

Section 16.3

Plastics

Until the middle of the nineteenth century, virtually all objects of everyday life were made from naturally occurring or naturally derived materials such as wood, glass, metal, paper, wool, and rubber. While this short list of available materials was sufficient for most purposes, there were situations that demanded something new. In 1863, a billiard ball manufacturing company, Phelan and Collander, offered a prize of \$10,000 to anyone who could find a substitute for natural ivory in billiard balls. In response to this offer, American printer John W. Hyatt and his brother Isaiah figured out how to form billiard balls out of a recently discovered synthetic chemical called nitrocellulose. By 1871, Hyatt had established two companies to work with this new material, under the name celluloid, and the plastics industry was born.

The word plastic has a wide usage and a broad definition. Most often it refers to materials that, while solid in their final forms, take on liquid or shapeable states during earlier phases. Modern plastics can assume many shapes and forms and exhibit a rich variety of physical and chemical properties. Most importantly, the development of plastics has made it possible to design materials that exactly suit their uses.

Questions to Think About: *Why do some plastics melt when heated while others simply burn? Why are some plastics flexible while others are hard and brittle? Why do clear plastics often turn hazy and white when you bend them too far? What makes Kevlar, the plastic fiber used in bulletproof vests, so strong? Are all plastics recyclable?*

Experiments to Do: *Plastic eating utensils are made of relatively hard, brittle plastics that soften considerably when you put them in boiling water. To see this softening in action, heat a plastic spoon until it melts. Find a safe location and hold the middle of the spoon above a candle flame. Keep the spoon and your fingers out of the flame itself. As the*

□ Polymers were discovered long before anyone understood what they were. It wasn't until 1920 that German chemist Hermann Staudinger (1881–1965) made his macromolecular hypothesis, suggesting that polymers are actually giant molecules formed by the permanent attachment of countless smaller molecules. Through careful experiments, he proved his hypothesis to be correct and was rewarded with the 1953 Nobel Prize in Chemistry.

spoon heats up, it will initially soften to a leathery consistency. At still higher temperatures, it will be elastic, like a rubber band. And at still higher temperatures the plastic will flow, first like chewing gum and then like syrup.

These five behaviors are characteristic of plastics, although not all plastics exhibit them clearly. Just which behavior a particular plastic exhibits depends on its composition and temperature. The plastic spoon is hard and brittle at room temperature. Can you find plastic items that exhibit one of the four other behaviors at room temperature?

Polymers

Plastics are based on **polymers**, enormous chain-like molecules containing thousands or even millions of atoms. Like all organic molecules, and the glasses of the previous section, the atoms in a polymer are held together by covalent bonds. But while propane, diesel fuel, and paraffin wax consist of chain-like molecules roughly 3, 16, and 30 carbon atoms long respectively, the chain-like molecules of high-density polyethylene (HDPE) are between 1000 and 3000 carbon atoms long (Fig. 16.3.1). Once a molecule is more than about 1000 atoms long, it's considered a polymer. (For a history of the understanding of polymers, see □.)

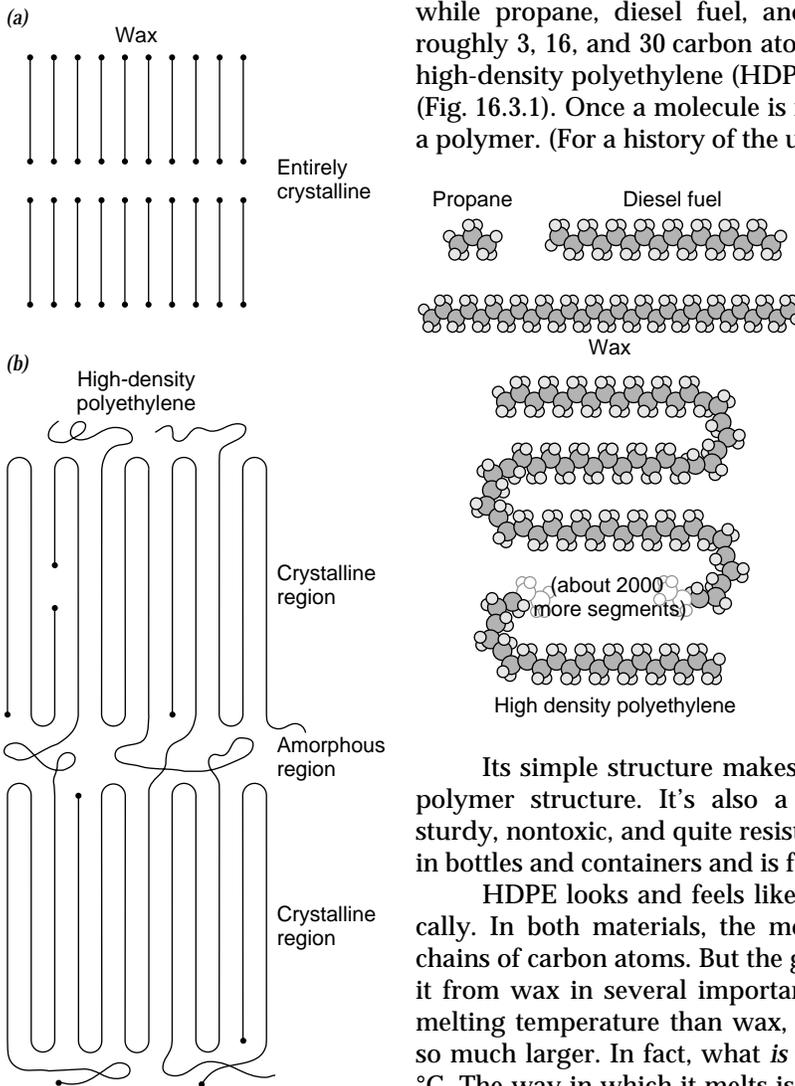


Fig. 16.3.2 - (a) Wax is a crystalline material, held together only by van der Waals forces. (b) High density polyethylene is about 80% crystalline and 20% amorphous, with entanglements helping to hold it together.

Fig. 16.3.1 - Paraffin chains are found in many materials. Each paraffin chain consists of a backbone of carbon atoms (the larger balls), decorated by pairs of hydrogen atoms (the smaller balls). A chain is terminated at each end by an extra hydrogen atom. Propane, diesel fuel, and wax contain relatively short paraffin chains while high density polyethylene, the plastic used in milk containers, contains paraffin chains of between 1000 and 3000 carbon atoms.

Its simple structure makes HDPE a good starting point for a discussion of polymer structure. It's also a commercially important polymer because it's sturdy, nontoxic, and quite resistant to chemical attack. HDPE is used extensively in bottles and containers and is familiar as the cloudy white plastic of milk jugs.

HDPE looks and feels like wax because the two are closely related chemically. In both materials, the molecules consist of hydrogen atoms attached to chains of carbon atoms. But the great lengths of these chains in HDPE distinguish it from wax in several important ways. First, HDPE has a substantially higher melting temperature than wax, which isn't surprising because its molecules are so much larger. In fact, what is surprising is that HDPE melts at only about 140 °C. The way in which it melts is complicated and is one of the reasons that polymers are so interesting.

Second, while wax is completely crystalline, HDPE is partly crystalline and partly amorphous (Fig. 16.3.2). In about 80% of the plastic, the molecules are neatly oriented like dry spaghetti in a box. In the other 20%, the molecules are coiled randomly and entangled with one another like cooked spaghetti. These amorphous regions are as unavoidable as the knots that appear in shoulder-

length hair. HDPE's mixed structure gives it a non-uniform index of refraction—its denser crystalline regions slow light more than its amorphous regions. This non-uniformity gives solid HDPE a milky haziness that disappears when the plastic melts to become a uniform liquid.

Third, HDPE doesn't crumble like wax when you bend it. The amorphous regions of tangled polymer chains provide the plastic with considerable flexibility. When you stress HDPE, its coiled chains unwind. They can't cross one another where they're entangled but they still allow the plastic to stretch by as much as 50% in length. The material responds elastically to small stresses but undergoes plastic deformation when the stresses are severe. If you push gently on a milk container, it will bounce back, but if you crush it, it will stay crushed.

Finally, HDPE has a much greater tensile strength than wax. Wax molecules are relatively short chains, clinging to one another only with van der Waals forces. **Van der Waals forces** are weak, non-directional intermolecular forces that are created by temporary fluctuations in the positions of electric charges in molecules. All molecules exert van der Waals forces on nearby molecules. Van der Waals forces are so weak that the wax molecules slide across one another easily and the whole crystal can be pulled apart. Although HDPE chains are also bound together only by van der Waals forces, their great lengths and frequent entanglements make the plastic hard to pull apart. You must actually break some of the molecules in order to divide the plastic at room temperature.

While low-density polyethylene (LDPE) is also built from long wax-like molecules, these molecules have short branches or side chains. Side chains get in the way of crystallization because they make it hard for the molecules to line up neatly. As a result, LDPE is about half amorphous—heaps of coils and tangles.

With its mechanical properties dominated by the amorphous regions, LDPE is limp and flexible at room temperature. However, it has considerable tensile strength because its entangled chains can't be separated easily. The major uses of LDPE are in trash bags, shopping bags, food and dry goods wrappers, and electric insulation.

CHECK YOUR UNDERSTANDING #1: All For One or One For All?

How does a polymer chain differ from a chain of many individual diesel fuel molecules?

Polymers and Temperature

At room temperature, low-density polyethylene is neither a solid nor a liquid. It bends almost effortlessly so it isn't a normal solid. It doesn't flow so it isn't a normal liquid. Instead, LDPE lies in between solid and liquid in what is called the *rubbery plateau regime*. There are five temperature regimes for most polymers and the rubbery plateau is the middle one. At lower temperatures, there are the *glassy regime* and the *glass-rubber transition regime* and at higher temperatures, there are the *rubbery flow regime* and the *liquid flow regime*.

These five regimes exist because the long polymer chains can't crystallize completely at low temperatures and can't avoid entanglements at high temperatures. With trouble forming either a normal solid or a normal liquid, a polymer's characteristics change rather gradually with temperature.

Within this evolving behavior, polymer scientists have identified the five separate regimes (Fig. 16.3.3). There are no sharp boundaries between these regimes, so a particular polymer moves smoothly from one to the next as it warms up. While the presence of crystalline regions in a polymer complicates this picture, those regions can be safely ignored in polymers that are substantially amor-

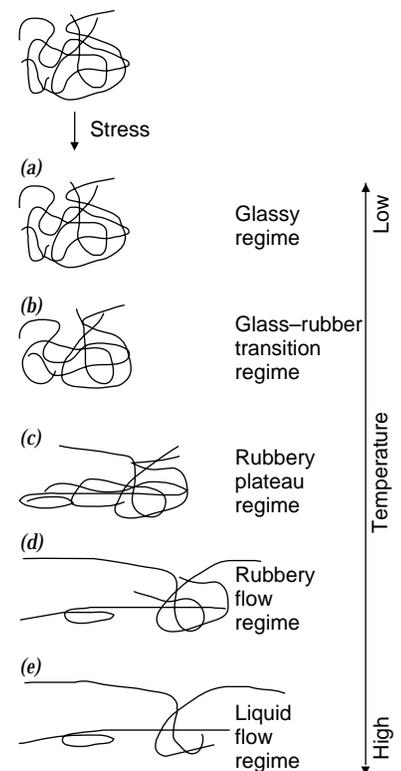


Fig. 16.3.3 - As you heat a polymer, it goes through the five stages shown here from top to bottom. (a) When cold, its atoms don't shift during stress so it's glassy. (b) When cool, its atoms shift slowly but the chains remain fixed so it's between glassy and rubbery. (c) At intermediate temperatures, its atoms and chains move but entanglements prevent them from getting past one another so it's rubbery. (d) When warm, the chains begin to untangle so it exhibits rubbery flow. (e) When hot, the chains easily untangle and it exhibits liquid flow.

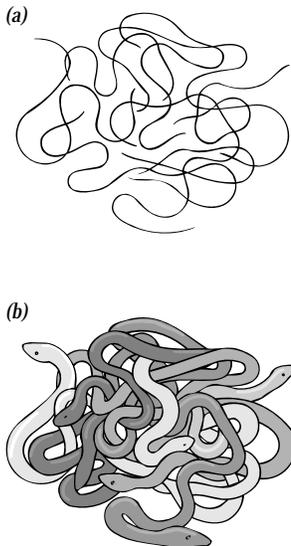


Fig. 16.3.4 - (a) Tangled polymer chains can only untangle themselves by moving forward or backward along their lengths. (b) Because this motion is reminiscent of snakes, it's called reptation.

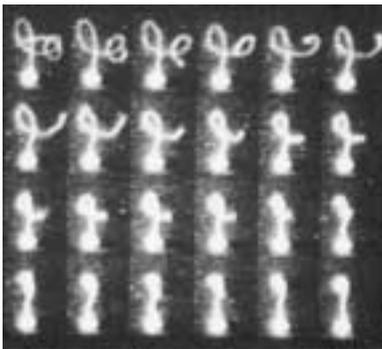


Fig. 16.3.5 - While the theory of reptation correctly predicted many features of polymer behavior, reptation itself wasn't directly observed until 1993, when American physicist Steven Chu first watched it through a microscope. Chu and his colleagues coated a single polymer molecule with fluorescent dye and used a laser beam to drag that molecule through another polymer. The molecular chain snaked its way through entanglements, just as predicted by reptation theory.

phous. We'll examine the five regimes in LDPE, which is amorphous enough that we won't have to worry about its crystalline regions.

At extremely low temperatures, LDPE is a hard, brittle solid. Because the atoms of LDPE can't move relative to one another when it's below its glass transition temperature (about $-128\text{ }^{\circ}\text{C}$), it's a glass (Fig. 16.3.3a). Your shopping bag never gets cold enough to reach this **glassy regime**, but there are many common polymers that are glassy at room temperature. One of the most important of these is poly(methyl methacrylate) or Plexiglas.

At about $-80\text{ }^{\circ}\text{C}$, the atoms in LDPE have enough thermal energy to move relative to one another. However, the overall chains still can't move (Fig. 16.3.3b). LDPE is in the **glass-rubber transition regime** and has a leathery character—stiff but pliable. A familiar polymer that is in this regime at room temperature is poly(vinyl acetate), the principal polymer in most latex interior house paints.

Near room temperature, LDPE is in the **rubbery plateau regime**, with its atoms moving freely and even its chains moving slightly. Because the chains are still too entangled with one another to permit flow (Fig. 16.3.3c), the plastic has a rubbery feel—flexible and elastic. The chains pull taut when you stretch it and snap back to normal when you let go. But if you pull too hard on the plastic, the chains break at the entanglements and the plastic stretches irreversibly or tears. These behaviors explain the familiar stretchiness of LDPE trash and shopping bags and the tearing that occurs when you overload them with sharp objects.

At about $100\text{ }^{\circ}\text{C}$, the chains in LDPE are mobile enough to disentangle themselves and the material is in the **rubbery flow regime** (Fig. 16.3.3d). The chains disentangle themselves through a process called **reptation**, in which thermal energy causes the chains to slide back and forth along their lengths until they leave entanglements behind them. This motion was first postulated by French physicist Pierre-Gilles de Gennes (1932–) and is named for its similarity to the motions of snakes (Figs. 16.3.4 and 16.3.5). A common polymer that is in this rubbery flow regime just above room temperature is chicle, the main constituent of chewing gum. Silly Putty, a silicon polymer, is also in this regime.

At higher temperatures, the chains in LDPE slide across one another freely and the polymer is in the **liquid flow regime** (Fig. 16.3.3e). Reptation occurs so rapidly in this regime that it's hard to distinguish a liquid polymer from any other viscous liquid. One polymer that exhibits liquid flow at room temperatures is poly(dimethyl siloxane), a silicon-based compound. Because its long molecular chains slide across one another so easily, this liquid makes an excellent lubricant.

Even at high temperatures, polymers exhibit unusual flow characteristics as a consequence of reptation (Fig. 16.3.6). Because the chains have to slither large fractions of their lengths to get past each entanglement, polymers with longer chains are more viscous than polymers with shorter chains. Reptation theory accurately predicts that a polymer's viscosity should be proportional to the third power of the average chain length.

It's sometimes possible to shift a polymer's behavior from one regime to another by adding chemicals to it. **Plasticizers** are chemicals that dissolve in a polymer and soften it. They lower its glass transition temperature (T_g) and usually decrease the sizes of any crystalline regions. Plasticizers added to poly(vinyl chloride) or "vinyl" convert it from a glassy solid at room temperature to the leathery material used in some upholstery. In hot weather, you can smell these plasticizers evaporating. When enough of them leave, the aging vinyl returns to its glassy state and becomes susceptible to cracking.

CHECK YOUR UNDERSTANDING #2: On An Unusually Cold Day...

How would the plastics you use behave if the temperature were $-100\text{ }^{\circ}\text{C}$?



Fig. 16.3.6 - When you place a spinning rod into normal liquids, the molecules of liquid are thrown outward and move away from the rod. But in a liquid polymer, entanglements draw the polymer chains toward the rod, creating the Weissenberg effect.

Thermoplastics and Thermosets

Because the molecules in HDPE and LDPE can move independently at high temperatures, these polymers behave as liquids when heated. They are both **thermoplastics**, a class of plastics that can be reshaped at high temperatures. While some thermoplastics burn or char before they melt, even those materials can usually be dissolved in solvents, reshaped, and allowed to dry.

But not all polymers can be reshaped. Some polymers have chemical cross-links between their chains that prevent them from reptating. These **thermosets** can't flow. They won't melt when you heat them and they won't dissolve in solvents unless those solvents destroy their molecular structures.

Because they can't be reshaped, thermosets must be produced in their final forms. Many thermosets begin as thermoplastics that are then cross-linked, a process generally called **vulcanization**. In other contexts, this cross-linking is known as tanning (leather), curing (resins), and drying (oil paints). Many important polymers are cross-linked, as we'll soon see.

Most polymer molecules are built by tacking together much smaller molecules. These small molecules are referred to as **monomers** and the tacking together process is called **polymerization**. The final chains are then named after their monomers (e.g. polyethylene from an ethylene monomer, and poly(methyl methacrylate), from a methyl methacrylate monomer).

In many cases, a single monomer is used over and over again to form a *homopolymer*. Representing that monomer as the letter "A", the finished homopolymer looks like "AAAAAAAAAA...." However, there are also cases in which several different monomers are incorporated in the same chain. Such chains are called *copolymers*. Representing two monomers by the letters "A" and "B", the finished copolymer might be "ABABABABAB...."

□ Most animals can't digest cellulose because they're unable to break its molecular chains into individual glucose molecules. Fortunately, bacteria and protozoans produce a catalytic enzyme that breaks up cellulose so that dead trees and plants decompose quickly. Cows and other ruminants carry bacteria and protozoans in their stomachs and let those tiny animals convert cellulose into small digestible molecules.

Distinguishing between homopolymers and copolymers is particularly important when the various monomers in a copolymer come together in random order. Then the finished copolymer might be "ABAABBBABAABBAAA...." The resulting molecular chains are different from one another and are unlikely to form crystals. Most of these *statistical copolymers* are amorphous.

Even homopolymers can be disordered if their monomers randomly adopt different orientations during polymerization. If a monomer can enter the chain as either "↑" or "↓" then the homopolymer might be "↑↓↑↑↓↑↑↓↑↓↑...." These *atactic homopolymers* are amorphous.

CHECK YOUR UNDERSTANDING #3: A Really Bad Hair Day

Hair is actually a thermoset composed of long protein chains that are cross-linked by sulfur atoms. At what temperature does hair melt?

Natural Polymers: Cellulose and Natural Rubber

□ Oxygen permeable contact lenses swell when wet, allowing oxygen molecules to dissolve in the plastic and diffuse to the surface of the eye. The plastic bottles used for carbonated beverages similarly dissolve water, oxygen, and carbon dioxide molecules. Because carbon dioxide and water slowly diffuse out of a bottle while oxygen diffuses in, the beverage it contains eventually goes flat.

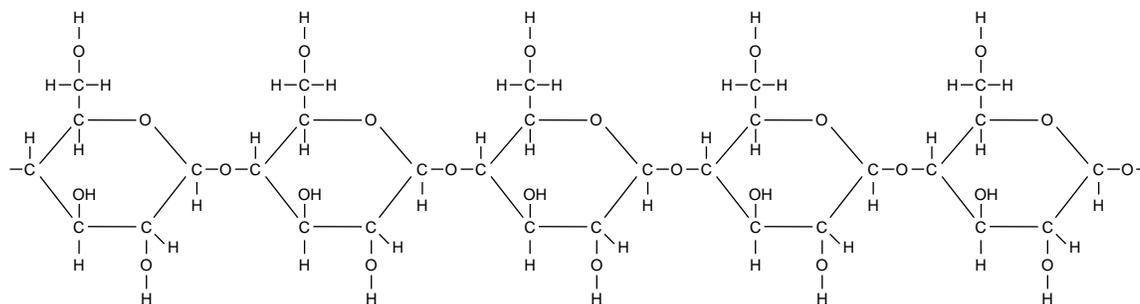
Several of the most important polymers occur naturally, most notably cellulose and natural rubber. Cellulose is the principal structural fiber in wood and plants and by far the most abundant polymer on earth. We use it as a building material, in making paper, clothing, rope, and chemicals, and as a fuel. Cellulose molecules are made of polymerized glucose sugar molecules (Fig. 16.3.7). These chains are unbranched and orderly so cellulose crystallizes easily. Because natural cellulose is about 70% crystalline and 30% amorphous, it appears translucent or white. But while it's built from sugar molecules, we can't digest it (see □).

The oxygen and hydrogen atoms in adjacent cellulose molecules form strong hydrogen bonds and bind the chains together so tightly that overheated cellulose decomposes instead of melting. That's why wood burns rather than turning into liquid in your fireplace. Cellulose's glass transition temperature is also quite high so wood is rigid. Cellulose is only flexible as extremely thin fibers, such as those in cotton. Cotton is nearly pure cellulose.

Since cellulose chains also form hydrogen bonds with water molecules, cellulose eagerly soaks up water. The water dissolves in cellulose, forming a solid solution. The fibers swell and soften as water enters them because water acts as a plasticizer. When the water dries up, the swollen fibers become hard and stiff again. These changes lead to the shrinkage that occurs when you launder cotton clothes in water. This shrinkage can be reduced by lubricating the fibers with fabric softeners. (For more on solid solutions in plastics, see □.)

Natural rubber forms when a chemical called isoprene polymerizes into long chains of *cis*-polyisoprene (Fig. 16.3.8). The prefix "*cis*-" indicates that the isoprene monomers alternate up and down, as shown in the figure. Natural rubber is extracted from the sap of several tropical trees, where it forms a *latex* of

Fig. 16.3.7 - Part of a cellulose molecule, showing five repetitions of the glucose monomeric units from which it's built. Each carbon atom (C) is bound to four other atoms, including oxygen atoms (O) and hydrogen atoms (H). The covalent bonds between the atoms are indicated by lines. Cellulose is a stiff, mostly crystalline solid at room temperature and is the main structural material in trees and plants.



Cellulose

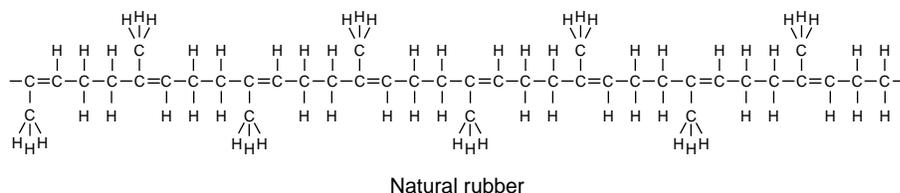


Fig. 16.3.8 - Part of a natural rubber molecule showing eight repetitions of the basic isoprene moneric units from which it's built. The orientations of the isoprene units alternate up and down. The chains coil up randomly on their own but straighten when you stretch the rubber. The rubber reaches its elastic limit when the chains are straight.

tiny polymer particles suspended in a watery liquid. As the sap dries, its remaining water pulls the polymer particles together and the rubber coagulates into an elastic solid.

Without oxygen atoms, the molecules in rubber can't form hydrogen bonds. They stick together so weakly that rubber's melting temperature is only 28 °C and its glass transition temperature is a frigid -70 °C. However, rubber rarely crystallizes at any temperature because its molecules naturally wind themselves up into random coils. These coils are what give rubber its wonderful elasticity. As you stretch a piece of rubber, its polymer molecules straighten out. When you let go, those molecules return to their randomly coiled shapes.

This coiling is an example of nature's tendency to maximize randomness and entropy. A straight rubber molecule is orderly. Once you stop pulling on it, thermal motions in its atoms give it a bend here and a twist there, and soon the molecule is wound into a jumble of random coils. While thermal motions could one day straighten that molecule back out, such an event is quite unlikely.

Rubber first came into use in 1820, when Englishman Thomas Hancock constructed the first rubber factory. Three years later, Scottish chemist Charles Macintosh began using rubber to waterproof fabrics. But natural rubber is sensitive to temperature and therefore hard to use. Moderate or cold weather puts rubber in the rubbery plateau regime, where it's a firm, elastic material. But hot weather takes it to the rubbery flow regime, where it's as gooey as glue.

The famous accident of the American inventor Charles Goodyear (1800-1860) changed all that. In 1839, after ten years of trying to prevent rubber from softening at high temperatures, Goodyear accidentally dropped a mixture of rubber and sulfur onto a hot stove. The material that formed was exactly what he had been looking for. It was stiff but elastic and remained that way regardless of temperature. He called this process *vulcanization*, after the Roman god of fire.

What Goodyear had done was to form cross-links between individual molecular chains in the rubber (Fig. 16.3.9). He had turned natural rubber, which is a thermoplastic, into vulcanized rubber, a thermoset. Since the chains in the vulcanized rubber were interconnected, they couldn't flow and the rubber couldn't melt—it was a single giant molecule.

Vulcanized rubber exhibits the elastic behavior of the rubbery plateau re-

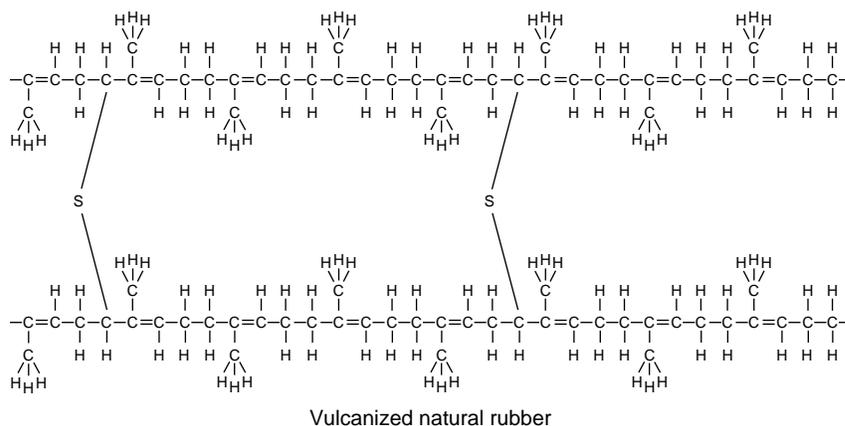


Fig. 16.3.9 - Vulcanized rubber is formed by heating a mixture of natural rubber and sulfur. The sulfur links individual rubber chains to form a thermoset. Vulcanized rubber no longer melts the way natural rubber does. The more sulfur that's added to the natural rubber, the harder the vulcanized rubber becomes.

□ Poly(dimethyl siloxane) is a particularly important silicon polymer, with an extremely low glass transition temperature and thus a low viscosity near room temperature. Silicone rubber sealants are based on this polymer, but with an added twist—the ends of each polymer chain are treated so that they cross-link in the presence of moisture. After you apply the liquid sealant, it undergoes room temperature vulcanization (RTV) in air to form a soft silicon rubber. This process releases acetic acid, the main ingredient in vinegar, so you can smell that the rubber is vulcanizing.

□ Genetic information is encoded in a naturally occurring copolymer called deoxyribonucleic acid or DNA, where it's contained in the exact sequence of monomers. Medical, biological, and forensic scientists can now produce this copolymer, using the polymerase chain reaction (PCR). This technique selectively polymerizes DNA monomers (nucleic acids) to copy portions of a particular DNA chain. PCR can locate particular patterns in the DNA and is coming into frequent use in trials as a genetic equivalent of fingerprinting.

Fig. 16.3.10 - Nitrocellulose is formed in a chemical reaction between cellulose and an acid mixture. Unlike cellulose, nitrocellulose can be shaped and was the first synthetic plastic. However, nitrocellulose is both flammable and explosive.

gime over a broad range of temperatures. As long as there aren't too many cross-links between chains, the random coils can still wind and unwind, and the vulcanized rubber still stretches when you pull on it. But the more sulfur you add to the mixture, the more cross-links are formed and the stiffer the rubber becomes. Sulfur content thus controls the stiffness of vulcanized rubber.

Because natural rubber is in limited supply, most modern rubber is synthesized from petroleum. While many of these synthetic rubbers or *elastomers* are chemically different from vulcanized natural rubber, they all have random coils in their polymer chains and cross-links between those chains. Their various molecular structures give them new and useful properties such as resistance to chemical attack and better stability at high temperatures. For a discussion of silicon rubber, see □, and for a note about another natural polymer, DNA, see □.

CHECK YOUR UNDERSTANDING #4: Wagon Wheels and Tires Don't Melt

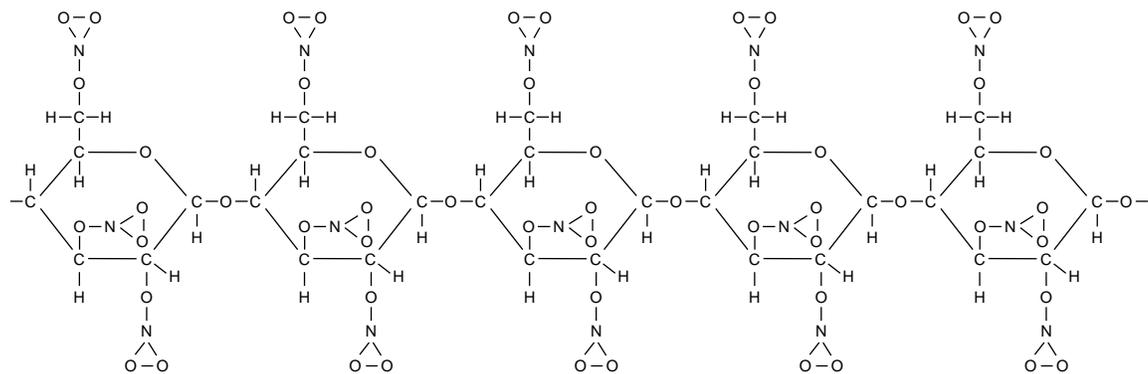
Neither cellulose nor vulcanized rubber can melt but for different reasons. What are those reasons?

Synthetic Polymers: Celluloid, Plexiglas, Nylon, and Teflon

When Phelan and Collander offered \$10,000 to anyone who could find a replacement for ivory in billiard balls, neither cellulose nor rubber was up to the task. Instead, the Hyatts used a chemically modified cellulose called nitrocellulose (Fig. 16.3.10) to produce the first practical synthetic plastic: celluloid.

In contrast to cellulose, which can't be reshaped, chemically softened or plasticized celluloid can be molded fairly easily. The objects that were produced with celluloid resemble those we use today, including transparent plastic films, combs, toys, and synthetic silk-like cloth. However celluloid darkens with long exposure to light and is extremely flammable. Nitrocellulose itself is a high explosive and the main constituent of smokeless gunpowder.

Instead of nitrating cellulose, chemists found that they could attach other useful chemical groups to cellulose to form useful and less dangerous plastics. Cellulose acetate was the first important alternative to nitrocellulose. Referred to as "acetate" or "triacetate", cellulose acetate continues to be used in many forms. Chemists also found that they could take cellulose through a series of chemical transformations that finally ended where it began, with regenerated cellulose. This chemical process allowed cellulose to be reshaped into fibers or films. Rayon and cellophane are both examples of regenerated cellulose.



Nitrocellulose or celluloid

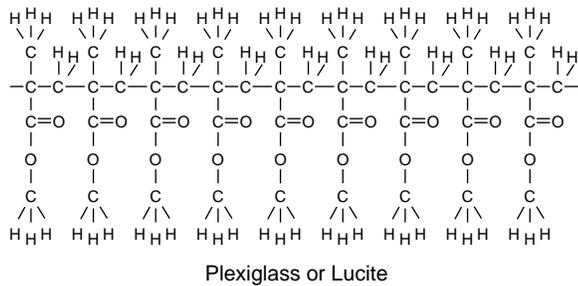


Fig. 16.3.11 - Plexiglas is long chains of poly(methyl methacrylate). These chains bind relatively strongly to one another to form a glassy, transparent material at room temperature.

Plexiglas and Lucite are made from the thermoplastic poly(methyl methacrylate) (Fig. 16.3.11). Like cellulose, poly(methyl methacrylate) contains oxygen atoms and forms hydrogen bonds between chains. These bonds are so strong that Plexiglas is a glassy solid below about 105 °C. It's hard, clear, and durable.

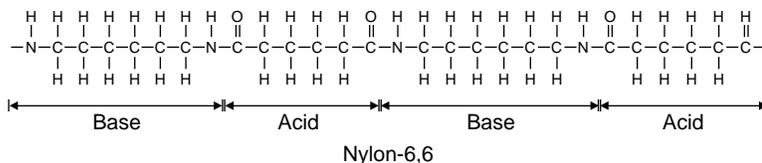
Instead of cracking like glass when you bend it too far, Plexiglas *crazes*. Voids appear on the stretched plastic surface but they're prevented from separating completely by taut polymer chains that span the open fissures. Because light's speed changes as it passes in and out of the voids, it reflects randomly from the crazed plastic and gives the plastic a hazy, whitish look. However, the Plexiglas doesn't break. This impact resistance makes Plexiglas an important alternative to glass.

Plexiglas has a number of close relatives that are also useful. Poly(methyl acrylate) is more flexible and elastic than Plexiglas and is the principal polymer in acrylic paints. Methyl cyanoacrylate is a monomer that polymerizes rapidly in the presence of moisture to form a hard, glassy plastic. It's the active ingredient in Superglue and Crazy Glue.

Nylon was developed at Du Pont in 1931 by Wallace Carothers □ and Julian Hill. Their work was based on the chemical reaction that occurs when an organic acid group (of atoms) on one molecule encounters an organic base group on another molecule. This reaction binds the two molecules together while releasing a water molecule. Carothers and Hill realized that hydrocarbon molecules with these reactive groups at both ends would tend to polymerize into long chains. To test their idea, they began producing double-ended organic acids and double-ended organic bases. Their work was a success. The acids and bases bound together to form chains of alternating monomers (Fig. 16.3.12). This strong, tough, elastic, and chemically inert copolymer was named nylon.

Because the acid and base groups in the chains allow them to hydrogen bond to one another, nylon's properties depend on the lengths of its monomer molecules. The shorter the monomer molecules, the more acid and base groups are incorporated into the nylon and the stiffer and harder the nylon becomes. Nylons are named according to the lengths of their base and acid monomers. Nylon-6,6 is made from a six carbon-atom long base and a six carbon-atom long acid and is stiffer than nylon-6,12, which uses a twelve carbon-atom long acid.

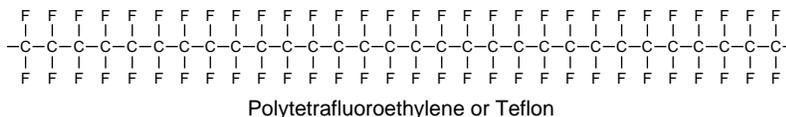
Another plastic that's extremely resistant to chemical attack is polytetrafluoroethylene, known as Teflon or PTFE (Fig. 16.3.13). Teflon's polymer chains resemble those in polyethylene except that its carbon chains are surrounded by fluorine atoms rather than hydrogen atoms. Because fluorine atoms are slightly larger than hydrogen atoms, they fully enclose the carbon backbones of the Tef-



□ At 31, American chemist Wallace Hume Carothers (1896–1937) left an instructor's position at Harvard University to head an extraordinarily successful research group at Du Pont. Not only did his group invent nylon, but they also prepared neoprene, one of the most important synthetic rubbers. His pioneering work even included polyesters, although his early fabrics melted during ironing. But despite his scientific successes, he was plagued by terrible bouts of depression. Following the sudden death of his sister and three weeks after applying for a patent on nylon, Carothers took his own life.

Fig. 16.3.12 - Nylon forms when a double-ended acid reacts with a double-ended base. The reaction permanently binds the acid to the base and they become alternating segments in long copolymer chains. This particular nylon is called 6,6 because the double-ended base monomer contributes 6 carbon atoms to the copolymer chain (the first 6) and so does the double-ended acid (the second 6).

Fig. 16.3.13 - Polytetrafluoroethylene or Teflon is composed of enormous carbon chains, completely surrounded by fluorine atoms (F). The fluorine atoms make Teflon harder and even more resistant to chemical attack than its hydrogen-based relative, polyethylene.



lon polymer chains. With its chains sheathed in fluorine atoms, Teflon is one of the most chemically inert materials in existence. It's also slippery and makes an excellent nonstick surface for cookware and laboratory equipment.

Unfortunately, Teflon pulls apart easily unless its molecules are at least 100,000 carbon atoms long. This length makes reptation so slow that Teflon is almost incapable of flowing. Even at its melting temperature of 330 °C, Teflon is so viscous that it appears solid. That's why Teflon objects are formed by filling a mold with powdered Teflon and heating it until it fuses together.

CHECK YOUR UNDERSTANDING #5: Hard to Get Hold Of

Why is Teflon more resistant to chemical attack than nylon?

Liquid Crystal Polymers: Kevlar

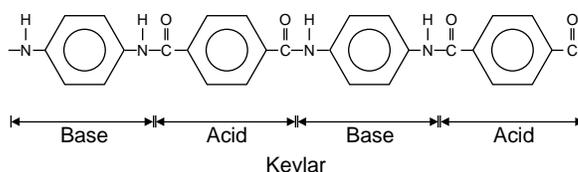
Not all polymers form tangles of random coils, even at high temperatures. Some polymers are stiff, rod-like molecules that line up with one another, even as they reptate forward and backward. As liquids, these polymers are liquid crystals and as solids, they are remarkably strong fibrous materials.

One of these liquid crystal polymers is poly(*p*-phenylene terephthalamide), also called PPD-T or Kevlar. This copolymer resembles nylon except that nylon's hydrocarbon chains are replaced by aromatic rings (Fig. 16.3.14). Because these rings don't bend, the copolymer chains are rigid and straight.

At room temperature, the molecules of Kevlar form long, uniform crystals that give it an enormous tensile strength. Because the molecules are already straight, they don't have to uncoil or disentangle themselves when the Kevlar is subjected to tensile stress along the direction of the chains. Instead, they all oppose the stress together. To break a Kevlar fiber, you must break all of its molecules at once. Because Kevlar and other liquid crystal polymers stretch very little and are extremely hard to break, they are used in bulletproof vests, sails, parachutes, and ropes, and as reinforcement in ultrahigh-strength composites.

Even ordinary polymers can be strengthened by straightening their polymer chains, a step that often occurs when a fiber is spun. Spinning is done by squirting a liquid out of a fine nozzle and allowing it to solidify. Some polymers, such as nylon, are spun from hot liquids and solidify by cooling. Others, such as acrylics, are spun from solutions and solidify as the solvent dries. Still others, such as rayon, are spun from a solution that reacts with a chemical outside the spinneret to produce the final polymer fiber. In each case, the synthetic fiber is drawn out of the nozzle under tension. This tension stretches the fiber along its length and unwinds many of its polymer chains. When the fiber solidifies, it retains this modified structure and is stronger as a result.

Fig. 16.3.14 - Kevlar resembles nylon, except that the flexible hydrocarbon chains of nylon are replaced by rigid aromatic rings. Each chain is stiff and straight, so the polymer forms a liquid crystal at high temperatures. When liquid Kevlar cools and solidifies, it becomes a fibrous material with extraordinary tensile strength.



CHECK YOUR UNDERSTANDING #6: You Can't Be Good at Everything

While a thin Kevlar fiber has an enormous tensile strength, a large block of solid Kevlar exhibits a similar tensile strength only along one direction. Explain.

Polymerization

Poly(methyl methacrylate) is made by polymerizing methyl methacrylate monomer (Fig. 16.3.15). The methyl methacrylate molecule includes a double covalent bond between carbon atoms that's easily attacked by a free radical. When a chemical that produces free radicals is added to methyl methacrylate and the mixture is heated, a free radical attacks the double bond between two carbon atoms. The double bond becomes a single bond as the free radical binds to one member of the carbon atom pair. The other carbon atom becomes a free radical itself and begins to seek out something with which to bind. It soon attacks another methyl methacrylate molecule, which then attacks another, and so on. With each step, the molecule increases in length and eventually a polymer chain is produced.

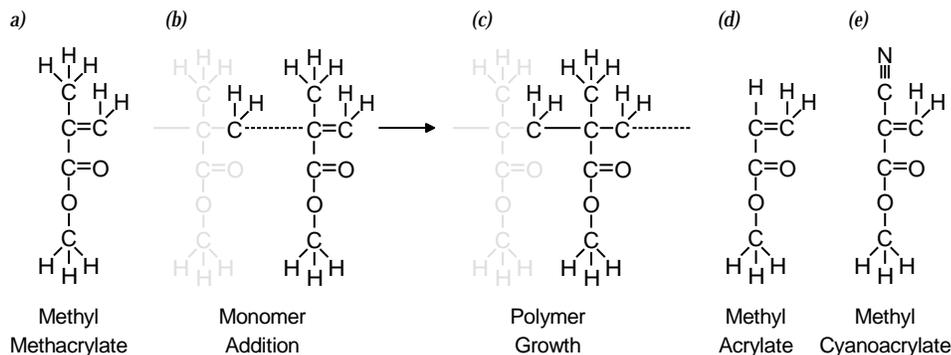


Fig. 16.3.15 - (a) Methyl methacrylate polymerizes in the presence of free radicals. (b) The free radical attacks the double bond between two carbon atoms and attaches itself to one of those carbon atoms. (c) The other carbon atom then becomes a free radical itself and begins searching for yet another monomer to attack. This process continues until a long chain is constructed. Alternative monomers include (d) methyl acrylate and (e) methyl cyanoacrylate.