3.5 POLYMERS

On his second voyage to the New World in 1493-1496, Christopher Columbus saw natives playing a game with balls made from the gum of a *Hevea* tree. Archaeologists suggest the use of such balls was common in the cultures of the Caribbean and Central and Southern America long before the arrival of European explorers. The native Americans gathered the milky exudate from cuts they made in a variety of trees. As it dried they fashioned it into balls, footwear and even bottles. In 1736 French explorers collected some of the condensed juice of the *Hevea* tree and sent it to Europe where it was analyzed by Joseph Priestly and other scientists. Priestly noted that the gum could "rub" pencil marks off paper, and thus the term "rubber" was coined. Although most eighteenth century scientists initially thought that rubber was just an interesting curiosity, its many valuable properties were later discovered and inventors eventually incorporated it in a wide variety of materials including tires, water-proofing and sporting goods.

Rubber is one of many naturally occurring polymers-- high molecular weight compounds consisting of up to millions of repeated low molecular weight units. The term "polymer" is derived from the Greek words "polys" meaning many and "meros" meaning parts, a term that aptly describes the structural nature of these substances. The most abundant organic molecules in the world are polymers. Cellulose and lignin (the main fibers in wood), starch (a natural storage form of sugar in plants), chitin (a key fiber in the cell walls of algae, fungi and arthropods), collagen (the fiber that holds soft tissues together in our bodies), DNA, RNA and proteins (key biological informational and structural molecules), and even cotton, wool, silk, and flax (natural fibers used in clothing) are polymeric.

Many polymers like starch, cellulose, and chitin are homopolymers, chains consisting of only one repeating sub-unit, or monomer (Figure A illustrates the beginning of the starch polymer.) Others, like DNA and protein are known as copolymers because they contain two or more different monomers. Copolymers are described as "random", "block", or "alternating" depending upon the arrangement of their constituent monomers. You can visualize these by putting differently colored pop-beads, gum drops, or other substances together in chains like those shown in Figure B.

In 1856 Andrew Parkes combined cellulose nitrate and camphor to invent the first man-made plastic (a plastic is a moldable high molecular weight organic polymer) known as celluloid. A variety of uses for celluloid were soon found, including billiard balls, piano keys, and photographic and motion picture film stock. Although the development of new plastics was initially very slow (it took more than fifty years for the development of the next synthetic polymer), the pace accelerated during the first half of the twentieth century as the German chemist Herman Staudinger (subsequently a Nobel prize winner in chemistry) and others provided a theoretical understanding of polymer chemistry. Armed with this new knowledge, chemists were able to develop a wide variety of useful polymers that have found their way into virtually every aspect of life.

Some polymers are linear, while others are branched or cross-linked (Figure B). Cellophane tape is an example of a product made of linear polymers, most of which lie parallel to each other the way strands of spaghetti lie in a pack. Just as it is easier to separate the pieces of spaghetti (between noodles) into two bunches than it is to break them into two bunches (across noodles), so it is easier to tear cellophane tape lengthwise (between chains) than crosswise (across chains).

Although there is no theoretical limit to the length of a polymer chain, most are composed of 1000, to 10,000 monomers and have molecular weights that vary from approximately 15,000 to 500,000 grams/mole. Most linear polymers such as polyethylene can be repeatedly softened or melted by heating and are known as thermoplastics.

Many polymers have branches or are cross-linked (Figure B). The strength and rigidity of a polymer generally increases with the number of cross-links. If all of the polymers in a substance are connected by cross-links, then that substance can be considered to be a single molecule. A bowling ball or a tire is essentially one molecule because all of the polymer chains are cross-linked with each other. Most extensively cross-linked polymers do not soften when heated because the polymer strands are not free to move. Such polymers are known as thermosets.

Polymers are made by step reactions and chain reactions. Figure A shows the formation of a starch molecule by a step reaction known as condensation because water is released each time a monomer binds. Wool, silk, cellulose, nylon, Dacron®, and Kevlar® are formed by condensation reactions.   Chain, or addition reactions involve the opening of double (or triple) bonds by the action of an initiator. The most common type of initiator is a free radical which contains an unbonded electron such as occurs in a split-peroxide (indicated as R* in our equations). A free-radical is a highly reactive species that contains an unpaired electron. Free radicals bind to a carbon in a double bond (or triple bond), breaking the extra bond and leaving an unpaired electron (active site) at the adjoining carbon. The process is repeated as this new unpaired electron breaks a double bond and creates another active site in yet another monomer.   Monomers only react with the active site and not with other monomers.   Figure C shows how polyethylene is made by a chain (addition) reaction. The chain reaction is terminated when another free radical reacts with the growing end of the chain to cap its growth.

Polymers are now an integral part of life in industrialized countries, and are widely used as adhesives, coatings, textiles, packagings, foams, elastomers, optic elements, electronic components, structural composites, engineering plastics, and in many other applications. In this chapter you will investigate this extremely important class of chemicals.

3.5.1 POLYMERIZATION

Concepts to Investigate: Polymers, monomers, polymerization, elastomers, allotropes.

Materials: Part 1: sodium silicate (water glass; avoid contact with skin), 95% ethyl alcohol (flammable: extinguish all flames), small paper cups, popsicle sticks or stirring rods, paper towels. Part 2: sulfur, beaker, test tube, test tube clamp, ring stand.

Safety: *Wear goggles, lab coat and gloves. Part 2 must be performed as a teacher demonstration only.*

Principles and Procedures: The Mayans of Central America were one of the first to use natural latex polymers from the rubber tree to produce elastic, bouncing balls. Archaeologists believe that the neighboring Aztecs apparently used rubber balls in ceremonial games. In this activity, you, like the ancient Mayans and Aztecs, will make a rubbery ball, but rather than making it from organic latex, will make it from the inorganic liquid sodium silicate.

Part 1: Silicone Rubber: *Put on a pair of disposable gloves*. Place 20 mL of sodium silicate solution in one paper cup. Slowly add 5 mL of 95% ethyl alcohol while stirring with a wooden stick. Continue stirring with a circular motion until the material polymerizes. Moisten your gloves with water and roll the polymerized material into a ball. Gently squeeze excess alcohol from the ball and wet it occasionally until its surface glistens. Sometimes the silicone tends to dry out and crumble. If this occurs, moisten your gloves and try to reform the ball as before. The product of this reaction is a silicone polymer (Figure D). The group in brackets is the monomer that is repeated numerous times to produce a long chain. The "R"s represent ethyl groups (CH_3CH_2-) contributed by ethyl alcohol. Try bouncing the ball. How high will it bounce when dropped from 1.0 or 0.5 meters? Calculate the rebound ratio by dividing the height of the rebound by the height from which it is dropped (Figure E). Compare the rebound ratios of this ball at a given height with those formed by others in the class. Is there any similarity between those that exhibit the highest rebound ratios?

Elastomers ("elastic polymers") are rubbery polymers. They are composed of long chains that recover their shape after being stretched or deformed. Is the silicone material that you made an elastomer?

Part 2: Polymeric sulfur *Note: Teacher demonstration only:* An allotrope is a different form of the same element. Sulfur has four allotropes: The normal, yellow sulfur that is found in large deposits in the Earth is known as rhombic sulfur. When heated, rhombic sulfur melts to form liquid lambda sulfur. If lambda sulfur is allowed to cool slowly it crystallizes into monoclinic sulfur, but if it is cooled rapidly it forms polymeric (plastic) sulfur.

Fill a beaker about 3/4 full of water and place in a fume hood. Fill a test tube two-thirds full with sulfur. Support this test tube with a metal clamp, place in a fume hood, and heat the sulfur gently until it melts. *Avoid igniting the sulfur vapors that emanate from the mouth of the tube*. Continue heating and notice that the color of the sulfur changes from yellow through orange, red, and brown to black. After the sulfur boils, pour it in a narrow stream into the center of the cold water (Figure F). A brown strand of plastic polymerized sulfur will form. Once it is cooled, remove the sulfur with tongs and examine its properties. What properties suggest that this form of sulfur is polymeric? Allow the polymeric sulfur to stand for a week or more. Does it appear to be as flexible as it was initially? At room temperature the only stable form of sulfur is rhombic, and so the plastic polymeric sulfur will eventually revert to the rhombic form. As the S-S bonds in the chain are broken, the monomer units S_8 re-form.

Questions:

(1) What was the rebound ratio of the silicone ball that you made?

(2) What characteristics are shared by those balls demonstrating the highest rebound ratios?

(3) Most commercial polymers are carbon-based. What similar properties do carbon and silicon share that may contribute to their abilities to polymerize.

(4) Plastics are made of organic (carbon-based) polymers. What similar properties does the silicone polymer in part 1 share with plastics.

(5) Perform some library research to identify practical applications of silicone polymers.

(6) Is polymeric sulfur a stable form of sulfur at room temperature? Explain, based upon your observations from part 2.

(7) What is the monomer unit in the sulfur polymeric chain in Figure G.

3.5.2 CROSS-LINKING POLYMERS

Concepts to Investigate: Cross-linking, polymers, cross-linking agents, viscosity, elastomers, thermoplastic polymers, thermoset polymers.

Materials: Part 1: Polyvinyl alcohol; sodium borate decahydrate (e.g. Twenty Mule Team Borax® Laundry Booster), Styrofoam cups, wooden stirring stick, plastic sandwich bags. Part 2: substitute white glue for polyvinyl chloride.

Safety: *Wear goggles, lab coat and gloves.*

Principles and Procedures: In 1839, American chemist Charles Goodyear discovered that rubber could be made much stronger by heating it in the presence of sulfur. Figure H shows how sulfur can cross link hydrocarbon polymer chains to form a stronger interlocking mass.

Goodyear recognized the potential industrial applications of his "vulcanization" process and applied for numerous patents. Although Goodyear's discovery was indeed revolutionary, he was unable to make money on the process and died in substantial debt. By the end of the 19th century technological and economic conditions were improved and the need for vulcanized rubber was growing with the growing popularity of the bicycle. An Ohio entrepreneur by the name of Frank Seiberling borrowed a few thousand dollars to develop a plant to make bicycle tires made of vulcanized rubber. Seiberling named his company in honor of the man who discovered the vulcanization process. The booming bicycle industry created huge sales and catapulted the Seiberling's Goodyear Tire and Rubber Company into international prominence. The rapid growth of the automotive industry in the twentieth century fostered Goodyear's sales, and by 1996 sales exceeded thirteen billion dollars a year! Polymer-cross-linking has proved to be a very lucrative business!

In the following activities, you will be investigating the influence that cross-linking has upon the nature of two polymers. Can you think of any possible practical applications for these cross-linked polymers?

Part 1: "Slime": Cross-Linked Polyvinyl Alcohol): Polyvinyl alcohol (Figure I) is a polymer used extensively in the plastics industry in molding compounds, surface coatings, and chemical resistant films. Sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) is a mineral used in cleaning compounds such as Twenty Mule Team Borax Laundry Booster . Both polyvinyl alcohol and sodium borate are water soluble, but when mixed, form a cross-linked polymer. Sodium borate acts as a cross-linking agent to bind polyvinyl alcohol chains together. This solidifies the polyvinyl alcohol and traps water, forming a slimy mass.

Sodium borate dissolves in water to form boric acid, H_3BO_3, which then accepts a hydroxide from water to become $B(OH)_4^-$.

$$H_3BO_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+$$

It is thought that $B(OH)_4^-$ then reacts in a condensation reaction with polyvinyl alcohol as indicated in Figure J. The water from this condensation reaction as well as the excess water from the two solutions gets trapped in the cross-linked polymer, producing the slimy, flexible properties.

Make a 4% polyvinyl alcohol solution by slowly stirring in 4 grams of polyvinyl alcohol powder into 96 mL of hot (approximately 80°C; not boiling!) distilled water (use a magnetic stirrer if possible). Do not add the polyvinyl alcohol rapidly or it may clump and form a sticky mass. Allow the solution to stand in a covered container. Make a 4% solution of sodium borate by dissolving 0.4 gram of sodium borate decahydrate (borax) in 9.6 mL of distilled water. Pour the polyvinyl alcohol solution into a Styrofoam or plastic cup and stir in the sodium borate solution.

Although the "slime" that develops is non-toxic and can be handled, stretched, and formed into various shapes (Figure K), you may wish to wear gloves to reduce the possibility of skin irritation. Be sure to wash your hands thoroughly after handling the polymerized slime. Repeat the procedure using twice as much sodium borate solution. What influence does the amount of sodium borate solution have upon the viscosity (thickness) of the slime? Describe the characteristics of the slime. You can keep the slime sealed in a plastic bag.

Part 2: "Silly Putty" : In 1943 a team of chemists developed a new putty-like polymer that could be repeatedly shaped, twisted, tied, stretched, flattened and rolled. The chemists were sure that the highly unusual properties of this polymer would make it useful for some new product, and distributed samples to thousands of engineers. Surprisingly, none of the engineers could find a practical use for this odd material until someone realized that it would make a great toy. Entrepreneurs soon packaged and sold the polymer as "Silly Putty®" which came to be one of the best-loved toys of the second half of the twentieth century. Although the real Silly Putty® is made from a relatively expensive siloxane polymer, we can make a cross-linked polymer that has many of the same properties using simple household materials.

Prepare a glue solution by adding equal quantities of water and white glue (Elmer's® glue works well) to a plastic or paper cup. Prepare a borax (sodium borate decahydrate) solution by dissolving 10 grams of borax in 90 mL of water. If you wish to make colored putty, add a couple of drops of food coloring to the glue solution. Mix equal volumes of the glue and borax solutions and stir for a couple of minutes. Roll the lump around in your hands until it ceases to be sticky.

White glue is a solution consisting of many small hydrocarbon globules suspended in water. It is viscous (thick) because all of the long molecular chains are tangled together just like a pot of stirred spaghetti. Sodium tetraborate acts as a cross-linker and ties the hydrocarbon chains together, resulting in an extremely viscous substance that exhibits properties of both a liquid and a solid. An elastomer has elastic properties and returns to its original shape after being twisted , pulled and compressed. Is the cross-linked glue-based polymer you made an elastomer? Does it bounce? Drop the ball from a height of 50 cm and measure its rebound ratio (Figure E). Compare the rebound ratio with those found by the other students in your class. Did everyone get the same rebound ratio? If your polymer ball cracks when dropped from this height, try measuring the rebound ratio when dropped from 25 cm. Place the ball in a refrigerator for 15 minutes and try bouncing again. How does temperature affect the elasticity of this substance?

If the rigidity of a polymer decreases as the temperature is raised past a critical temperature, it is said to be a thermoplastic polymer. If, however, the polymer chemically decomposes before it softens it is known as a thermoset plastic. Place the polymer clump in a beaker and heat gently and slowly on a hot plate (Figure L). Does this appear to be a thermoset or a thermoplastic polymer?

Questions:

(1) Describe the unusual properties of the cross-linked polyvinyl alcohol.

(2) Describe the characteristics of the slime once it has been allowed to dry.

(3) A polymer is a string of repeating monomers. What is the monomer in polyvinyl alcohol?

(4) Is the rebound ratio for the polymer ball in part 2 the same for everyone in the class? If it is significantly different, what variables might explain this difference?

(5) Does the glue-based polymer in part 2 appear to be a thermoplastic or thermoset polymer? Explain.

(6) How would your polymer be different if more sodium tetraborate were added? Try it!

(7) Why will a car tire sometimes "bump" in cold weather but roll smoothly after the car has been driven for a short distance?

3.5.3 USES OF POLYMERS

Concepts to Investigate: Uses of polymers, commercial polymers, neoprene, polyacrylonitrile, polychlorotrifluoroethylene (Teflon®), polyester, high density polyethylene (HDPE), low density polyethylene (LDPE), polyethylene terephthalate (PET, PETE), polyolefin, polystyrene, polysulfone, polytetrafluoroethylene, polyurethane, polyvinyl alcohol, polyvinyl chloride, polyvinyl fluoride, polyvinylacetate.

Materials: (none required)

Principles and Procedures: Historians and anthropologists have described the stages of civilization in terms of the most important and advanced building materials employed. The Stone Age was first and was followed by the Bronze, Iron, and Steel Ages, and now we are in the Age of Polymers, a time in which synthetic polymers are the material of choice for a large variety of industrial and domestic applications.

In 1907 Leo Bakeland patented Bakelite®, the first fully synthetic polymer. This hard plastic was used as an electrical insulator and paved the way for the more than 60,000 different synthetic plastics on the market today. Each year companies manufacture more than 30 million tons of plastics that are used in myriad of applications. We wear clothes containing polyester and nylon fibers, eat food packaged in polyethylene containers, drink water delivered through polyvinyl chloride pipes, walk on carpets made of polyolefin fibers, and sleep on mattresses made of polyurethane foam. The variety of applications of synthetic polymers is mind-boggling. Table 1 lists some of the major classes of polymers and describes some of their useful properties and uses. Examine the list of applications and circle each item you have used in the last week. For example, if you have been a passenger in a car, then you would circle the word "radiator hose" under "neoprene" because automobiles use radiator hoses (unless it was an old air-cooled automobile such as the original Volkswagen Beetle!).

Table 1 Uses of Polymers

polymer	*properties*	*applications*
neoprene	very chemical resistant, rubbery	shoe soles, hoses, radiator hoses, wetsuits
polyamide (nylon)	fibrous, strong, durable, moisture resistant	parachutes, carpet, ropes, form-fitting skiwear, hosiery, swimware, boat sails
polyacrylonitrile	resinous, fibrous, or rubbery, combines with butadiene and styrene to form hard, tough ABS copolymer	ABS plumbing pipe, structural panels, kettle handles, housewares; Orlon fabric
polychloro-trifluoroethylene	can be molded by extrusion, chemically resistant	gaskets, linings for containers, parts for valves and pumps
polyester	fibers recover quickly after extension and absorb very little moisture.	filters, conveyor belts, sleeping bag insulation, coat insulation, tire cords. Brand name polymers include: Dacron, Fortrel, Terylene; Mylar & Lexan.
polyethylene (high-density) HDPE	can be easily formed into lightweight containers	milk, water, and juice containers; toys, liquid detergent bottles
polyethylene (low-density) LDPE	can be stretched into fine, tough, films.	bread bags, frozen food bags, grocery bags
polyethylene terephthalate (PET, PETE)	strong, easily moldable, chemically resistant, light-weight	soft drink bottles, peanut butter jars, salad dressing bottles, nonbreakable bottles
polyolefin	fiber composed of at least 85% polyethylene or polypropylene	hosiery, sportswear, undergarments, pile fabrics, upholstery, outdoor furniture, indoor carpeting, indoor-outdoor rugs and carpets, filters, marine cordage, automobile seat covers, electrical insulation, carpet backing
polystyrene	thermoplastic; resists attack by acids, alkalis, and many solvents, does not absorb water; excellent electrical insulator.	Styrofoam cups, grocery store meat trays, fast-food sandwich containers, video cassette cases, compact disk jackets, cafeteria trays, refrigerator insulation
polysulfone	tough, strong, stiff, chemically and thermally resistant	household and plumbing items, various automotive parts, wire coatings
polytetrafluoro-ethylene (PFTE)	strong, tough, waxy, nonflammable, chemically resistant, slippery surface, thermally stable	Viton: gaskets, bearings, linings for containers and pipes. Teflon: non-stick cookware, cooking utensils, pump valves, plumbing tape.
polyurethane	flexible foams, highly elastic quick drying fibers, or hard-drying films	flexible foams: upholstery material, mattresses rigid foams: cores for airplane wings fibers: spandex clothing fiber, support hosiery; Lycra, Numa, Spandelle, and Vyrene. hard films: polyurethane varnishes
polyvinyl alcohol	colorless, water-soluble, flammable resin	component in: adhesives, emulsifiers, lacquers, coatings, and films
polyvinyl chloride	rigid when unplasticized; flexible when plasticized	unplasticized form: water pipe, plumbing fittings, phonograph records, synthetic floor tiles, credit cards plasticized form: raincoats, shower curtains, and packaging films.
polyvinyl fluoride	resistant to attack by chemicals or	protective films for: building sidings, pipes,

	by weathering	corrosive chemical containers
polyvinylacetate	water-insoluble resin	carpet backings; film-forming ingredient of water-based (latex) paints, adhesives, lacquers, and cements

Questions:

(1) Which categories of polymers do you use most often on a weekly basis?

(2) The price of most polymers is tied to the price of petroleum. Explain.

(3) Nylon, polyester, olefin, and other synthetic fibers have replaced many natural polymers for use in clothing, carpets and similar applications. Which natural fibers have they replaced?

(4) Name ten applications of synthetic polymers that are not already listed in the table.

3.5.4 RECYCLING PLASTIC POLYMERS

Concepts to Investigate: Recycling, polymers, solid waste, polymer characteristics.

Materials: Part 1: variety of empty plastic household containers such as: detergent containers, ketchup bottles, peanut butter jars, etc. Part 2: 400 mL beaker, acetone, stirring rod, Styrofoam® cup, Styrofoam® packing material.

Safety: *Part 2 must be performed as a teacher demonstration. Wear goggles, lab coat and gloves.*

Principles and Procedures: In the 40 years between 1960 and 2000, the total annual solid waste in the United States doubled from approximately 80 million tons to 160 million tons. Many communities have run out of suitable locations to bury their trash and must pay to ship it out of the area. Currently approximately 20% of the volume of trash (approximately 10% of the mass) that is dumped into land-fills is composed of plastics. Plastic trash is not only a serious problem for landfills, but it is also an eyesore. Unlike paper and garden debris, plastics are not bio-degradable and thus persist in the environment indefinitely unless someone picks them up. The persistence of plastic trash in the environment, the looming shortage of petroleum reserves, and the shortage of landfill space have increased the urgency to recycle plastics. By 1990 Americans were recycling approximately one third of waste aluminum and one quarter of waste paper, but only 2% of waste plastic. Today more and more communities are adopting mandatory recycling programs in which citizens must separate recyclable plastic trash so it can be reprocessed into new products.

Environmentalists both within and outside the plastics industry have become very concerned about the waste problems caused by synthetic polymers. In an effort to recycle these polymers more effectively, the plastics industry adopted a coding system to identify the type of plastic so that they could be categorized for recycling purposes. Plastic containers are now labeled with a letter code that appears inside the recycling symbol.

Part 1: Identifying classes of polymers: Examine as many disposable plastic items as available and look for the recycling figure. Classify each product (i.e. shampoo bottle, grocery bag, etc.) under one of the 7 recycling codes. After examining 3 or more samples of a polymer try to describe its characteristics. For example, does it float (make sure you fill the container) in water? Is it crinkly? Does it appear glossy? Is it flexible or rigid? Complete the table below.

Table 2 Recycling codes

recycling code	*polymer resin*	*description*	*sample products*
1 PETE	Polyethylene Terephthalate (PET or PETE)		
2 HDPE	High density Polyethylene (HDPE)		
3 PVC	Polyvinyl Chloride or Vinyl (PVC-V)		
4 LDPE	Low density Polyethylene (LDPE)		
5 PP	Polypropylene (PP)		
6 PS	Polystyrene (PS)		
7 OTHER	Multi-layer Plastics		

Part 2: Recycling: When you turn plastics in for recycling they are reprocessed and made into new products. Synthetic polymers can be recycled by burning (to produce energy in a

incineration-generator), by melting (to reform a similar polymer), by shredding (to produce fibrous filling), or by treatment with chemicals. The following summarizes the principal recycled products:

(1) Polyethylene Terephthalate (PET or PETE): Most of the recycled PET is from beverage containers. Recyclers are able to make 99% pure, granulated PET that sells at approximately half the cost of new PET. Approximately 50% is used as fiberfill for jackets and strapping. The remainder is used to make such things as liquid soap bottles, surfboards, paint brushes, fuzz on tennis balls, and more soft drink bottles.

(2) High density Polyethylene (HDPE): The process for recycling HDPE is well-developed. Recycled HDPE finds its way into drainage pipes, flower pots, plastic lumber, trash cans, automotive mud flaps, kitchen drain boards, beverage bottle crates, pallets, signs, stadium seats, re-cycling bins, traffic barrier cones, golf bag liners, and toys.

(3) Polyvinyl Chloride or Vinyl (PVC-V): Recycled PVC has been used in drainage pipes, pipe fittings, floor tiles, bottles, door mats, hoses, and mud flaps. It is generally not burned in incinerators because it releases hazardous fumes such as dioxins and furans.

(4) Low density Polyethylene (LDPE): LDPE is burned in incinerator-powered generators to produce electrical energy. It is also recycled into items in which color is not critical such as garbage can liners, grocery bags, paint buckets, fast food trays, lawn mower wheels, and automobile battery parts.

(5) Polypropylene (PP): Recycled polypropylene is used in license plate holders, desk top accessories, hanging files, food service trays, flower pots, and trash cans.

(6) Polystyrene (PS): One of the most challenging polymers to recycle is polystyrene, the material from which Styrofoam cups and Styrofoam packing material are made. Although some methods for recycling are in place, chemists are still looking for more effective ways to recycle the huge amounts of waste polystyrene.

Teacher demonstration only: *Wear goggles, lab coat and gloves*. One of the techniques that may be used in recycling Styrofoam is to first "melt" it using acetone. Place a Styrofoam cup in a 400 mL beaker and place in a fume hood or other well-ventilated location. Add 30 mL of acetone to the Styrofoam cup. What happens to the Styrofoam? What happens if you stir the acetone? Place 30 mL of acetone in a second beaker and add a Styrofoam packing kernel. How many kernels can you add before they no longer melt? Using a glass stirring rod pick up the styrene clump and place it on a paper towel and flush the acetone down the drain with excess water. What new properties does this styrene clump have compared to the original Styrofoam? Can you think of any potential uses for this from of styrene?

Questions:

(1) Describe the properties of each polymer.

(2) List the types of containers commonly made from each class of polymer.

(3) Which plastics are accepted for recycling in your community? Call the waste disposal service if you are not certain.

(4) Why do waste disposal or recycling companies want you to crush all waste plastic containers?

FOR THE TEACHER

3.5.1 Polymerization

Discussion: Challenge the students to determine how to make the most elastic polymer balls. In this process, students will begin to understand some of the mechanical and chemical variables involved in the making of practical polymers. If ethyl alcohol is not available, you may substitute 2-propanol (rubbing alcohol is approximately 70% 2-propanol, also known as isopropyl alcohol) but it may not work as well.

A dramatic demonstration of polymerization may be performed using a two-component (A:isocyanate, B:polyol) polyurethane foam kit available from many plastic supply companies (e.g. TC-300 hard coat polyurethane foam from BJB Plastics). *This should be performed only as a teacher demonstration. Read product warnings and directions carefully before proceeding. Perform in a fume hood and wear goggles, lab coat and gloves.* Add components A and B in the specified quantities and mix as directed. The polymerization reaction is quite exothermic and produces carbon dioxide and water vapor which are trapped in the polyurethane as it forms, creating many tiny bubbles. Heat from the reaction causes the bubbles to expand and the foam to grow to perhaps ten times its original volume. Within a few minutes the foam cools and hardens, and can then be cut and shaped with a knife. Hard coat polyurethane foams are used extensively for insulation and cushioning. They are also used in the entertainment industry to make light-weight stage props that can be easily carried from set to set.

Answers:

(1) Student responses.

(2) Student responses.

(3) Carbon and silicon are in the same family in the periodic table, and both form four bonds which allows them to form long chains with cross branches

(4) Most plastics and this silicone polymer are flexible, elastic, water-repellent, electrical insulators and thermal insulators.

(5) Silicones are relatively unreactive and thermally stable and are therefore useful in applications where there are extreme variations in temperature. They are used as lubricants, hydraulic fluids, and electrical insulators, and also to treat fabrics to make them waterproof.

(6) As the plastic sulfur is allowed to stand at room temperature, it slowly reverts back to the crystalline rhombic form, indicating that the plastic form of sulfur is unstable at room temperatures.

(7) The monomer unit is an 8-sulfur atom chain. Some students might think that the monomer is simply single sulfur atoms, but when allowed to stand, plastic sulfur reverts to rhombic sulfur (S_8), indicating that the monomer is actually S_8.

3.5.2 Cross-linking and polymers

Discussion: To make this activity more colorful, you may wish to add food coloring to the polyvinyl alcohol prior to the addition of the sodium borate solution. If you allow the polyvinyl alcohol solution to stand uncovered, a thin film will develop on the surface as the water evaporates. You may wish to show your students this polymerized film. If time is limited, it is recommended that the instructor make stock solutions of the polyvinyl alcohol and sodium borate. Results seem to be best if the polyvinyl alcohol solution has been allowed to stand for one or two days. Both solutions will keep for more than a year if hermetically sealed.

You will find the polymer in part 2 described as "Silly Putty" in many books and on many web pages. It should be realized that the white glue based polymer shares some of the properties of the commercial Silly Putty (Dow Corning 3179 Dilatant Compound) which is a complex mixture made primarily of hydroxy-terminated polymers of dimethyl siloxane.

If you do not have access to the materials listed in these activities, you may wish to make a "Gak "-like starch-based polymer by mixing 2 parts Elmer's glue with 1 part liquid Sta-Flo starch. Put on gloves, add a couple of drops of food coloring, and kneed with your hands for 5-10 minutes. If it is too sticky add a little starch. If it is too runny add some glue.

Answers:

(1) A gel develops almost immediately. It can be rolled into an elastic ball and stretched into long strands.

(2) The linked polyvinyl alcohol returns to a solid phase. It is relatively rigid and somewhat transparent.

(3) (-CH_2CH(OH)-)

(4) Student responses.

(5) Thermoplastic. It softens with gentle heating.

(6) Increasing the number of cross-links increases the rigidity of the polymer.

(7) The artificial rubber in the tires is a thermoplastic polymer and softens upon frictional heating.

3.5.3 Uses of Polymers

Discussion: The market for polymers has grown rapidly since Bakeland's discovery. Today, chemists are examining the potential for new applications of polymers including molecular information storage and the conduction and storage of light and electricity. More than half of American chemists and chemical engineers are employed by polymer-related industries. The polymer industry in the United States employs more than three million and contributes more than one hundred billion dollars to the U.S. gross national product. Students should be aware of the vast economic significance of the polymer industry.

Answers:

(1) Student answers will vary.

(2) The vast majority of synthetic fibers are by-products of petroleum. Thus, when the price of crude petroleum increases, the cost of making polymers increases and this cost is generally passed on to the consumer.

(3) Cotton, hemp, sisal and flax.

(4) Student answers will vary.

3.5.4 Recycling Synthetic Polymers

Discussion: Students are impressed with the way Styrofoam melts in acetone. You may wish to compare the apparent "solubility" of Styrofoam packing material with newer environmentally-safe corn-starch packing material. The corn-starch material dissolves easily in water, but not in acetone while the Styrofoam material does not dissolve in water, but "melts" rapidly in acetone. Students should recognize that the starch packing material is more environmentally friendly because it will dissolve with the first rainstorm while the Styrofoam material will persist in the environment until heavily oxidized and mechanically broken down. The following table lists some examples of the most commonly recycled plastics.

Table 3 Examples of products made of recyclable polymers

recycling code	*polymer resin*	*description*	*sample products*
	Polyethylene Terephthalate (PET or PETE)	usually clear or green; sinks in water; rigid	peanut butter jars, salad dressing bottles, soft drink bottles
	High density Polyethylene (HDPE)	semi-glossy, crinkly, may be hard when thick	toys, liquid detergent bottles, motor oil containers, toys, plastic bags; milk, water, and juice containers

3 PVC	Polyvinyl Chloride or Vinyl (PVC-V)	semi-rigid, glossy, sinks in water	clear food packaging, shampoo bottles, vegetable oil bottles, blister packages
4 LDPE	Low density Polyethylene (LDPE)	flexible, not crinkly	frozen food bags, grocery bags, shrink-wrap, garment bags, bread bags
5 PP	Polypropylene (PP)	semi-rigid, low gloss	yogurt containers, margarine, tubs, medicine bottles, refrigerated containers, most bottle tops
6 PS	Polystyrene (PS)	often brittle, glossy	coffee cups, throw-away utensils, cafeteria trays, grocery store meat trays, fast-food sandwich containers, video cassette cases, compact disk jackets
7 OTHER	Multi-layer Plastics	squeezable	"squeezable" containers, ketchup bottles, syrup containers.

Answers:

(1) See chart.

(2) See chart.

(3) Student answers may vary. The most commonly recycled plastics are polyethylene terephthalate (PETE) and high density polyethylene (HDPE).

(4) Plastics occupy approximately 20% of the trash volume in many communities. Crushing containers produces significantly less volume and simplifies transport.

APPLICATIONS TO EVERYDAY LIFE

Household plastics: All of the plastics in your home are made of polymers. Refer to section (3.5.3) for examples.

Thermoplastics: Thermoplastics are easily moldable at high temperatures and may be heated and shaped into a wide variety of forms. Thermoplastics are used in a wide variety of molded products and applications such as soft drink containers, electricians tape, food packaging, and insulation.

Thermoset Plastics: Thermoset plastics are extensively cross-linked and do not deform or soften upon heating. As a result, thermoset plastics are used extensively in machinery where they must retain their shape even under conditions of high temperature. They are also used in kettle handles, epoxies, and plywood adhesives.

Toys: All plastic toys are made of polymers. Some polymers such as those in Slime, Silly Putty, and Silly String are sold as toys simply because of their fascinating (slimy, bouncy, stringy) properties. Sodium polyacrylate is a super-absorbent polymer used in many "disappearing water" tricks (as well as disposable diapers) because of its ability to absorb 500 to 1000 times its own weight of water. Polyacrylamide is used in Grow Beasts and other toys that expand dramatically when placed in water.

Employment: Polymer chemistry dominates today's material industry. More than half of the nation's chemists and chemical engineers work in polymer-related industries! It is estimated that the polymer field contributes in excess of one hundred billion dollars to the gross national product each year.

Politics: Polymers are used in products necessary to virtually every conceivable industry in today's world, yet almost all polymers and plastics are derived from petroleum and other fossil fuels. An petroleum shortage not only affects the price we pay for gasoline and other fuels, but also the price we play for all petroleum-based products. Because of the significance of petroleum to the fuel and polymer industries, the governments of industrialized countries are particularly concerned about maintaining political stability in petroleum producing regions of the world so as to prevent an petroleum crisis and a "polymer crisis".

Agriculture: Polymeric materials are added to agricultural soils to improve aeration (air circulation in soils).

Medical Plastics: A variety of high-tech plastics are being developed for specific surgical applications. Dacron®, Teflon®, and polyurethane-based plastics are already being used for such things as heart valve replacements, blood vessel repair, and hernia support meshes.

Sporting Goods: Virtually every sport uses equipment made of synthetic polymers: football helmets, tennis rackets, hockey pucks, uniforms, balls, motorcycle windshields, skis, bicycle tires, and backpacks are but a few of the many sporting goods composed partially or completely of synthetic polymers.

Substitute Building Materials: Synthetic polymers are used in place of traditional building materials: Corian® countertops replace ceramic ones, fiberglass shower stalls replace tiles, elastomers replace inorganic grout, fiberboard replaces wood, PVC and ABS replace copper and steel for plumbing pipes, nylon and olefin replace wool in carpets, and Plexiglas® and Lucite® replace glass for windows.

Clothing: Read the manufacturer's labels on the clothing you are wearing and you may find that many are made of polymers. Nylon, olefin, polyester, rayon, and polyurethane are a few of the artificial polymers commonly used in clothing. Cotton, wool, flax, and silk are the most common natural polymeric substances used.