

CHAPTER 13. DECODING MACROMOLECULE STRUCTURES: POLYMERS

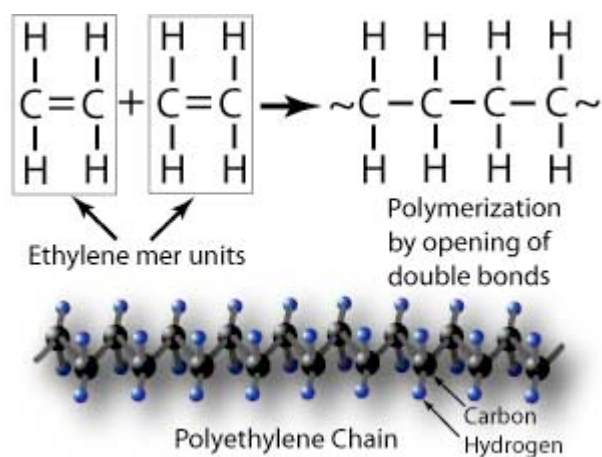
What Is a Polymer?

The large molecules, or macromolecules, called **polymers** provide much of the physical structure of our world. The cellulose molecules which form the leaves and stems of plants are polymers, as are the protein molecules which make up animal tissues. Chemists have learned to mimic the macromolecules that form the natural fibers of silk, cotton, and wool to make synthetic polymers like rayon, nylon, polyethylene, and polypropylene. These synthetic polymers have become a familiar part of our surroundings in myriad ways: clothing, carpeting, building materials, and consumer products are only a few of the everyday uses for the many polymeric materials produced today.

At first look, a polymer molecule can look dauntingly large and complex. One polymer molecule can have thousands of atoms, and the polymer molecules in a material can vary in size. How can we hope to know the structures of these giant molecules? The key to understanding the structures of polymers lies in the fact that they are long chains made of smaller units which repeat throughout the molecule. Understanding this principle, we can gain insight into the structures of these molecules whether they are found in the tissues of our own bodies or in the petroleum-based synthetic polymers which we encounter every day.

Polyethylene from Ethylene

A good starting point for learning about polymer structures is **polyethylene**, the most popular of the synthetic polymers. In the 1967 film "The Graduate" Dustin Hoffman as a new college graduate was taken aside by his uncle to be told "I have one word to say to you. Just one word: plastics." From plastic sandwich bags to plastic milk cartons to plastic toys, many of the everyday objects we encounter under the name "plastic" are made of polyethylene. Polyethylene is an example of an **addition polymer**. When the molecule ethylene, C_2H_4 , is heated under pressure in the presence of oxygen, the double bond between the two carbon atoms is partially broken, and ethylene molecules link up to one another, forming a long chain.



This process is called **polymerization**. The small molecule, like ethylene, that reacts to form the units of the polymer chain is called a **monomer**.

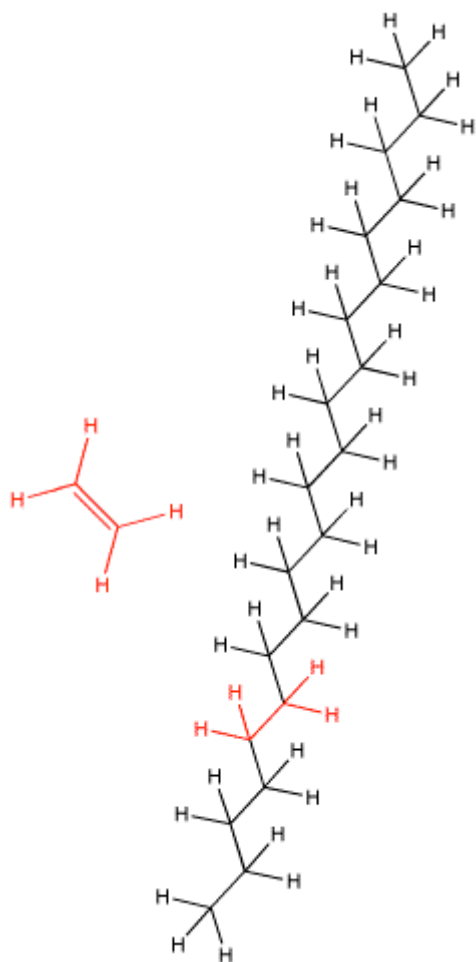
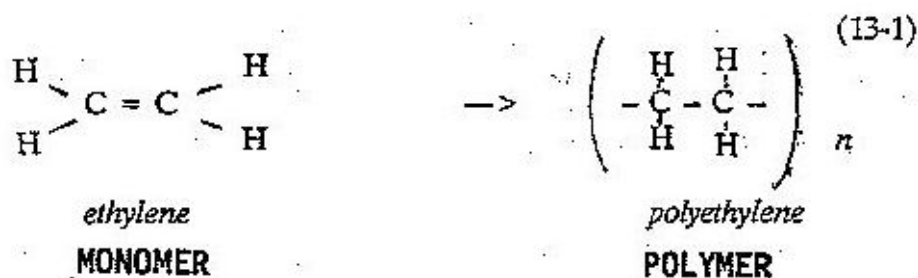


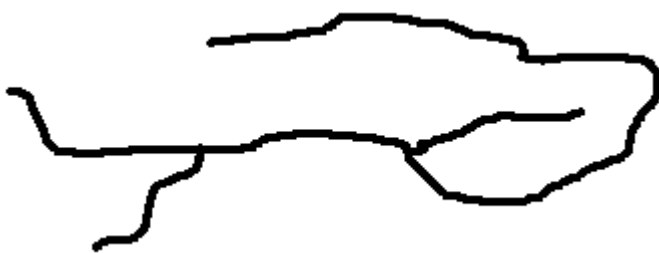
Fig. 13-1. Many molecules of ethylene C_2H_4 monomer link up to form polyethylene, a polymer.

The polyethylene polymer chain can take various forms depending on the polymerization reaction conditions. In the presence of chromium oxide, a "straight" or linear chain is formed as shown in Fig. 13-1. As the molecular model shows, because of the tetrahedral bonds to each carbon, the resulting shape of the "straight" chain actually looks more like a zig-zag in the actual molecule.

In order to save space, we can write this polymer formation equation with n being the number of ethylene units in the polymer:



The number of ethylene units n in linear polyethylene can vary between about 500 to about 10,000, and these very long, flexible units can be envisioned as looking very much like cooked spaghetti. These linear, spaghetti-like molecules can pack closely together, forming the plastic material known as **high-density polyethylene, or HDPE**. This material owes its high density and rigidity to the close packing of its molecules. Plastic milk bottles and motor oil containers are among the containers made of this material.



The HDPE chains can pack closely together, maximizing attractive forces and forming a material that is more tightly bonded together and hence stronger.

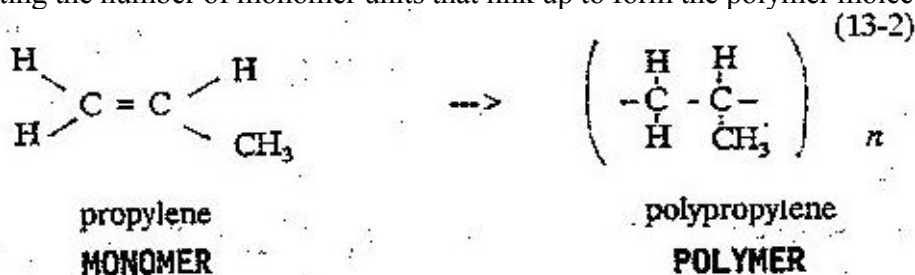
LDPE, or low-density polyethylene, is formed when reaction conditions for the polymerization of ethylene are such that the molecules link up to form branched chains instead of straight ones. Branching patterns of LPDE are random, forming macromolecules that are irregular in shape. As a consequence, the molecules cannot pack together as efficiently as the linear molecules of HDPE. The material is less dense than HDPE because the inefficient packing leads to empty spaces in the material's structure. LDPE is also less rigid than HDPE; because it is so flexible, it finds its main use in plastic films like those used for sandwich bags.



The random branching on the LDPE molecule prevents the polymer molecules from packing together tightly, resulting in weaker attractive forces and a more flexible molecule with less strength.

Polypropylene from Propylene

A whole family of addition polymers, each with its own characteristic properties, is made, like polyethylene, from monomers with carbon-carbon double bonds which link up to form long-chain molecules. Each monomer, listed in Table 13-1, can be considered to be a **derivative** of ethylene, or an ethylene molecule which has another group or groups attached to it. Looking in Table 13-1 at propylene, for example, we see that it looks like an ethylene molecule with a methyl group, $-\text{CH}_3$, attached. Like ethylene, propylene can be made to polymerize; the name of the polymer formed is polypropylene. This reaction can be expressed in a chemical equation like (13-1), with n representing the number of monomer units that link up to form the polymer molecule.



Polypropylene is a strong material which is well-suited not only for making molded objects like the casings for automobile batteries, but also for fibers that go into products like indoor-outdoor carpeting. Synthetic fibers like polypropylene are made by forcing the polymer “soup” through tiny holes in a device called a **spinneret**, forming a fine, thread-like **filament** in which the polymer molecules are all aligned in the same direction. Two or more filaments can then be twisted together to make a thread which can be woven into a fabric, or, sometimes, used to reinforce the strength of a molded plastic.

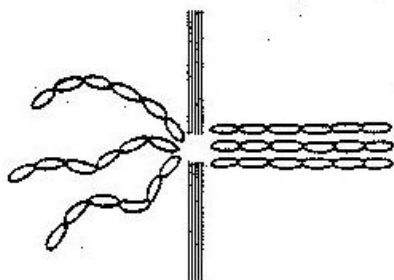


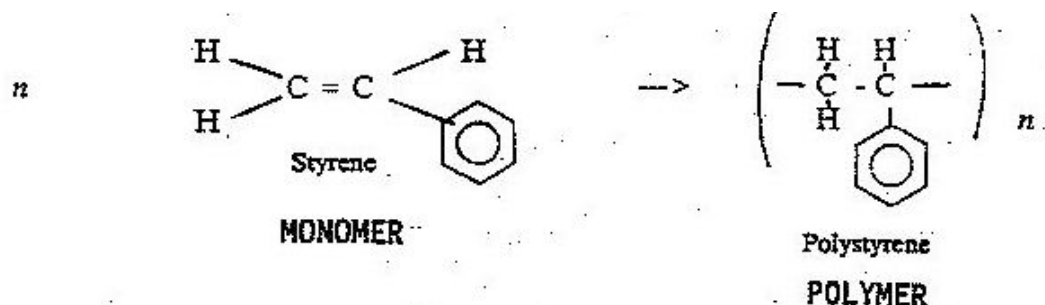
Fig. 13-3 A spinneret, designed after a spider's web-spinning apparatus, produces fine filaments when the polymer is forced through small holes. From Saferstein's Criminalistics (Prentice-Hall, 4th ed., 1990).

Table 13-1. Ethylene Derivatives and Their Addition Polymers

MONOMER Formula	Monomer Common Name	Polymer Name (Trade Names)	Uses
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	Ethylene	Polyethylene (Polythene)	Squeeze bottles, bags, films, toys and mold objects, electrical ins tion
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{CH}_3 \end{array}$	Propylene	Polypropylene (Vectra, Herculon)	Bottles, films, indoor- outdoor carpets
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{C}_6\text{H}_5 \end{array}$	Styrene	Polystyrene (Styrene, Styrofoam, Styron)	Food and drink cooler building material in tion
$\begin{array}{c} \text{F} & & \text{F} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{F} & & \text{F} \end{array}$	Tetrafluoroethylene	<i>Polytetrafluoroethylene</i> (Teflon)	Gaskets, insulation, b ings, pan coatings
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{Cl} \end{array}$	Vinyl chloride	Polyvinyl chloride (PVC)	Floor tile, raincoats, p phonograph records
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{CN} \end{array}$	Acrylonitrile	Polyacrylonitrile (Orlon, Acrilan)	Rugs, fabrics

Polystyrene from Styrene

The compound formed when a benzene ring is attached to an ethylene molecule is called **styrene**, and the polymer it forms is called **polystyrene** (Table 13-1).

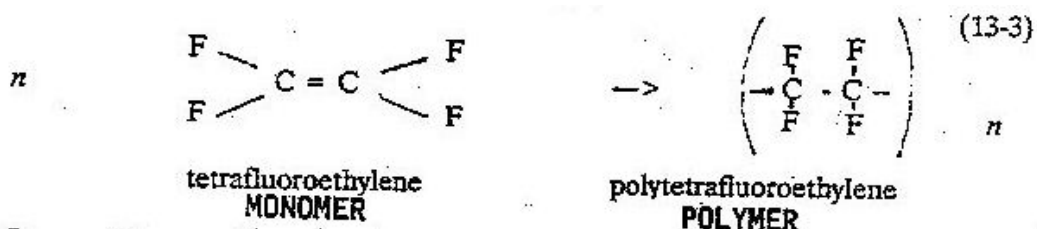


Polystyrene is used for a variety of uses, from furniture, appliance components, and toys to insulating material; in its pure form it is a clear, hard, colorless solid. When gas bubbles are trapped into the styrene molecules in the production process, the white, spongy material called **styrofoam** is formed. Styrofoam has good insulating properties and is used for disposable coffee cups and fast food containers meant to keep foods hot, as well as in coolers and insulating panels for the home. Its light weight and spongy texture have made it popular as a packing material. Styrofoam, especially when used as fast-food packaging, has been a source of controversy, not only because of its high-volume contribution to the waste stream when styrofoam objects are disposed of, but because the gas bubbles used to expand the plastic have frequently been the CFC's, or chlorofluorocarbons which are implicated in the destruction of the protective ozone layer of the atmosphere (Ch. 16). Largely as a result of consumer pressure, the use of CFC's to manufacture polystyrene has decreased; in 1989 the Food Service and Packaging Institute announced that more than 99% of all foam food service products were being manufactured without the use of CFC's.

Fig. 13-4. Photo showing a clear styrene drinking cup and a polystyrene cup. Caption: *Trapped gas bubbles make the physical properties of polystyrene different from those of pure styrene.*

The Teflon Story

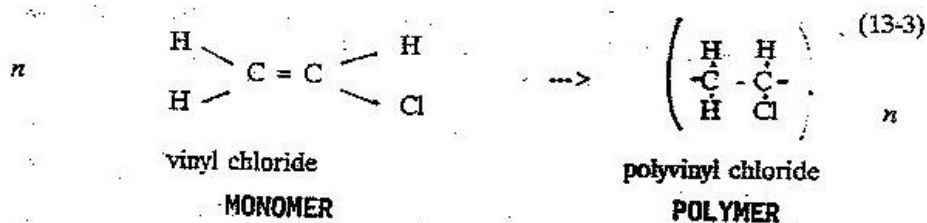
One of the addition polymers based on the ethylene molecule was an unplanned discovery. In the DuPont chemical laboratories in 1938 a chemist was preparing to use some tetrafluoroethylene gas. On opening the valve of the pressurized metal cylinder which contained the gas, he found that no gas would come out, even though the weight of the cylinder showed that tetrafluoroethylene gas should still be inside. Out of curiosity, he sawed open the cylinder and found that it contained a white solid material. This material was highly unreactive and heat-resistant, surviving temperatures up to 300° C. It was found to be a polymer of tetrafluoroethylene, named polytetrafluoroethylene, or Teflon in its abbreviated trade name. The chemical equation for its formation is similar to those for the formation of other ethylene-based addition polymers:



Its special unreactive properties have made Teflon useful in a number of applications. It is familiar as a nonstick coating on frying pans, but is also used to make corrosion-resistant tubing, Gore-Tex athletic wear, and even in surgical use for artificial veins and arteries.

The PVC Story

When vinyl chloride, an ethylene molecule with a chlorine atom attached, polymerizes, it forms an addition polymer called polyvinyl chloride, or PVC:

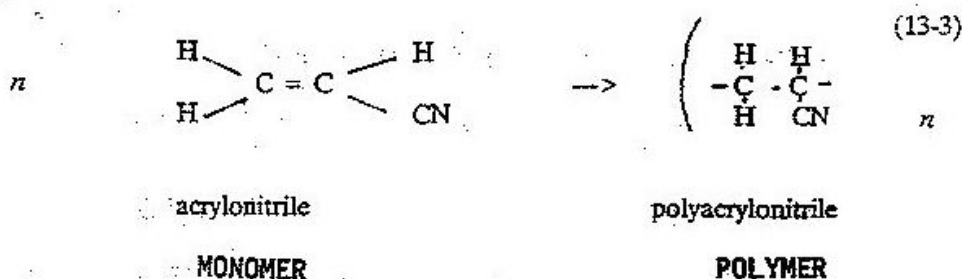


PVC plastic is tough and resilient, useful for materials like floor tile, plastic pipe for plumbing, pool liners, and trash bags. Over nine billion pounds of PVC were made in the U.S. in 1990. In the

1970's, however, PVC production plants made tragic history. Chemical plant workers who had been exposed to high levels of vinyl chloride, as great as 500 parts per million in the air, over periods of from 14 to 27 years, developed a rare form of liver cancer called angiosarcoma. The link between chemical exposure and cancer found in these workers caused a major retooling of PVC production plants to minimize worker exposure to hazardous vapors. In addition, this landmark case in occupational health was responsible for a heightened awareness of the risks of worker exposure to industrial chemicals.

Polyacrylonitrile: a Polymer with a Problem

Acrylonitrile is a monomer consisting of an ethylene molecule with a -CN group attached. This group is called the cyano, or nitrile, group. The polymer produced from acrylonitrile is called polyacrylonitrile.

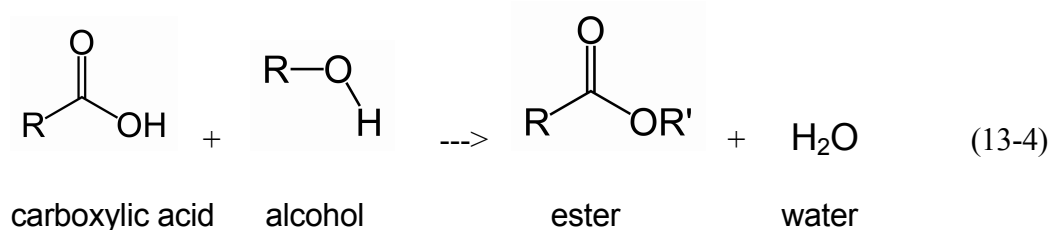


Polyacrylonitrile is a popular fiber material for both clothing and carpeting, best known under trade names like Orlon and Acrilan; it can be made into a variety of fiber types which take dyes well and are soft to the touch. Acrylic polymers are also used extensively in paints. When heated, acrylic enamels form an extensively cross-linked network that is both hard and solvent-resistant. Acrylic enamels adhere well to surfaces and are effective in controlling corrosion. They are used extensively as automobile topcoat finishes.

When polyacrylonitrile is burned, the cyano group can form the extremely deadly gas hydrogen cyanide. The possible presence of hydrogen cyanide gas released in the air has been one reason for objections to solid waste facilities which burn waste. Polyacrylonitrile fibers should not be used in carpeting or upholstery in airlines, office buildings, or other enclosed public spaces because of the toxic gas that might be released in case of fire.

Polyester: a Condensation Polymer

In Chapter 12 we learned that when a carboxylic acid group reacts with an alcohol group, an ester group is formed which links together the two reacting molecules, and a molecule of water is formed as well. If R and R' are used to represent the rest of the two reacting molecules, we can focus in on the reacting groups and write the equation for this type of reaction as



Reactions like this in which a molecule of water is "split out" of the reacting molecules are called **condensation reactions**. Condensation reactions can be used to link together molecules and form polymers. The resulting polymers are called **condensation polymers**. When condensation reactions which produce ester linkages are used to form a polymer, the resulting polymers are called **polyesters**.

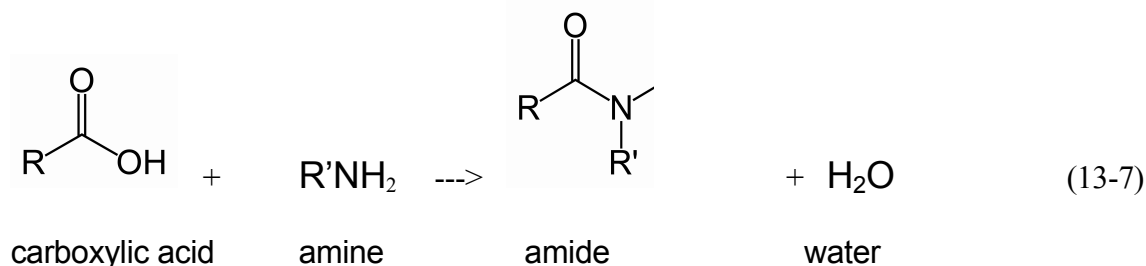
The first polymer formed with ester linkages was made by Carothers in the 1930's by reacting ethylene glycol, HOCH₂CH₂OH, with adipic acid, HOOCCH₂CH₂CH₂CH₂COOH. (13-5)

The polyester that resulted from this reaction produced a strong fiber, but its melting point was so low that it could be melted when pressed with a hot iron. In the early 1940's Whinfield and Dickson tried making a polyester by replacing the adipic acid with the aromatic dicarboxylic acid, terephthalic acid.

(13-6)

Nylon, the Polyamide Condensation Polymer

Another type of condensation polymer of major industrial importance is **nylon**. The linkages holding together the nylon polymers are **amide** groups, which we learned in Chapter 12 are formed by the condensation reaction of a carboxylic acid with an amine:



The discovery of nylon was the result of the research of Wallace H. Carothers (1896-1937), a DuPont chemist whom we have already mentioned in connection with the development of Orlon.

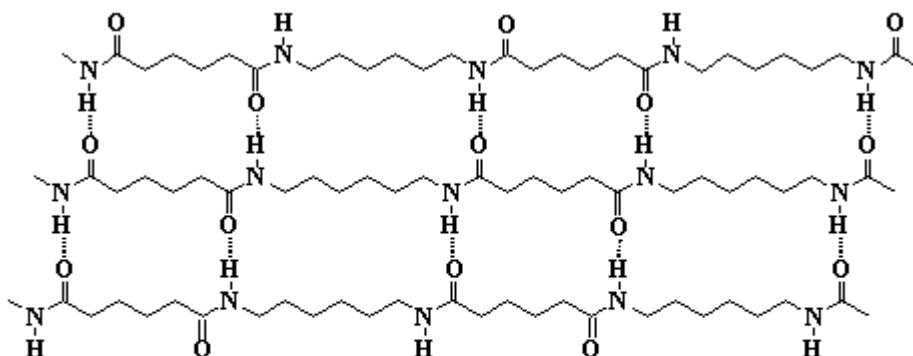
The first nylon product to be marketed was nylon stockings for women, a DuPont product first marketed in 1939. The stockings were instantly popular as a replacement for silk hosiery. When the U.S. entered World War II, nylon stockings became a scarce and precious commodity as the production of nylon parachutes, rope, and other military equipment replaced civilian goods production.

Nylon filaments are made by forcing the molten polymers through spinnerets. The cooled filaments are then drawn by winding them on pulleys at high speeds, producing a silkier, stronger material. The discovery of cold-drawing fibers, made in Carothers' laboratory, was one of the happy accidents of the early days of polymer chemistry. Julian Hill, working with a polyester material, noticed that if he gathered a small ball of the polymer at the end of a stirring rod and pulled it out of the rather messy mass in the reaction vessel, the resulting stringy material was silky in appearance. The story is told that one day while Carothers was out of the laboratory, Hill and his fellow workers tried to see how far they could stretch the polyester material by holding onto a piece by one end and running down the hall with it. The strong, silky string produced by this rather lighthearted experiment led the scientists to the realization that drawing out the fiber had aligned the polymer molecules, increasing the strength of the material. The polyesters being produced in Carothers' laboratory at that time, however, were too low-melting to be useful as fibers. Applying the cold-drawing technique they had observed with polyester to the amide polymer they had made from adipic acid and hexamethylenediamine led the experimenters in Carothers' laboratory to the first commercial synthetic fiber, nylon-6,6.

Why is the cold-drawn nylon fiber so strong and relatively high-melting? The concepts of intermolecular forces we have already learned in studying smaller molecules (Chapter 5) explain the

properties of macromolecules as well. If properly aligned, the amide groups in the nylon chains are able to hydrogen bond to amide groups on other chains (Fig. 13-5), and the strong intermolecular force of **hydrogen bonding** thus holds the chains together, resulting in a strong, high-melting material.

Fig. 13.5



In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

Kevlar, the Bullet-Proof Polyamide

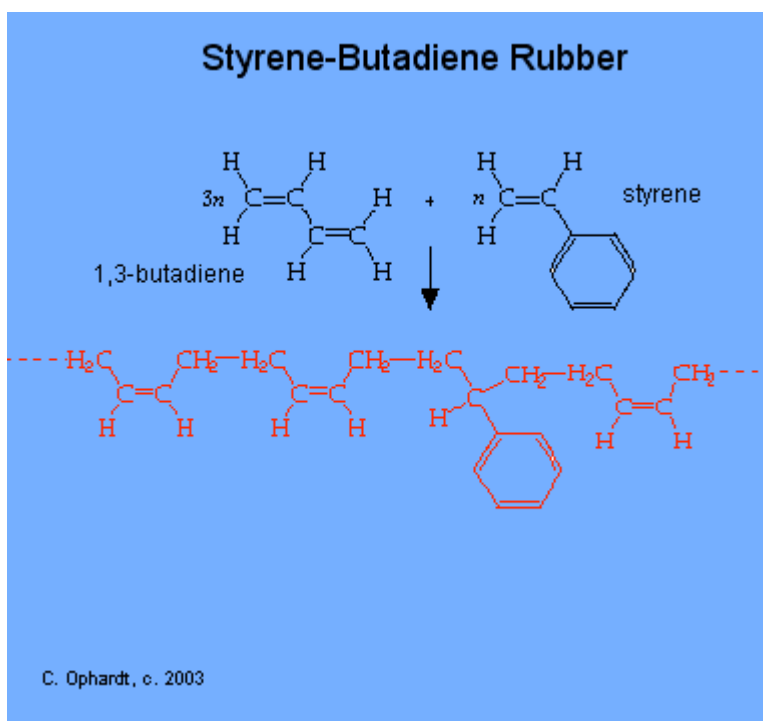
Another polymer using amide linkages is **Kevlar**, made from p-phenylenediamine and terephthalic acid. If you are interested in the Kevlar structure, check out <http://pslc.ws/macrog/aramid.htm> Fibers made from Kevlar are stronger, ounce for ounce, than steel cord. Kevlar is used for tire cord, for bulletproof vests, and for other civilian and military uses such as aircraft construction that benefit from its strength and light weight.

Rubber: Elastic Material from Nature and from the Laboratory

Rubber is a material we are all familiar with, from rubber bands to automobile tires. Actually, numerous chemical compounds fall under the category we call "rubber." As with much of the chemistry we learn, there is a rich history behind the development of the everyday material we take for granted. The name was given to the naturally occurring material by Joseph Priestly, the contemporary of Thomas Jefferson and Benjamin Franklin who, when he fled England for persecution for his Unitarian beliefs, became one of the first chemists in America. Observing the material's ability to rub out pencil marks, he gave it the name which it carries today. Though we still

Laboratories, Esso (now Exxon), and Dupont were among the industrial contributors of researchers. The war effort which led to the development of synthetic rubber paralleled the research efforts in other polymers, and during the 1940's the polymer industry grew to be one of America's leading industries. In Germany, a traditional center of organic chemistry research, chemistry laboratories were focused as well on the problem of developing synthetic rubber. The first synthetic rubber produced in the United States was polychloroprene, or neoprene, a polymer of chloroprene. Neoprene rubber is resistant to solvents and is still used today in automotive and conveyor belts, garden hoses, shoe soles, gaskets, and adhesives.

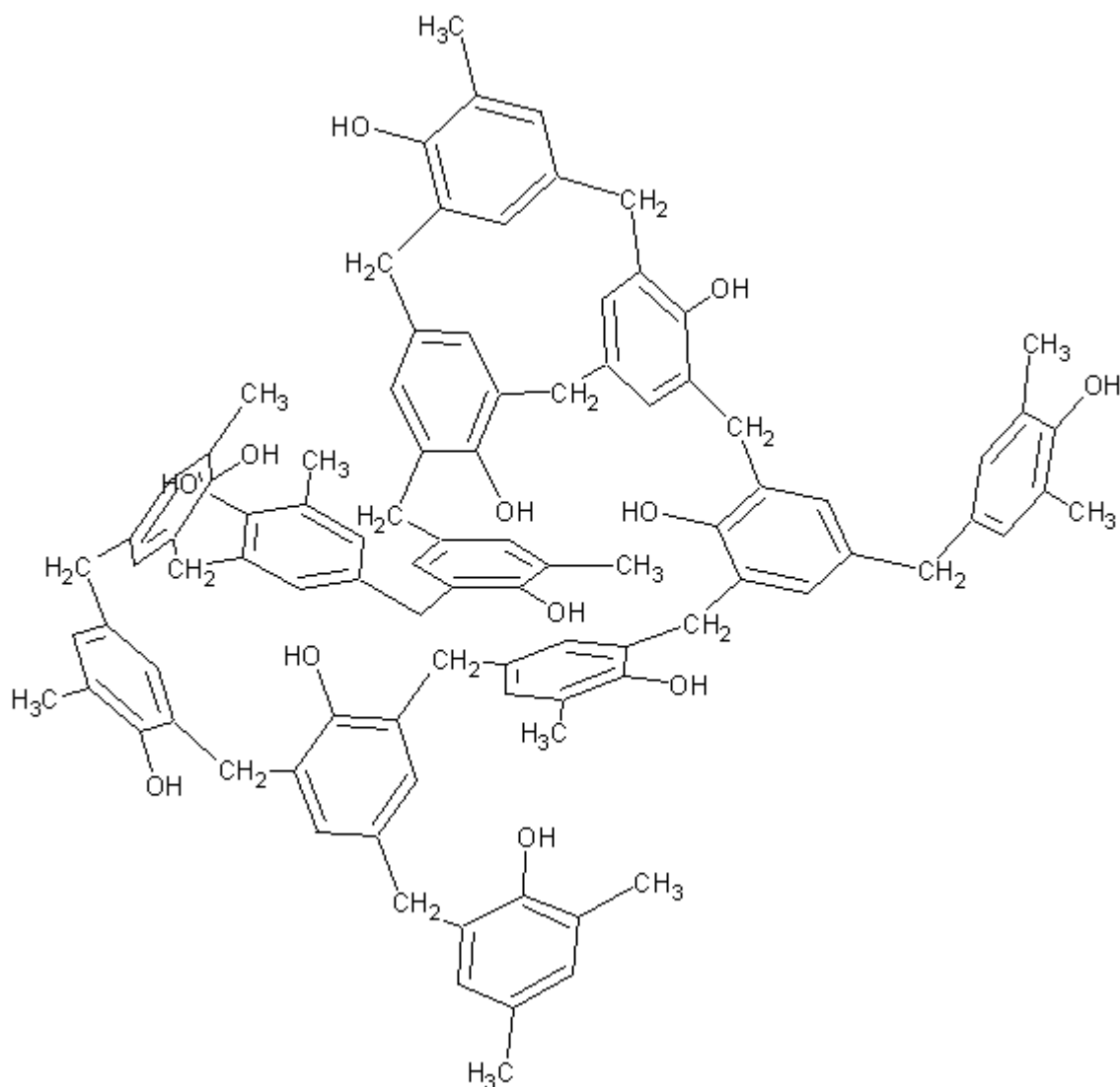
After the war a team of American chemists visited Germany to learn what processes had been developed there for making synthetic rubber. German chemists had been working on a polymerization reaction to make a copolymer of styrene and butadiene. American chemists modified the reaction procedure for this process, resulting in the synthetic rubber which is still the standard rubber for passenger car tires:



(13-12)

Formaldehyde Resins

One of the earliest plastics to be marketed was the condensation polymer formed by phenol and formaldehyde, called Bakelite. This three-dimensional polymer is extensively cross-linked:
(13-13)



Notice the 3-d structure of this polymer compared with the “spaghetti-like” ethylene and rubber. The covalent bonds of the three-dimensional cross-linking in Bakelite make the polymer very strong and hard. It became immediately popular when first developed in 1909 as a material for consumer goods like radio casings and telephones, and is still used in products like radios, buttons, and electric insulators. Bakelite is a thermosetting plastic, which means that heating causes the material to harden permanently, as heating produces the strongly bonded cross linkages. By contrast, polymers like nylon, polyethylene, and polyvinyl chloride soften when heated and become harder when cooled.

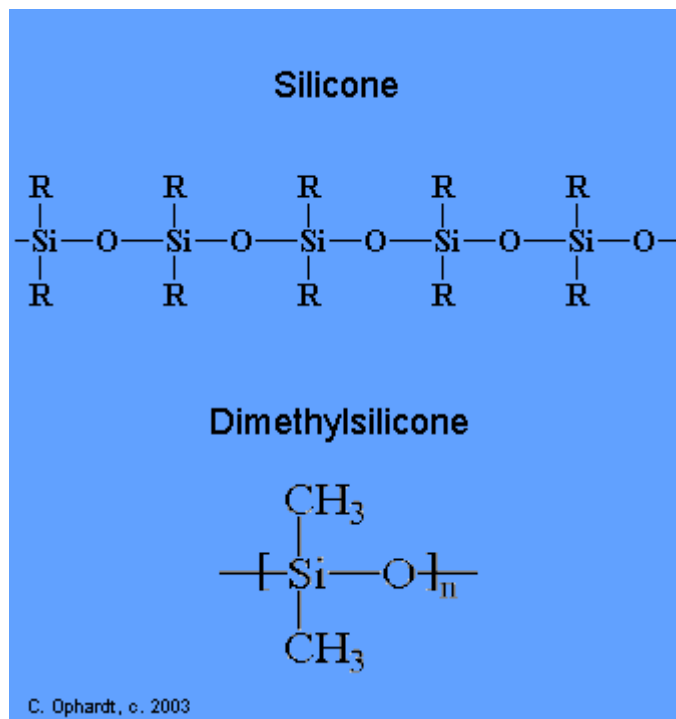
Bakelite was followed by other formaldehyde resins that have become extremely important in our everyday lives. Their thermosetting properties make them valuable as building materials of all kinds. When the cyclic amine melamine undergoes a condensation reaction with formaldehyde, a melamine-formaldehyde resin is formed which is used for Formica brand countertops and Melmac brand dinnerware. Urea forms a condensation polymer with formaldehyde called urea-formaldehyde resin which has seen wide application in the construction industry. Urea-formaldehyde resins are used as adhesives or binding agents in many plywoods, particle boards, and fiberboard. Both melamine-formaldehyde resins and urea-formaldehyde resins are used as adhesives, and both are used as coatings for paper and for permanent-press fabrics. The urea resins, however, see greater use because they are less expensive. In the 1970's urea-formaldehyde foam insulation was used until increasing evidence included that irritating formaldehyde gas was being emitted from the material, especially when new. A typical inexpensive cabinet, even if it appears to be wood-grained, is likely to be sawdust held together with a strong formaldehyde resin glue and covered with a Formica-type covering.

In 1987 the Environmental Protection Agency determined that formaldehyde was a probable cause of cancer in humans, prompting a re-examination of materials that might emit formaldehyde into the air. Garment workers (because of formaldehyde perma-press coatings) and occupants of new mobile homes are among the groups who may be particularly at risk. In addition to the possibility of cancer risk, levels of formaldehyde in the air as low as 0.1 part per million (ppm) can cause eye, nasal, and throat irritation in sensitive individuals. In new buildings or newly renovated buildings with poor ventilation, formaldehyde originating in urea-formaldehyde resins may be partially responsible for a condition called "sick building syndrome" in which sensitive individuals suffer from a variety of complaints. The chemical concept that formaldehyde is a highly reactive molecule that promotes cross-linking in other molecules has long been known. Embalming, for example, depends on the use of formaldehyde to cross-link the proteins in the body. Though studies to determine the relationship between formaldehyde exposure and certain forms of cancer is still in an early stage, limiting exposure to formaldehyde vapors by a combination of appropriate choice of building materials and adequate ventilation is desirable. "Out-gassing" of formaldehyde gas from building materials and fabrics is most likely when they are new, and decreases with time as the gas monomer is released from the heavy molecules of the polymers.

Silicones: Non-Organic Polymers

Because of the unique ability of carbon to form long chains of covalent bonds, most polymers are organic compounds. Silicon, found in Group 4 with carbon, is able to form covalent networks alternating with oxygen; sand is made of such a covalent network. Synthetic polymers using the ability of silicon to form this kind of bonding are called **silicones**:

(13-16)



silicone polymer

Silicones are chemically and thermally stable and find a variety of uses, from "Silly Putty" to industrial and medical uses. Dimethylsilicones, with a linear polymer structure like that shown in reaction (13-16), are oils. Cross-linked silicon polymers are solid, forming silicon rubber. Its heat-resistant properties make it especially useful for use in aircraft and in the space program, and its chemical inertness has made it a choice for plastic surgery implants. The case of silicone gel-filled breast implants remains controversial. Banned because of lawsuits claiming adverse health effects, they were approved by the FDA in 2006 with the caveat that frequent testing be made to test for ruptures of the implant that would release the silicone into the body.

Plastics Recycling

While synthetic polymers form an indispensable part of modern life, the fact that they are made from fossil materials like petroleum and coal means that there is not an unlimited supply of starting material. The same shrinking pool of fossil fuels that we rely on for transportation, heat, and to power our industries is the source of our plastics and synthetic fibers. At the same time, the

mountains of solid waste we produce have led to a scarcity of room in landfills, and made solid waste disposal increasingly difficult and expensive. Plastics recycling, then, makes economic as well as ecological sense. The chemical principles that we have learned about the formation of polymers helps to explain how plastics recycling works.

Recycling works best for the **thermoplastic polymers**, which melt when heated, then assume their original solidity. The melted plastic can be separated from any solid impurities, then molded into the desired shapes. Polyethylenes and polyesters from which bottles are made are examples of thermoplastics polymers. **Thermosetting polymers**, by contrast, harden permanently when they are first heated because of the formation of cross-linked bonds. The formaldehyde polymers from which building materials are made are examples of thermosetting polymers. To facilitate sorting plastics waste materials, manufacturers now add symbols printed or molded on the bottom of containers (Table 13-2). These recycling symbols, a number in a triangle of three bent arrows with a product code, are being made mandatory with the passage of packaging laws in 27 states.

Table 13-2. Plastics Recycling Codes and Their Meaning

<i>Code number</i>	<i>Product code</i>	<i>Plastic type</i>
1	PETE	Polyethelene-terephthate
2	HDPE	High-density polyethylene
3	V	Vinyl or polyvinyl chloride
4	LDPE	Low-density polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	Other	All other plastic resins

The Plastics Industry, Present and Future

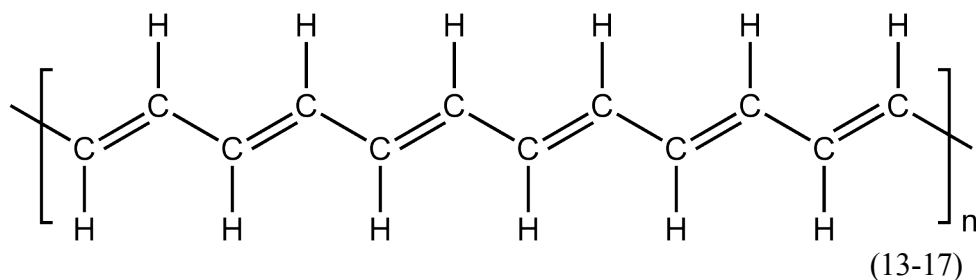
Since its beginnings the plastics industry has continued to grow rapidly, as the many synthetic polymers played a more and more dominant role in our everyday lives. Plastics appear

not only in the more visible forms like packaging and furniture, but in many other uses like building and construction components and adhesives, electrical equipment, and appliance parts. Despite Dow Corning's original bankrupting experience with silicone breast implants, in 2007 medical plastics were a \$1 billion dollar a year market, and growing at 10 to 20 per cent a year. This demand is largely driven by the demand of an aging population for artificial hips and knees, but artery-opening stents and pacemakers are also a growing and critical market.

What kind of future can we predict for the use and production of plastics? The market for thermoplastic-type resins constitutes by far the larger volume, with packaging is the single greatest use for thermoplastics. As recycling becomes more popular, more recycled resins will become available, diminishing at least in part the drain on fossil fuel feedstocks for synthesizing thermoplastics. Demand for many types of plastic materials, for building materials and transportation, for example, will be linked to the rate of growth of the economy.

The history of the plastics industry, however, has historically featured the development of new materials like polyethylene, nylon, and polyester that rapidly found consumer uses and became high-volume products. Current research has produced fascinating new polymeric materials; only time will tell which will become indispensable to us in the future.

Polyacetylene, produced by the addition polymerization of acetylene, has the ability to conduct electricity.



Experimental work varying the conditions under which polyacetylene is made has produced a shiny substance which can be made into films and which has a conductivity similar to metals. The commercial possibilities for electrically conducting plastics are limitless, since plastic batteries would be very light in weight.

Since the scientists in Carothers' laboratory experimented by seeing how far they could pull a polymeric strand down the hall, polymer chemists have known that oriented polymers are stronger than randomly scattered ones. Current research with oriented polymers is aimed at producing plastics stronger than steel and resistant to heat, chemicals, moisture, and corrosion. Kevlar, the "bullet-proof polyamide," owes its strength to an oriented structure. Kevlar is made from units called "rigid rods," which are dissolved or melted and then squeezed into an ordered solution called a liquid crystal. Kevlar is five times as strong as steel, but only in the direction of alignment. For

that reason it is used in the form of a fiber rather than a solid. Another type of polymer called liquid crystals has found consumer use first in digital watches and clocks, and then in computer flat panel displays, as application of an electric field causes collections of the polymer molecules to realign and change the optical properties of the material.

New processes are being developed to make materials called **molecular composites** in which rods of super-rigid polymers are interspersed through a material to make a strong, lightweight product that would be of particular usefulness in the aerospace industry. Molecular composites appear to have the potential be stronger and more useful than traditional composites, in which the strengthening material is glass or carbon fibers.

Producing oriented polymers from conductive polymers involves a new set of challenges, but a whole new set of potentially rewarding applications is encouraging workers in this area. Commercial rechargeable batteries using conductive polymers have already appeared, and more powerful ones are being planned. Conductive polymers might make shields that would make planes invisible to radar or protect them from lightning. Mercuri Kanatzidas of Michigan State University and others are working on conductive polymers that change from a conductive to a nonconductive state and even change color with small changes in temperature or radiation. These polymers could result in "smart" windows that would regulate the light-transmitting and insulating properties of windows according to the amount of sunlight being received.

Which of these research projects will result in products that change our everyday lives remains to be seen. Optimistic researchers predict a second plastics revolution with an impact as great as the original one. You may have seen these breakthroughs referred to as "materials science" – but the main science employed is.... You guessed it- chemistry.

The Truth About Plastics

Plastics have become an integral part of our everyday lives. They're unbreakable, light weight, colorful, inexpensive, and easy to mold. But recent studies have shown that some plastics may cause adverse health effects, especially to children whose small bodies are still developing. While much of the evidence concerning plastics and food is still inconclusive, we'd like to provide you with some guidelines for using plastics safely.

CHOOSE FOOD GRADE PLASTICS. Choose food and drink containers that have been FDA-approved for food use. Plastic items not intended for contact with food might contain harmful materials. (Our plastics have all been FDA-approved for food use.)

CLEAN CONTAINERS THOROUGHLY. Thorough cleaning between

uses prevents bacteria from growing.



MICROWAVE RESPONSIBLY. Never heat food in plastic containers not intended for food use. If you microwave in plastics, make sure the containers are FDA-approved for microwave use. Choose polyethylene or polypropylene, which do not contain plasticizers. Do not microwave in polystyrene (Styrofoam), single-use plastic containers, or plastic wrap.

PURCHASE THE SAFEST PLASTICS AVAILABLE. Plastics can be identified by their recycle codes 1-7. The following is a summary of what we know about plastic safety and recyclability:

BEST CHOICES:

#5 - Polypropylene (PP) has no known adverse health effects.

#2 - High Density Polyethylene (HDPE) has no known adverse health effects.

#4 - Low Density Polyethylene (LDPE) has no known adverse health effects.

WORST CHOICES:

#3 - Polyvinyl Chloride (PVC) often contains plasticizers which are added for flexibility. PVC contains phthalates and other suspected endocrine disrupters. PVC is used in many products including plastic wrap, bottles, and children's toys. Some PVC contains lead. PVC is difficult to recycle because of its high chlorine content and high levels of toxic additives. Separation and collection costs are high, material quality is greatly reduced after recycling, and the demand for virgin PVC remains high compared to the recycled material.

#6 - Polystyrene (Styrofoam) contains suspected carcinogens and endocrine disrupting

chemicals. Consuming fatty foods or alcoholic drinks from these containers is not recommended. Polystyrene is generally not recyclable.

#7 - Polycarbonate (PC) contains Bisphenol-A, a known hormone disruptor. It can damage reproductive organs and have adverse effects on breast tissue and prostate development. PC, or lexan, is used in some Nalgene brand water bottles (the hard colorful ones), some baby bottles, and in the lining of some aluminum cans. It is also found in dental fillings and sealants, including some used to prevent tooth decay in children.

#1 - Polyethylene Terephthalate (PETE or PET) is used mostly in single-use drink bottles--like those containing water, soda, and juice. These bottles are not intended for re-use and should not be stored for long periods of time or exposed to heat. While these bottles are highly recyclable, in reality few actually make it to the recycling center. According to the Container Recycling Institute, in fact, 50 billion single-use plastic bottles are used annually, but only 10 billion are recycled. The other 40 billion end up in landfills, incinerators or as roadside litter. Please make the switch to a reusable bottle.

The source of this information is

www.laptoplunches.com/newsletters/DecemberNewsletter_2005.html.

CONCEPTS TO UNDERSTAND FROM CHAPTER 13

For an excellent video introduction to these concepts, visit The Age of Polymers, #22 in the World of Chemistry video series: <http://www.learner.org/resources/series61.html>

Polymers are long-chain molecules made of smaller units which repeat throughout the molecule.

Polymerization is a reaction in which small units called **monomers** link up to form a macromolecule, or polymer.

An **addition polymer** is formed when monomer molecules containing a double bond polymerize. In this polymerization reaction the double bond is partially broken, and the resulting polymer product is linked by single bonds.

A family of addition polymers, each with its own characteristic properties, can be considered to be derivatives of the ethylene polymer polyethylene. Some of these polymers, their respective monomers, and their commercial uses, are listed in Table 13-1.

The molecular structures of polymers affect their physical properties. For example, the close-packed linear form of polyethylene is more dense and rigid than the less efficiently packed branched molecules of low-density polyethylene.

Homopolymers are made from only one type of monomer.

Copolymers are formed when two or more kinds of monomers are reacted together. Types of copolymers are:

Alternating copolymers: ABABABABABABABABABABABABABABABAB

Block copolymers: AAAAAAAAAABBBBBBBBAAAAAAAAABBBBBBBB

Ideal copolymers: AAABBABBAAABABBBAAABBABBAAABB

Polymers formed from **condensation reactions**, in which a water molecule is formed as one of the products, are called **condensation polymers**. Examples of condensation polymers are nylons, which are joined by amide linkages, and polyesters, which are joined by ester linkages.

Thermosetting polymers are those in which heating causes the material to harden permanently, because of the formation of cross-linked bonds. **Thermoplastic polymers** soften when heated because the weaker intermolecular forces between the molecules can be broken by heat energy; when cooled, they resume their original form.

The ability of silicon to form covalent networks with oxygen makes possible both natural materials like sand and synthetic inorganic polymers called **silicones**.

The fossil fuels that we rely on for transportation, heat, and power supply the materials to synthesize plastics and synthetic fibers. Recycling plastics not only reduces the amount of solid waste that must be disposed of, but helps to conserve our limited supplies of fossil fuels.

A SKILL TO LEARN FROM CHAPTER 13

Polymers are large molecules built from repeating units. When decoding the structure of a polymer molecule, **look for the repeating unit**.

SOME FACTS TO KNOW FROM CHAPTER 13

Polyacrylonitrile fibers like acrilan should not be used in enclosed public spaces because they release toxic hydrogen cyanide when burned.

There are several types of synthetic rubber; the type used for auto tires is a copolymer of styrene and butadiene, or SBR.

The strong cross-linked resins formed from condensation reactions with formaldehyde make many useful products, including construction adhesives, and permanent-press finishes. New products using these materials should be used with adequate ventilation because of the possible presence of formaldehyde, an irritant and probable carcinogen.

The code numbers and symbols on the bottoms of plastic containers refer to the type of plastic, and are used in sorting containers for recycling. The meanings of the codes are listed in Table 13-2.

Conducting plastics like polyacetylene and oriented polymers, in which the alignment of the molecules produces a stronger material, are among the current research projects that may lead to totally new uses for plastics.

Your Name _____

The Date _____

CHAPTER 13 PROBLEMS

1. Name the synthetic polymer most likely to be found in the following:

- a. Indoor-outdoor carpeting
- b. A soft-textured sweater that releases cyanide when burned
- c. An automobile tire
- d. Panty hose
- e. A “fleece” vest made from recycled soft-drink bottles
- f. A soft-drink bottle
- g. A non-stick pan coating
- h. A bullet-proof vest
- i. A kitchen counter
- j. Laminated plywood
- k. Plastic plumbing
- l. Swimming pool liners

2. Name all the natural polymers in the clothing you are now wearing.

Name the synthetic polymers you are wearing.

3. Name the synthetic polymers that you can see in the room you are now in. Are there likely to be synthetic polymers in the room's construction that are not immediately visible? What are they?

4. Name the monomer which is used to make each of the following addition polymers:

- a. Polyethylene
- b. PVC
- c. Teflon
- d. Orlon
- e. Polypropylene
- f. Polystyrene

5. How does the structure of LDPE differ from that of HDPE? How does this affect the properties of the two substances?

6. Fill in the blanks in the following table.

MONOMER NAME	MONOMER STRUCTURE	POLYMER NAME	POLYMER STRUCTURE
Ethylene			
			$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array} \right)_n$
		Polypropylene	
Tetrafluorethylene			

7. Explain in your own words what the following terms mean:
- Spinneret
 - Vulcanized rubber
 - Homopolymer
 - Condensation reaction
 - Cold-drawn fiber
 - Oriented polymer
8. Name the two monomers which form the copolymer SBR rubber.
9. Why needs of this country during World War II that resulted in the discovery of
- Nylon
 - Synthetic rubber
10. What chemical and physical characteristics of thermosetting plastics makes formaldehyde resins useful as construction adhesives?
11. What characteristics of thermoplastic polymers make them especially good candidates for recycling?
12. What precautions should be taken in factories in which formaldehyde resins are used to make perma-pressed fabrics and building materials? What are the reasons for the precautions?
13. Why are Acrilan fabrics unsuitable for use in airplanes?

14. What chemical property of formaldehyde makes it useful for embalming?
15. Name a non-organic (non-carbon-containing) synthetic polymer and give some of its uses
16. Give the common chemical names which correspond to the following abbreviations or trade names:
- Teflon
 - PVC
 - HDPE
 - LDPE
 - LLDPE
 - PETE
17. Using A and B as symbols for polymer units formed from two monomers which form a copolymer, show the patterns for the following types of copolymers:
- Alternating copolymer
 - Ideal copolymer
 - Block copolymer
- 18.
- What is the most common use of thermoplastics?
 - What is the most common use of thermosetting resins?
 - Which is produced in greater quantities, thermoplastic or thermosetting resin?

19. Name three situations in which polymer chemists observed unexpected happenings and used their observations to develop new polymer products.

20. If you are currently using a plastic water bottle, find out what kind of plastic it must be made of by reading *The Truth About Plastics*. Assess the possible risk from using the bottle. If you are not using a bottle currently, tell what kind you would choose based on this information.