CHAPTER 5: STRUCTURE OF POLYMERS

"The time has come," the Walrus said,
"To talk of many things:
Of shoes--and ships--and sealing-wax--
Of cabbages--and kings--"
Lewis Carroll, *Through the Looking Glass* (1872)

shoes, ship, sealing wax, cabbage, and a king

The "many things" listed by the Walrus are actually very similar in chemical composition and structure. If we consider only wooden ships, then all of the things on the list are composed of large carbon frameworks called **polymers**. Since 1872 chemists have identified the common polymers produced by plants and animals, primarily **proteins** (collagen, keratin) and **carbohydrates** (cellulose, starch). Chemists have also learned to synthesize new polymers from simple chemicals, creating a vast array of plastics and synthetic fibers.

5.1 PROPERTIES OF POLYMERS

In Chapter 1 it was shown that metals, polymers and ceramics have contrasting physical and chemical properties. Cotton t-shirts and plastic spoons do not have much in common with bicycle frames or coffee mugs. Polymers have low densities; do not reflect or absorb light (they are white or colorless); do not conduct electricity; and are flammable.

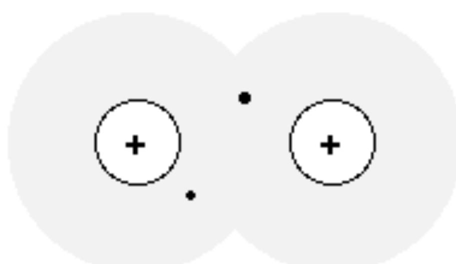
A primary reason that polymer properties are different is because the chemical compositions of metals, polymers and ceramics are totally different. Polymers are composed of non-metallic elements, found at the upper right corner of the periodic table. Carbon is the most common element in polymers. The chemical bonds in polymers are also different than those found in metals and ceramics.

5.2 COVALENT BONDS

Non-metallic elements have a high number of valence electrons (four or more) and prefer to gain electrons, not lose them, in chemical reactions. They often form anions. In a compound of only nonmetals there are no elements willing to become cations, so ionic bonds are not possible. Instead, two nonmetallic atoms can share valence electrons with each other. This type of electron sharing, called covalent bonding, keeps the shared electrons close to both atomic nuclei. One pair of shared electrons makes one **covalent bond**. A **molecule** is a group of atoms held together by covalent bonds.

This type of bonding contrasts with metallic bonding, in which valence electrons are not associated with a particular nucleus, and move easily throughout a sample.

Each hydrogen atom has one proton in its nucleus, and one electron.
The electron moves randomly in a spherical space around the nucleus.



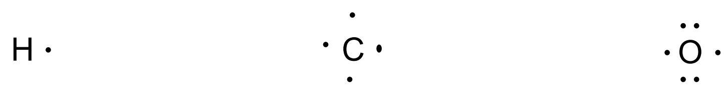
When a covalent bond forms, two hydrogen nuclei move close together.
Although the electrons still move around the molecule, usually they are near both nuclei.

To determine how many covalent bonds can be formed between atoms, first the number of **valence electrons** must be counted. This can be determined by using a periodic table. The group number matches the number of valence electrons.

Example: Carbon is element 6. It is found in Group IV so has four valence electrons.
Oxygen is element 8. It is found in Group VI so has six valence electrons.
The molecule carbon dioxide has the chemical formula CO_2.
4 electrons from C + 2(6) electrons from O = 16 valence electrons

5.3 LEWIS STRUCTURES

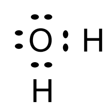
Rather than writing a sentence for the number of valence electrons on an atom, it can be more useful to draw a picture containing this information. A Lewis structure for an atom starts with a chemical symbol, with a dot added for each valence electron.



Since the highest possible number of valence electrons is eight (for noble gases) the dots representing valence electrons are traditionally arranged on four sides of the symbol, with at most two electrons on each side.

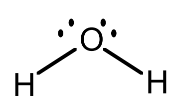
Experiments have shown that most nonmetallic nuclei are satisfied when they are near eight valence electrons. That is known as the **octet rule**. Carbon has four valence electrons, and needs to find four more to share. Oxygen has six valence electrons, so it only needs two more. Hydrogen is an exception to the octet rule; its nearest noble gas, helium, has only two electrons. Hydrogen nuclei form molecules with two nearby electrons, a **duet rule**.

To show a covalent bond, two chemical symbols are put near each other with two dots, representing a pair of electrons, between them. For example, a water molecule has one oxygen atom covalently bound to two hydrogen atoms.

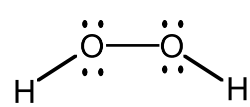
water 

Nuclei do not have to share all of their valence electrons. Note that two pairs of the oxygen's valence electrons are not shared with any other atoms. Those electrons are called **lone pairs** or **nonbonded pairs** and can influence the chemical properties of a molecule.

Because dots can be difficult to see, it is common to draw a line segment for each bond (two electrons). The Lewis structure of a water molecule then looks like

water 

Hydrogen peroxide is a different compond of hydrogen and oxygen, with chemical formula H_2O_2. Since hydrogen atoms only need a duet of electrons they are found at the outside of the molecule; the two oxygen atoms need to be in the center where they can form more bonds. In this textbook that structural information will be given by underlining the central atom(s) in the chemical formula: $H_2\underline{O_2}$.

hydrogen peroxide 

Sometimes nuclei will need to share more than one pair of electrons to achieve an octet with the available valence electrons. One shared pair of electrons is a **single bond**. Two shared pairs (four electrons) makes a **double bond**, and three shared pairs (six electrons) makes a **triple bond**. The more electrons that are shared, the stronger the bond will be. The neighboring elements carbon, nitrogen and oxygen commonly use double and triple bonds. For example, both nitrogen and oxygen are usually found as diatomic gases, N_2 and O_2. The nitrogen molecule has 2x5 = 10 valence electrons, and oxygen molecule has 2x6 = 12. Nitrogen needs a triple bond to achieve octets for each atom, but a double bond is sufficient for the oxygen molecule.

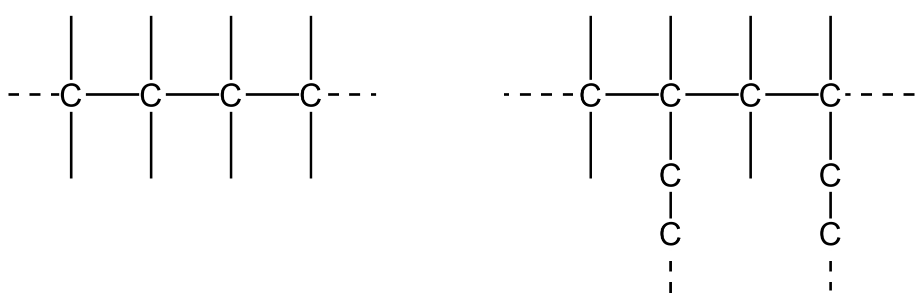
The type of covalent bond affects the shape of a molecule. The nuclei move closer together if they share more electrons. This means that a triple bond is shorter than a double bond, which is shorter than a single bond. The bond angles are also very specific in a covalently bond molecule. The shared electrons want to be near the two positively charged nuclei, but try to stay away from negatively charged lone pairs.

This structure is quite different than that created by metallic bonds, which do not have a particular orientation. Covalent molecules can flex a bit under stress but prefer to "bounce back" to their original positions.

Although a Lewis structure is a good way to show covalent bonds between atoms, it is not as effective at showing a molecule's three dimensional shape. Chemists use model kits and chemical graphics programs to visualize the positions of atoms in molecules.

5.4 FUNCTIONAL GROUPS IN POLYMERS

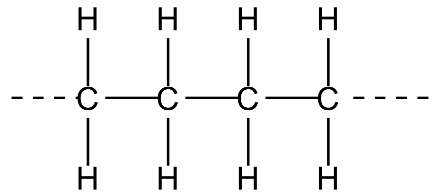
Carbon is the most important element in polymers. Because it starts with only four valence electrons, and wants to share four more, carbon forms a wide variety of covalent bonds. Most importantly, carbon forms strong bonds with itself. Long, strong chains or nets made of thousands of carbon atoms form the backbone of a polymer.



carbon backbones

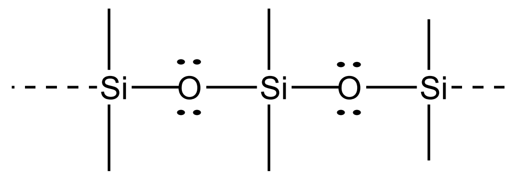
Polyethylene is the simplest polymer. In addition to the carbon backbone, only hydrogen atoms are used to achieve four covalent bonds per carbon atom.

polyethylene



Although silicon is in the same group as carbon, it does not form strong bonds with itself. **Silicones**, long chains of alternating silicon and oxygen atoms, can be synthesized.

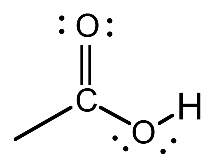
silicone



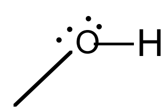
Many different nonmetal atoms could be covalently attached to a polymer backbone. Groups of atoms that contribute something besides C-C and C-H bonds are called **functional groups**. They affect the chemical and physical properties of a polymer.

Examples of Functional Groups

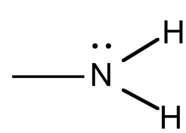
acid group (-COOH)



alcohol group (-OH)



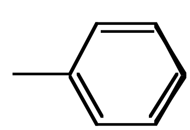
amino group (-NH_2)



chloride (-Cl)

fluoride (-F)

styrene (-C_6H_6)



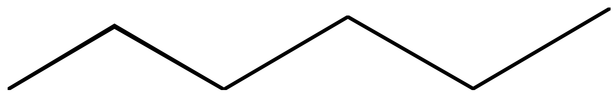
The primary experimental method used to identify functional groups in polymers is Infrared Spectroscopy (IR). This technique is described in Chapter 14.

SKELETON STRUCTURES

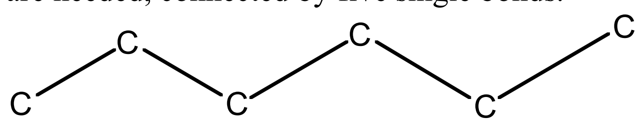
Simplified or "skeleton" structures can be used to emphasize the functional groups. Carbon-carbon bonds of the framework are represented by line segments. Each vertex is the location of a carbon atom. Most hydrogen atoms and all lone pairs are omitted. This type of diagram deemphasizes the hydrocarbon skeleton; since it is so strongly bonded as to be unreactive, it does not affect the chemical properties of the polymer.

Polyethylene is the simplest polymer. Since it has no functional groups, the skeleton structure of a polyethylene fragment looks like it does not have any atoms! (Remember that a real polyethylene molecule is more often 100 or 1000 atoms long.)

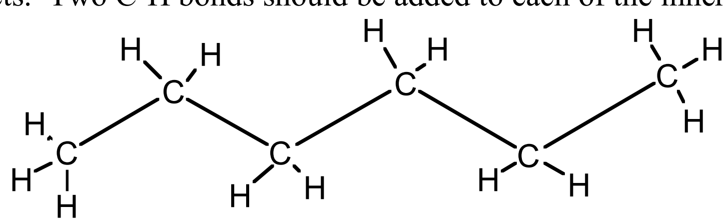
polyethylene



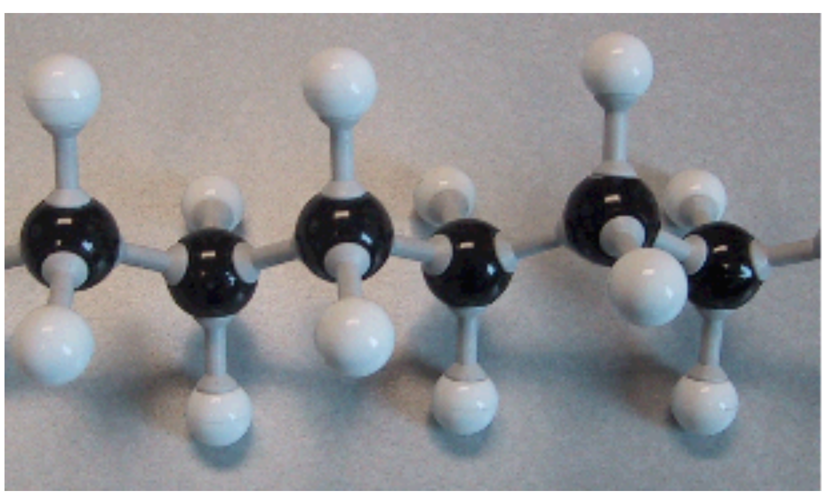
It is possible to figure out the missing information. There should be a carbon atom at the end of each line segment; six are needed, connected by five single bonds.



Since each carbon atom must have four bonds in a molecule, there must be missing bonds to hydrogen atoms. For the carbon atoms on the ends of the molecule, adding three C-H bonds to each will achieve octets. Two C-H bonds should be added to each of the inner carbons.



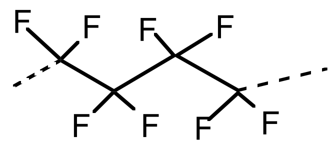
complete Lewis structure for polyethylene fragment



three dimensional model of polyethylene

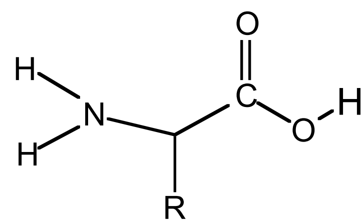
When functional groups are added to a simplified backbone it is easy to notice the change in structure. Polyfluoroethylene, often sold as Teflon, is similar in structure to polyethylene except that all the hydrogen is replaced with fluorine. It is a very slippery polymer.

polyfluoroethylene

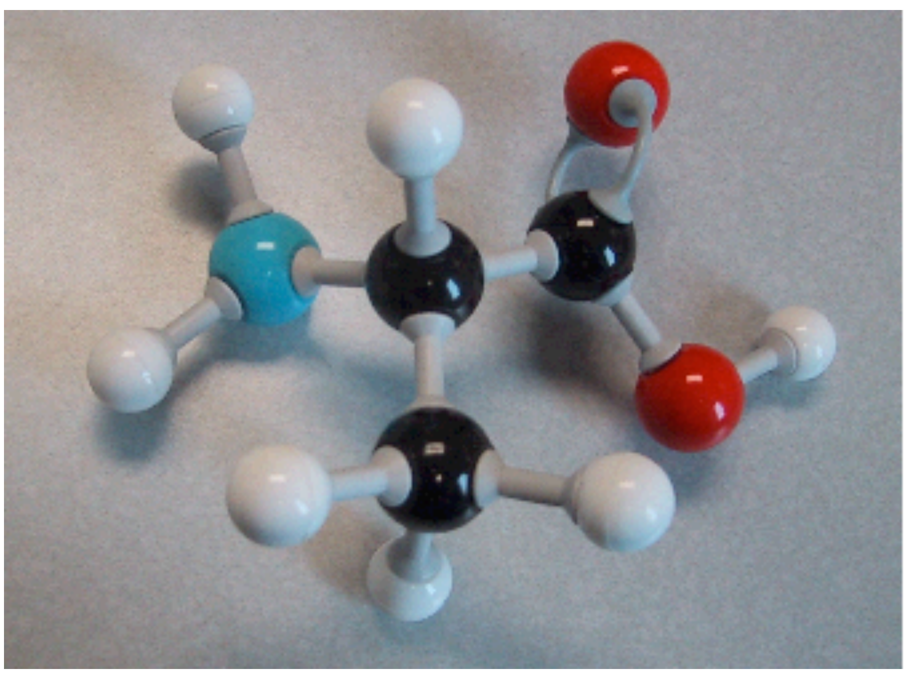


Amino acids, the monomers that build **proteins**, contain amino groups and acid groups, separated by one carbon. In the model nitrogen atoms are blue and oxygen atoms are red. The carbon between the amino group and the acid group always has one hydrogen on it (pointing up in the model) but the fourth group is variable. The symbol R is used when the exact identity of the group is not important. More than twenty different groups, as simple as a single hydrogen atom, are found on amino acids in nature.

amino acid



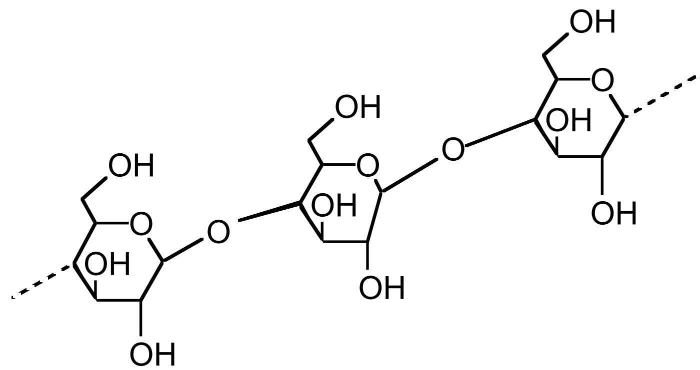
The photo shows a model of alanine, which has a $-CH_3$ group.



three dimensional model of amino acid alanine

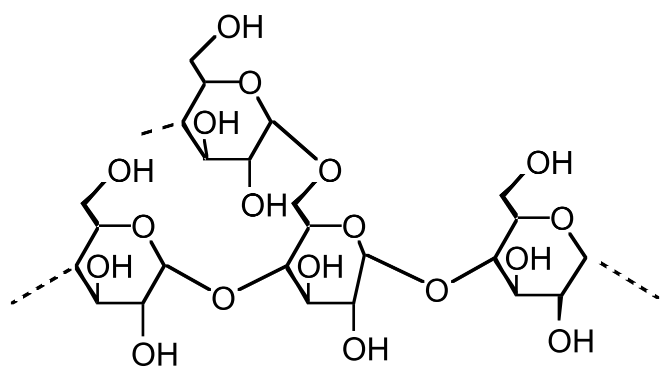
Polysaccharides are sugar polymers. **Cellulose** (found in wood, cabbages, cotton, and linen) is composed of long chains of sugar rings. They are covered with alcohol groups.

cellulose



Starch contains the same functional groups, but the sugar rings are connected at different angles. The structural change makes it possible for the human digestive system to digest the polymer into sugar. Starch polymers are often branched.

starch



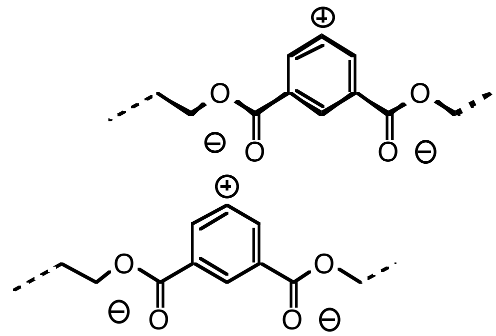
5.5 INTERMOLECULAR FORCES

A molecule is a group of atoms connected by covalent bonds. Chemical reactions are required to form or break covalent bonds. Weaker attractions often form between molecules, encouraging them to stick together in groups. The weaker attractions are called **secondary bonds** or **intermolecular forces**. These can be overcome by adding heat or dissolving in a liquid. The functional groups on a polymer determine the type(s) and strength of its secondary bonds.

POLAR INTERACTIONS

The valence electrons moving around a molecule may not be symmetrically distributed. The nonmetallic elements closest to the right top corner of the periodic table - nitrogen, oxygen, fluorine and chlorine - tend to shift shared electrons away from carbon and hydrogen. When there is a functional group with one of those elements, it has a slight negative charge and the rest of the molecule (carbon and hydrogen) is slightly positive. The molecule is polarized (or **polar**, for short). Its positive sections are attracted to negative sections of neighboring polymers.

poly(ethylene terephthalate)
"PET"



Poly(ethylene terephthalate) or PET, a polymer used to make bottles for carbonated beverages, has oxygen-containing functional groups that make it polar. Protein and cellulose chains are also polar.

Polyfluoroethylene is **nonpolar** (not polar) because it is completely covered with fluorine atoms; there is no exposed positive section to interact with a neighboring molecule's negative section.

Positive and negative charges can be localized on a covalent molecule since they have no path for conduction of electrons. The carbon atoms in the backbone always follow the octet rule with four covalent bonds, so can't pass extra electrons along the chain. If polymer fibers are rubbed together they can build up a static electricity charge.

HYDROGEN BONDS

Molecules with either -N-H or -O-H groups will form strong secondary bonds. This phenomenon is responsible for the relatively high boiling point of water, and for the fact that its solid form (ice) is less dense than its liquid form. Polymers with hydrogen-bonding groups will soak up water.

Fabric softeners are added to laundry to change the properties of cotton and linen fabrics. The fabric softener molecules have one end that binds to OH groups on cellulose. The other end of the fabric softener is a long, nonpolar chain. This exposed end feels smooth and slippery. Softened fabrics are less able to build up a static charge. However softened fabrics will not absorb as much water. This is an issue for the performance of cotton towels.

NONPOLAR INTERACTIONS

As valence electrons move around the nuclei in a nonpolar polymer, like polyethylene or polyfluoroethylene, they can become temporarily imbalanced. For a brief moment of time one part of a molecule would be negative, another part positive; it is temporarily polar. These occasional imbalances are enough to allow nonpolar molecules to attract each other, but the interaction is much weaker than that observed for polar or hydrogen bonding polymers.

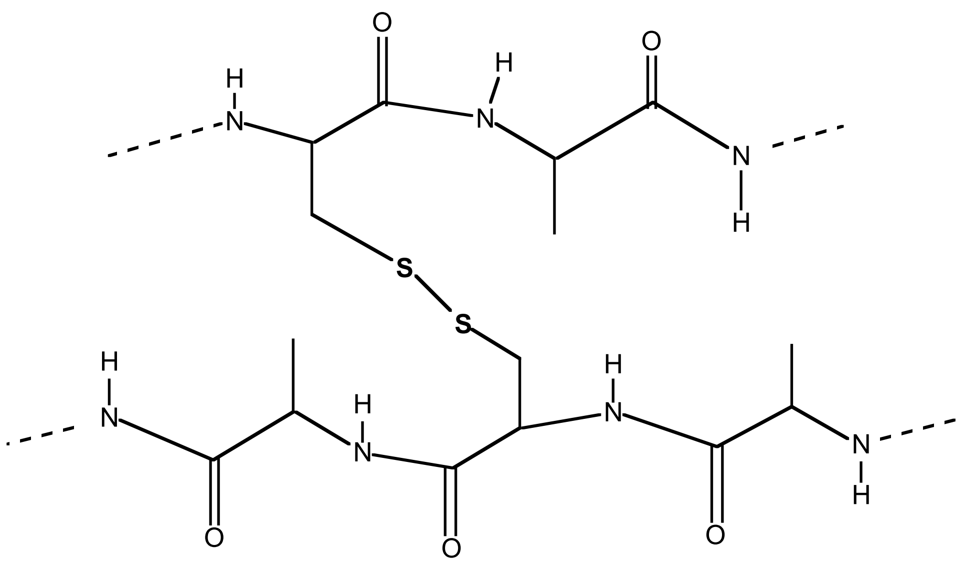
5.6 POLYMER CLASSES

The most common carbon polymers can be divided into four classes based on the structures of their carbon backbones, and the resulting physical properties.

FIBERS

Fibers are thread formers, often used to make cloth. Silk, nylon, polyester, and cotton are all fibers. They are usually flexible, and can be tightly woven without breaking. At the molecular level they are composed of long carbon chains with few or no branches.

In a fiber strand, multiple polymer molecules line up in parallel. Their intermolecular forces encourage an ordered, rather crystalline, arrangement. If you pull on both ends of a strand, it will not stretch very much since the chains are already aligned. Wool is an exception to this; sulfur atoms in adjacent chains find each other and form **sulfur bonds**, **crosslinking** the chains. This gives wool its crinkly texture.



Sulfur bonds crosslink chains of amino acids

THERMOPLASTICS

The name **thermoplastic** is given to polymeric materials that are flexible at high temperatures. Usually they are simply referred to as **plastics**. For example, a polyethylene milk jug can be dented without much force. Polymers such as polyethylene can form either fibers or thermoplastics, depending on how they are processed. A thermoplastic sample has chains going in random directions, held together by weak secondary bonds. A small amount of force can make the chains slide around, thus changing the shape of the sample.

If a plastic is cooled it will become stiffer, and eventually brittle. The temperature at which a plastic becomes brittle is its **glass transition temperature**. At low temperatures the polymer chains will not slide past each other because they do not have enough energy to overcome the secondary bonds.

Small molecules called **plasticizers** are often mixed into thermoplastics. They reduce the number of secondary bonds that can form between long polymer chains, making it easier to modify the shape. The glass transition temperature for a sample with plasticizer is lower. Plasticizers may evaporate over time (a process that is faster at high temperatures), increasing a sample's brittleness.

Samples of polymer classes, clockwise from top left:
skeins of wool (fiber), polyethylene jug (thermoplastic),
rubber bands (elastomer), polycarbonate lenses (thermoset).

ELASTOMERS

Stretchy polymers like rubber and spandex are **elastomers**. They demonstrate the property of **elastic deformation**: when force is applied the fiber stretches, but when the force is removed the fiber returns to its original shape and size. The molecular structure includes chains that prefer being tangled. If they are stretched and straightened, a restoring force pulls them back into the shorter, tangled position. Some chains in elastomers may be crosslinked. Rubber can be **vulcanized** by heating with sulfur, to create new sulfur crosslinks. This changes flowing latex into a stiffer material, suitable for automobile tires.

THERMOSETS

With certain polymers, heat can cause crosslinks to form irreversibly. The sample hardens so its shape is "set." Epoxy resins and some polycarbonates belong in this category. Unlike thermoplastics, thermoset samples will not soften upon heating.

Learning Goals for Chapter 5

After studying this chapter you should be able to:

composition & structure

- Understand the types of bonds found in polymers.
- Draw Lewis structures of simple molecules.
- Recognize functional groups found in natural and synthetic polymers.
- Use structures to sort polymers into classes.

properties

- Know properties of polymer classes.
- Explain how properties relate to polymer structure.
- Predict type of secondary bonding for each functional group.
- Describe effects of crosslinking on polymer properties.
- Describe effects of plasticizers on polymer properties.

performance

- Know applications of common polymers.

Compare *composition, structure, properties* and *performance* of polymers and metals.

Vocabulary list

amino acid	carbohydrate	cellulose
covalent bond	crosslinking	crystallinity
density	double bond	duet rule
elastic deformation	elastomer	fiber
functional group	glass transition temperature	hydrogen bond
intermolecular force	lone pair	molecule
monomer	nonbonded pair	nonpolar
octet rule	plasticizer	polar
polymer	polysaccharide	primary bond
protein	secondary bond	single bond
starch	sugar	sulfur bond
thermoplastic	thermoset	triple bond
valence electron	vulcanization	