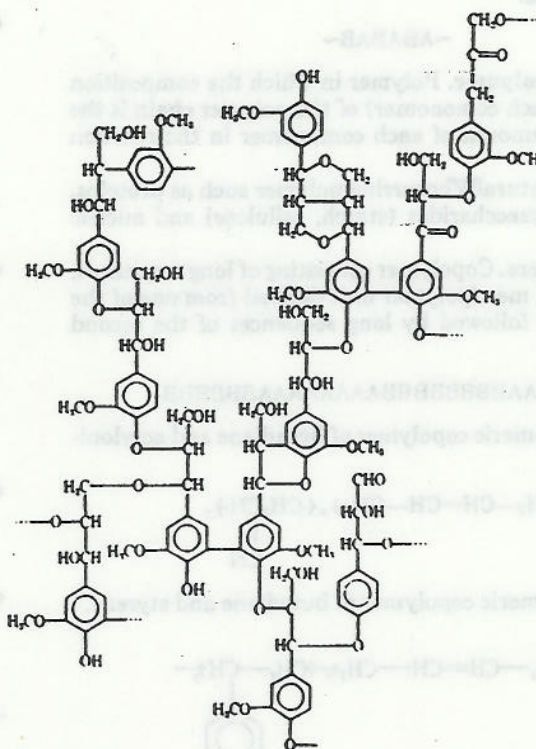


homopolymer. Polymer composed of only one repeating unit, in contrast to a copolymer that is made up of two or more different repeating units.

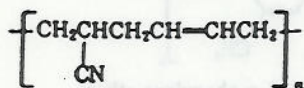
ideal copolymers. Copolymer where the units are present in a statistically random order.



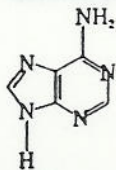
lignin. Structural support and adhesive material in plants; constitutes about 25% of wood; used as dispersants and wetting agents; used in oil-well drilling muds, adhesives, road binders, industrial cleaners, leather tanning, manufacture of vanillin, and cement products.



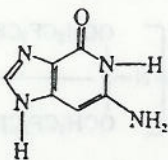
nitrile rubber (NBR). Printing tools, footwear, hoses, gaskets, seals, adhesive—80,000 tons.



nucleic acids. Consist of the condensation products of nucleoside triphosphates and contain a heterocyclic base (adenine, guanine, thymine, cytosine (DNA); and adenine, guanine, uracil, cytosine (RNA)), a sugar (deoxyribose (DNA); ribose (RNA)), and a phosphate moiety per unit; carry and transmit genetic information, involved in protein biosynthesis.

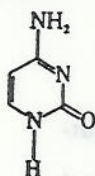


adenine
(in DNA and RNA)

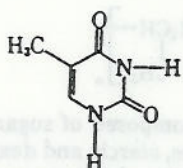


guanine
(in DNA and RNA)

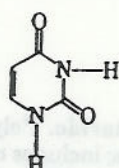
Pyrimidines



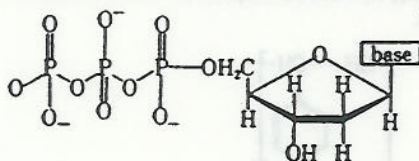
cytosine
(in DNA and RNA)



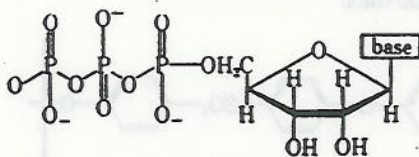
thymine
(in DNA mainly)



uracil
(in RNA)



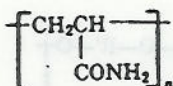
a deoxyribonucleotide
(monomer of DNA)



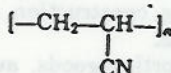
a ribonucleotide
(monomer of RNA)

oligomer. Polymer chain in which the number of repeating units is small, typically 2 to 10.

polyacrylamide. Paper treatments, water-treatment coatings, binder for pigments, adhesives, flocculant—50,000 tons.

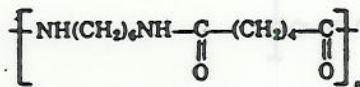


polyacrylonitrile. House furnishings, apparel, rug pile, shirts, socks, blankets, simulated fur, craft yarns, draperies—350,000 tons.



polyamides (nylons).

nylons 6,6 and *nylon 6.* Home furnishings, apparel, tire cord, rug fibers, filaments (fishing line and threads)—1,300,000 tons.

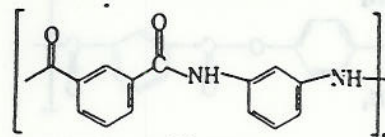


nylon 6,6

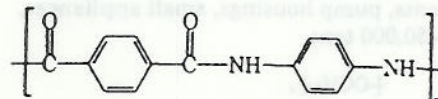


nylon 6

aromatic polyamides. heat-resistant clothing, stack filtration, fishing rods, tennis rackets.

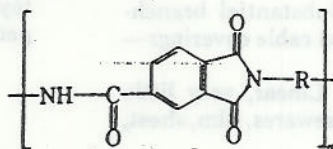


Nomex

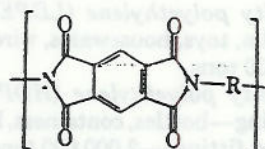


Kevlar

polyamide imides and polyimides. film, molded parts, wire enamels.



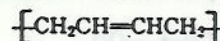
poly(amide imides)



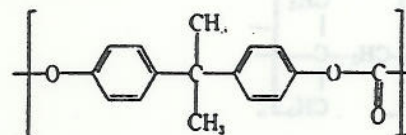
polyimides

polyblend. Typically are heterogeneous systems containing a polymer network, matrix in which another polymer is imbedded.

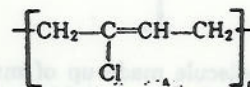
polybutadiene (butadiene rubber, BR). Tires, metal can coatings, hoses, belts—400,000 tons.



polycarbonate (PC). Glazing, lighting, transportation, appliances, signs, returnable bottles, solar collector application—120,000 tons.

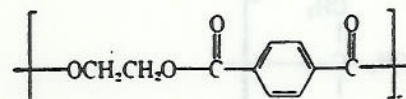


polychloroprene. Highway joint seals, bridge mounts, and expansion joints; automotive belts, hoses, and weather stripping; conveyor belts, wire and cable jacketing—120,000 tons.

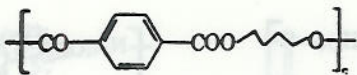


polyesters.

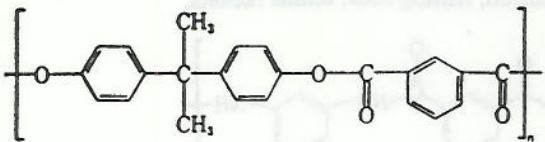
poly(ethylene terephthalate) (PET). Apparel, tire cord, magnetic tape, food packaging (including boil-in-bag food pouches), beverage bottles, coatings for microwave and conventional ovens, home furnishings—2,000,000 tons.



poly(butylene terephthalate) (PBT). Automotive exterior parts, under-the-hood parts, fuse cases, pump housing, small appliances—25,000 tons.



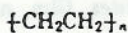
urated polyesters. Appliances, construction, corrosion-resistant products, transportation—500,000 tons.
matric polyesters. Abradable seals, plasma coatings.



ther (polyoxymethylene; polyacetal). Molding of phone components, pump housings, small appliances, mechanical parts—50,000 tons.



ethylene (PE).



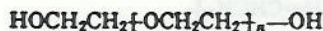
low-density polyethylene (LDPE). Substantial branching—film, toys, housewares, wire and cable coverings—500,000 tons.

high-density polyethylene (HDPE). Linear, very little branching—bottles, containers, housewares, film, sheet, pipe and fittings—2,000,000 tons.

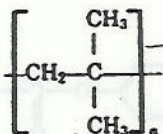
linear low-density polyethylene (LLDPE). Moderate branching—films, sheets.

ultra-high molecular weight polyethylene (UHMWPE). Packaging, films.

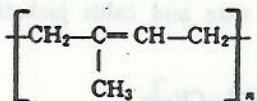
polyethylene glycol (PEG). Used in the manufacture of polyurethane elastomers, lubricants, thickeners, surfactants, plasticizers—600,000 tons.



polyisobutylene (PIB). Lubricating oils, sealants, butyl rubber, blending agents, adhesives—125,000 tons.

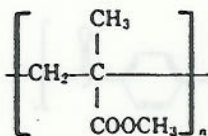


isoprene. Sporting goods, sealants, caulking compounds, car and truck tires, footwear—75,000 tons.

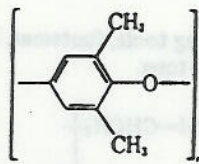


protein. A giant or macromolecule made up of multiple repeating units, such as polyethylene, in which at least 100 ethylene units $\left[\text{CH}_2\text{CH}_2 \right]$ are joined together by covalent bonds. The word is derived from the Greek words meaning "many parts".

poly(methyl methacrylate) (PMMA). Lighting fixtures, automotive lenses, solar panels, signs, glazing—450,000 tons.

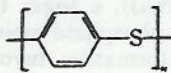


poly(phenylene oxide) (PPO). Automotive, appliances, business machines, electrical parts—70,000 tons.

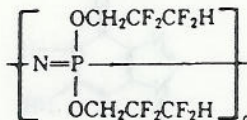


poly(2,6-dimethyl-p-phenylene ether)

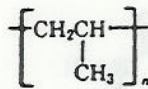
poly(phenylene sulfide) (PPS). Electrostatic coatings, electrical and mechanical goods—2,000 tons.



polyphosphazenes. Aerospace, medicine, oil exploration.

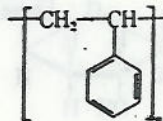


polypropylene (PP). Carpet backing, upholstery, fabrics, toys, carpet yarn, interior automobile trim, housewares, packaging—1,800,000 tons.

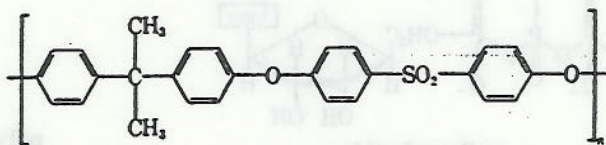


polysaccharide. Polymer composed of sugar-type repeating units; includes cellulose, starch, and dextran.

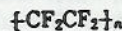
polystyrene (PS). Packaging, housewares, recreational products, electronics, toys, appliances, building and construction (insulation), furniture, disposable food containers—1,900,000 tons.



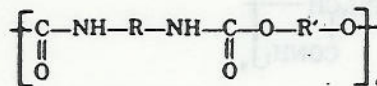
polysulfone. Electrical connections, small appliances, mechanical parts—5,000 tons.



polytetrafluoroethylene (PTFE). Liners, nonsticking surfaces, components for chemical processing equipment, molded electrical components, bushings, seals, cable insulation—7,000 tons.



polyurethane.



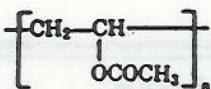
flexible foam. Transportation, bedding, furniture "stuffing", carpet backing, packaging—100,000 tons.

rigid foam. Commercial refrigeration, spray-on roof and tank insulation, pipe, building, construction, and cryogenic insulation—300,000 tons.

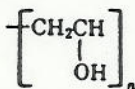
elastomers. Fabric coating, sporting goods, automotive parts, footwear—100,000 tons.

coatings. Industrial coatings—40,000 tons.

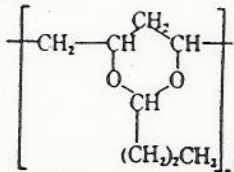
poly(vinyl acetate) (PVA). Labeling, packing, consumer adhesives (white glues), latex paints—400,000 tons.



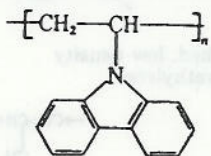
poly(vinyl alcohol) (PVAL). Textile and paper treatment—70,000 tons.



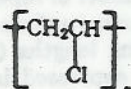
poly(vinyl butyral) (PVB). Adhesive in manufacture of laminated safety glass.



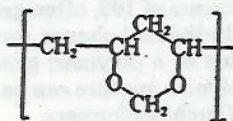
poly(vinyl carbazole). Formulation of photopolymer systems, photoconductive material in xerography.



poly(vinyl chloride) (PVC). Pool liners, pipe fittings, electrical outlet boxes, roof coatings, automotive bumpers, phonograph records, wire and cable insulation, clear film for meat packing, stretch film—3,000,000 tons.



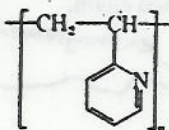
poly(vinyl formal) (PVF). Manufacture of enamels for heat-resistance wire insulation



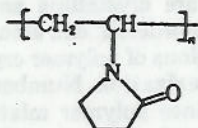
poly(vinylidene chloride). Film and sheeting for food packaging, container liners; coatings for paper, fabric and films—90,000 tons.



poly(vinyl pyridine). Adhesives to bond textile fibers to natural and synthetic rubbers in the manufacture of tires, rubber goods—14,000 tons.



poly(vinyl pyrrolidone). Cosmetics, textile treatment, adhesives, plasma volume extender.



prepolymer. Low molecular weight material (oligomer) capable of further polymerization.

proteins. Composed of α -amino acids; play an essential role in all living cells; act as carriers, catalysts (enzymes), chief

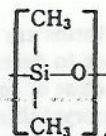
constituents of structural materials such as skin, hair, cartilage, muscle, and bone and in immunological mechanisms.

random copolymer. Copolymer where there is no definite sequence of the different mers or building blocks.

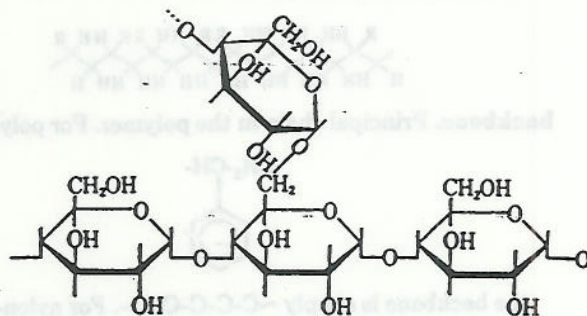
ABAABABAABBABBAB

rayon—regenerated. Reprecipitated cellulose in the form of filaments.

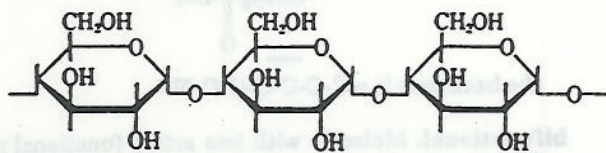
silicones (siloxanes). Greases, waxes, dielectric encapsulation, seals, gaskets, caulks, rubber molds, cosmetics, biomedical implants and devices, insulation, glass sizing agents, surfactants, antifoaming agents, hydraulic fluids, heat exchange fluids, masonry additive, water repellents—70,000 tons.



starch. Common food-reserve polysaccharide for plants; size, shape, and specific properties vary with botanical source; consists mainly of two components—amylose (which is largely linear chains of α (1-4)-linked-D-glucopyranose units) and amylopectin (highly branched containing chains of glucose units linked by α (1-4) bonds being cross-linked through α (1-6) bonding; industrially used in food industry as a thickener and gelling agent for soups, mayonnaise, and many desserts; derivatives used in the textile, paper, and laundry industries; used to make adhesives and in the laundry industry to stiffen and give finish to clothing and household linens.

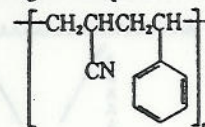


amylopectin—details of branch-point

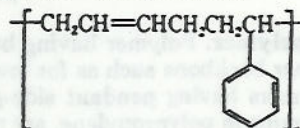


linear amylose

styrene-acrylonitrile copolymer (SAN). Manufacture of ABS blends, glass-reinforced dashboard components, blender bowls, dishwasher safe housewares, vacuum cleaner parts, detergent dispensers—60,000 tons.



styrene-butadiene rubber (SBR). Foam backing for carpets, adhesive tires—1,400,000 tons.



Physical Aspects of Polymer Structure

A Dictionary of Terms

Charles E. Carraher, Jr.

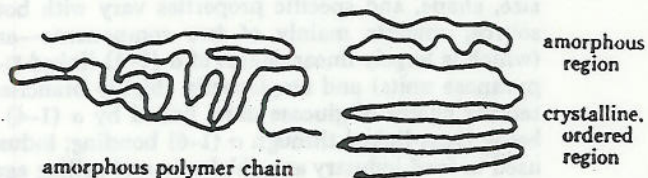
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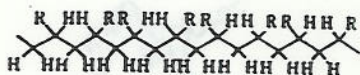
University of Southern Mississippi, Hattiesburg, MS 39406

The following terms are commonly used by those working in polymer science to describe the physical features unique to polymers as a class of compounds.

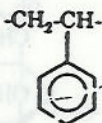
amorphous. Noncrystalline polymers or noncrystalline areas in a polymer; polymer chains are arranged in a less-than-well-oriented manner.



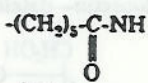
atactic. Polymer where there is a random arrangement of the pendant side-chains on each side of the chiro carbon. Thus, for a polymer of general structure $\text{CH}_2\text{-CHR-}$, the chain can be represented as



backbone. Principal chain in the polymer. For polystyrene



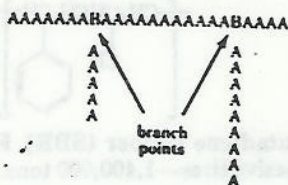
the backbone is simply $\sim\text{C-C-C-C}\sim$. For nylon-6,



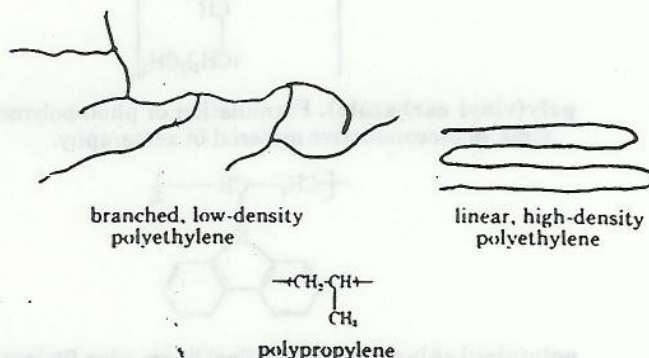
the backbone is $\sim\text{C-C-C-C-C-N}\sim$.

bifunctional. Molecule with two active functional groups. The functional groups can be the same, as in the case of 1,6-hexanediamine, or different, as in the case of alpha-amino acids.

branch point. Atom on the polymer chain where additional chain extension occurs, thus producing a branch (like on a tree).



branched polymer. Polymer having branches attached to the polymer backbone such as for low-density polyethylene. Polymers having pendant side-groups, such as the methyl groups in polypropylene, are not considered to be branched.



capping. Reacting the end-groups of polymer chains to produce an end that may be a stable, nonreactive end-group, or capable of further reaction under specified conditions.

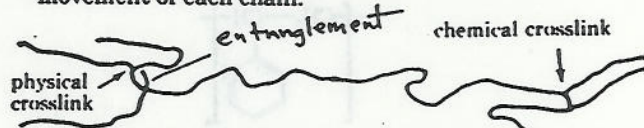
chain length. Number of repeating units (mers) composing a chain. Since many polymer mixtures are composed of chains of varying lengths (number of mers), the chain length is often expressed in terms of an average value called the average chain length. For a polymer chain composed of 20 units, as AAAAAAAAAAAAAAAAAAAAAA, the chain length is 20. Polymers typically have average chain lengths in excess of 100, often greater than 1000.

conformer. Individual shapes produced by changes in the conformation of a polymer; generally the actual average shape of polymer mixture can be pictured as an average of a variety of such conformers.

contour length. Fully extended length of a polymer chain; equal to the product of the length of each repeating unit (l) times the number of units or mers (n), i.e., the full contour length is then ln . This contour length can be corrected for bond angle (C-C bond angle is about 109°), for random-walk-associated factors and for steric factors.

coupling. Joining together of two polymer chains.

crosslinks. Covalent bonds connecting two or more polymer chains or physical entanglement acting to associate the movement of each chain.



crystalline polymer. Polymer with ordered structure that has been allowed to form crystals. Many polymers contain portions that are crystalline and other areas that are amorphous, nonordered; c.f., amorphous.

crystallites. Regions of polymer crystallinity.

degree of polymerization. Number of units, mers, composing a chain. Since polymer mixtures are typically composed of chains of varying lengths, the term average degree of polymerization, \overline{DP} , is often used with the bar over the DP designating the value as an average; c.f., chain length.

end-group. Groups at the chain ends such as carboxyl group that may occur at the end of polyester chains.

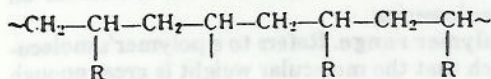


end-to-end distance. Distance between end-groups in a polymer chain. Typically, this is reported as an average end-to-end distance.

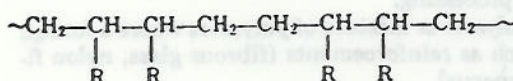


functionality. Number of reactive groups in a molecule (HO-CH₂-CH₂-OH, ethylene glycol—two functional groups).

head-to-tail configuration. Normal sequence of mers where the pendant groups are regularly spaced.

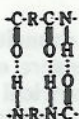


head-to-tail configuration
usual



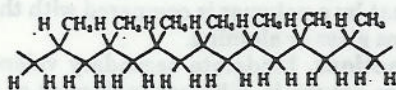
head-to-head, tail-to-tail configuration
abnormal

hydrogen bonding. Strong secondary valence forces between a hydrogen atom in one molecule and an oxygen, nitrogen, or fluorine atom in another molecule. These forces may also exist between hydrogen atoms in one location and oxygen, nitrogen, or fluorine atoms in another in the same molecule. Intermolecular hydrogen bonds are responsible for the high strength of fibers. Helices are the result of intramolecular hydrogen bonds. These forces are typically present for fibers derived from nylons and polyesters but are absent for rubbers.



intermolecular forces. Secondary, van der Waals forces (including dipole-dipole, hydrogen bonding, and dipole-induced dipole) between different molecules. Intramolecular forces are the same except within the same polymer chain.

isotactic. Polymers where the pendant groups are all of the same configurations as in isotactic polypropylene.



macromolecule. Large molecule. Typically used interchangeably with the term polymer. Even so, some will use the term "polymer" for a material such as polystyrene that has an exact repeating unit and the term "macromolecule" for natural materials such as hemoglobin, proteins and nucleic acids where a general repeat unit is present (for the latter two) but where there exists some variation such as in the base of nucleic acids and nature of the alpha substituent for the alpha-amino acid derived units for proteins.

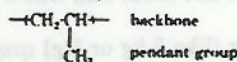
mer. Repeating unit in a polymer chain.

number-average molecular weight, \bar{M}_n . Arithmetical mean value obtained by dividing the sum of the molecular weights by the number of molecules. The basis for determining \bar{M}_n 's is derived from the realization that for dilute solutions, the activity of the solute in a solution is directly related to its mole fraction as the solute concentration goes to zero. When the activity of an added material is directly related to the mole fraction of material present, the property is referred to as a colligative property. Colligative property methods employed for determining molecular weights includes boiling-point elevation (ebullimetry), freezing-point depression (cryoscopy), osmotic pressure (membrane and vapor phase osmometry), and end-group analysis. Thus any analytic technique that determines the number of moles present in a sample of known weight, regardless of their size, gives a \bar{M}_n . It is also possible to measure the average molecular weight in terms of the weights, sizes of molecules present in the sample. This latter molecular weight is called the weight-average molecular weight, \bar{M}_w , and is determined typically by light-scattering photometry. For a mixture of polymer chains of varying lengths, \bar{M}_n is the first moment in the molecular weight distribution, analogous to the center of gravity in physics. The \bar{M}_w is the second moment of the distribution corresponding to the radius of gyration. Practically, the \bar{M}_n can be thought of as simply being related to the probability of drawing out particular lengths of rope from a paper sack containing a mixture of lengths of rope (polymer chains of varying lengths) emphasizing the number of ropes, i.e., the probability of drawing out a short length of rope is the same as the probability of drawing out a long length of rope. If the drawing of rope segments from the bag is dependent on the size of each rope segment (i.e., it is more probable to draw out a long chain compared to a shorter chain), then the probability is referred to as a weight-average property. Mathematically these two probability dependencies can be expressed in terms of N_i , the number of chains (or rope segments) of weight (or number of repeating units) M_i as follows:

$$\bar{M}_n = \frac{\sum M_i N_i}{\sum N_i} \quad \bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

For homodisperse mixtures of smaller molecules (e.g., camphor, phenylmethylketone, and certain proteins, enzymes, and nucleic acids), $\bar{M}_n = \bar{M}_w$. For heterodisperse samples (composed of chains of differing lengths), such as those of almost all synthetic polymers, $\bar{M}_w > \bar{M}_n$.

pendant group. Nonhydrogen group attached to the main polymer chain or backbone like the methyl group in polypropylene.

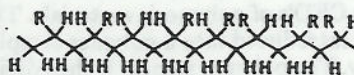


polydisperse. Polymer mixture consisting of molecules of different chain lengths.

polymer. Giant molecule or macromolecule made up of multiple repeating units joined together by covalent bonds.

radius of gyration. Average distance between chain ends and the polymer chains center of gravity, mass.

syndiotactic. Ordered polymer where the pendant groups are arranged alternately on each side of the polymer backbone.



tacticity. Arrangement of the pendant groups in space such as isotactic, syndiotactic or atactic.

Polymer Properties and Testing—Definitions

Charles E. Carraher, Jr.

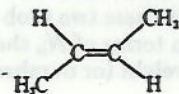
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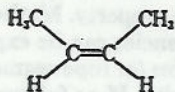
Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406

ASTM. American Society for Testing and Materials; responsible for checking, compiling and publication of standardized testing procedures; not a governmental agency. (Example: A producer of alabaster glass may say that his product is in fact alabaster glass as defined by ASTM test C162, C-14—an optional test to determine if the glass does in fact diffuse visible light without fiery color and that it is milky white in appearance. A governmental agency responsible for glass may or may not specify that in order for white glass to be called alabaster glass that it must score a certain minimum value in the ASTM test C162, C-14.) The ASTM is composed of over 100 technical committees each responsible for a specific area. For instance, ASTM C-14 is responsible for glass and glass products (thus the C-14 notation above for the alabaster glass); D-6, paper and paper products; D-7, wood; D-11, rubber; D-13, textiles; D-14, adhesives; D-20, plastics; D-23, cellulose and cellulose derivatives; F-9, tires.

configuration. Refers to shapes, arrangements related to the actual chemical bonding such as the possible cis and trans configurations of 2-butene.



trans-2-butene



cis-2-butene

conformation. Refers to arrangements related to rotation about single bonds such as a semirigid rod conformation for proteins versus a random coil conformation of polystyrene in a good solvent.

calendar. Machine for producing polymeric sheets; contains counter-rotating rollers.

casting. Production of films or sheets generally from concentrated polymer solutions through evaporation of solvent, from melts or by situpolymerization.

ceiling temperature. A characteristic temperature above which polymerization does not occur and where the polymer decomposes.

charge. Amount of polymer (like 5 kg or 5 g) used in each fabrication cycle.

cloud point. Temperature at which a polymer begins to precipitate from solution as the temperature is lowered.

coextruded film. Film produced by the simultaneous extrusion of two or more polymers.

cohesive energy density (CED). Heat of vaporization per unit volume; used as a means of matching polymers with potential solvents such that a polymer is more apt to be soluble in liquids that have CED's similar to that of the polymer. Since polymers do not vaporize without fragmentation, comparative swelling experiments are often carried out to obtain CED's of polymeric materials. Thus, a few cross-links are introduced into a polymer sample to insure its insolubility. The polymer sample is then divided into samples that are placed in liquids with known CED's. The polymer is assigned a CED corresponding to the CED of the liquid in which the sample shows the greatest swelling.

cold drawing. Stretching of a fiber or fibers in one direction; acts to increase tensile strength through alignment of the polymer chains in the direction of the stretching.

colligative properties. Properties of a solution that are dependent on the number of solute molecules present and are usually related to the effect of these molecules on vapor pressure lowering.

commercial polymer range. Refers to a polymer's molecular weight such that the molecular weight is great enough for the polymer to exhibit good physical properties, such as tensile strength, but not so high as to preclude ready, economical processing.

composite. Polymer or mixture of polymers where a foreign material such as reinforcements (fibrous glass, nylon fibers) are dispersed.

compressive strength. Measure of resistance to crushing forces.

creep. Long-term flow of material under a mild stress, including gravitational forces; also describes the elongation or deformation of a sample after an applied stress is removed.

critical chain length. Minimum chain length required for the physical entanglement of polymer chains.

cross-links. Covalent bonds connecting two or more chains.

cryometry. Technique of measuring molecular weight employing the freezing point depression resulting from the presence of molecules such as polymer molecules; molecular weight obtained is referred to as a number-average molecular weight.

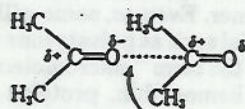
dielectric constant. Ratio of the capacitance of a material to that of air or a vacuum; measure of a tendency of a molecule to align itself as an electrical charge is applied; measure of polar nature and "flowability" of a material.

dielectric voltage. Maximum applied voltage that can be applied to a material before material destruction, breakdown occurs. Also known as dielectric strength.

differential scanning calorimetry (DSC). An instrumental thermal analytical technique in which the difference in the amount of heat absorbed or released by a sample and a standard is measured as the temperature is increased.

differential thermal analysis (DTA). A thermal instrumental analytical technique in which the rate of absorption or release of heat by a polymer is compared with that of a standard such as glass or alumina.

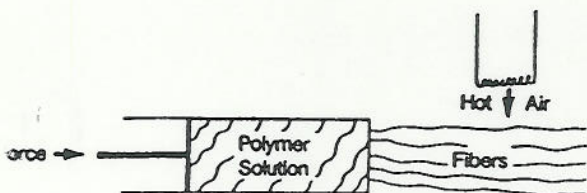
dipole-dipole interactions. Moderate secondary valence forces between polar groups in different molecules or in different locations in the same molecule.



dipole-dipole interactions

dry spinning. Process for obtaining fiber by forcing a solution of a polymer through holes in a spinneret followed by evaporating (such as through blowing hot air past the

drying polymer fibers) the solvent from the extruded (fibrous) polymer.



cross-linking. Term used to describe the cross-linking of a polymer typically containing sites of unsaturation). Term used principally by coating technologists.

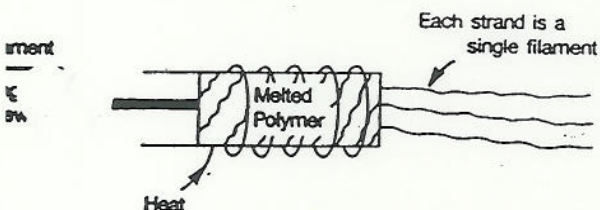
ebulliometry. Measure of the number-average molecular weight employing the elevation in the boiling point of a solution containing a polymer compared to the pure liquid itself.

electrodeposition. Use of an electric charge to deposit solid or dissolved polymer onto a metal surface; used to coat, paint appliances and automobiles by charging the metal surface with one charge and the coating material with the opposite charge.

end-group analysis. Measurement of the number-average molecular weight obtained through determination of the number of end groups per mass of polymer; nature of the end groups must be known.

extrusion. Fabrication process in which a heat-softened polymer is forced by a screw through a die; similar to forcing toothpaste through a toothpaste tube.

filament. Individual extrudate (extruded material) when a polymer is forced through a hole in a spinneret.



intrinsic strength. Measure of a material's resistance to bending.

fractionation of polymers. Separation of polydisperse polymer mixtures into fractions of similar molecular weight.

glass transition temperature (T_g). A characteristic temperature where the glassy, amorphous regions of polymers become flexible or rubberlike due to the onset of local, segmental motion when the temperature is increased.

brittle state. Region where a material is hard, brittle.

toughness. Measure of toughness.

isotropic. Having similar properties in all directions. Thus for bulk, amorphous nylon-6,6 properties such as refractive index, tensile strength, toughness are the same regardless of the orientation of the sample. For cold-drawn nylon-6,6 these properties are different (i.e., anisotropic) along the pull axis compared to properties measured at the other angles.

lamination. Plying of sheets which can be various materials such as paper, plastic, and wood; construction is much like making a double-decker cheese sandwich; examples include automotive windshields, where the glass is sandwiched about poly(vinyl butyral) and laminated counter-tops in which sheets of paper are held together by phenolic resin with urea or melamine resins used for the decorative finish of plywood.

colloidal dispersion of a polymer such as poly(methyl methacrylate) in water.

melt spinning. Process for obtaining fibers by forcing molten, melted polymer through holes in a spinneret followed by cooling of the filaments produced.

modulus. Ratio of stress (applied force) to strain (elongation, bend); ratio of magnitude of applied force to elongation; a measure of the stiffness of a polymer.

molding powder or compounds. Premix of resin and other additives used as the material is added to a mold or extruder.

osmometry. Determination of number-average molecular weight from the measure of vapor phase or membrane osmotic pressure differences. (See *number-average molecular weight*.)

piezoelectric. Conversion of mechanical forces, such as applied pressure, into electrical energy.

plasticizer. A material that reduces the intermolecular forces in polymers permitting the polymer segments to exhibit flexibility. For synthetic polymers this material is usually a nonvolatile additive or may be part of a polymer chain that encourages the formation of amorphous regions. Water serves as a plasticizer in natural polymers. By forming secondary bonds with the polymer chains and spreading them apart, the plasticizer reduces the polymer-polymer chain secondary bonding and provides more room for the polymer segments to slide past one another. Both factors act to provide a softer, more easily deformable, less brittle material.

power factor (or dissipation factor). A measure of the energy dissipated per cycle. The actual power absorbed per cycle is the product of the dielectric constant and dissipation factor.

pultrusion. Process in which filaments are dipped into (coated with) liquid prepolymer, passed through a die, and subsequently cured, cross-linked.

rheology. Science of flow of material.

rovings. Multiple untwisted strands of filaments.

shear (stress). Deformation in which parallel planes in a material remain parallel but are relatively displaced in a direction parallel to themselves; deformation where polymer chains in a material are displaced relative to one another.

solubility parameter. Numerical value equal to the square root of the cohesive energy density; used to predict polymer solubility through trying to match the solubility parameter of the polymer with that of a liquid.

spinneret. A plate in which multiple holes have been formed.

stress. Force per unit area.

stress relaxation. Measure of the relaxation of a stressed specimen with time at constant extension.

tensile strength. Resistance to pulling stresses.

thermogravimetric analysis. Measurement of the change (normally loss) in weight when a material is heated or temperature is held constant.

thermoplastic. Linear or branched polymer which may be softened by heat.

thermoset plastic. Network polymer usually obtained by cross-linking a linear polymer; insoluble; does not soften on reheating.

transfer molding. A process in which a preheated briquette or preform is forced through an orifice into a heated mold cavity.

ultracentrifugation. A high-speed centrifuge employed for the separation of submicroscopic particles such as polymer chains; depending on the type of calculation and experimental procedure used, several types of molecular weight values can be obtained.

¹ Carraher, C. E.; Seymour, R. B. *J. Chem. Educ.* 1986, 63, 418-419.

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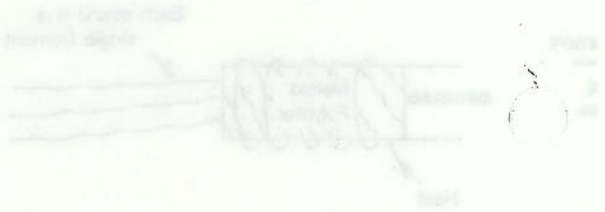
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