2.2 Synthetic Addition Polymers

addition polymer a very long organic molecule formed as the result of addition reactions between monomers with unsaturated carbon–carbon bonds

If you have ever stuffed used sports clothing in a plastic bag, or cooked eggs in a non-stick pan, you have handled an addition polymer. An **addition polymer** is the result of the reaction between monomers with unsaturated carbon–carbon bonds, similar to the addition reactions previously discussed for alkenes. Many plastic bags are made of polyethene, a very common addition polymer. (See Section 2.1, Figure 2.) Similarly, when tetrafluoroethene is the monomer, the resulting polymer is polytetrafluoroethene, PTFE (**Figure 1**). The brand name of this compound is Teflon: the slippery surface that prevents eggs from sticking to the pan.

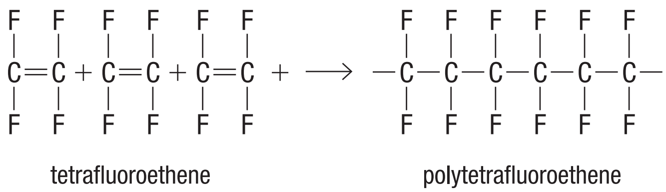


Figure 1 The formation of polytetrafluoroethene (PTFE)

The discovery of Teflon illustrates the role of chance in chemical research. In 1938, DuPont chemist Roy Plunkett was studying the chemistry of gaseous tetrafluoroethene. He synthesized about 50 kg of the chemical and stored it in steel cylinders. When the valve on one of the cylinders was opened to release some of the gas for testing, nothing happened. Rather than assuming that the cylinder was empty and discarding it, Plunkett decided to cut the cylinder open. Inside, he found a white powder: a polymer of tetrafluoroethene. This substance was eventually developed into Teflon. Why is Teflon such an inert, tough, non-flammable material? These properties are the result of the strong C–F bonds of the polymer molecule. These bonds are very resistant to chemical change. Because of its lack of chemical reactivity, Teflon is widely used for electrical insulation, non-stick coatings on cooking utensils, and low-friction surface coatings. CAREER LINK

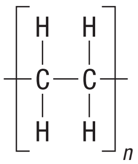
Other addition polymers can be made from monomers containing chloro–, methyl–, cyano–, and phenyl– substituents (**Table 1**). In each case, the carbon–carbon double bond in the substituted ethene monomer becomes a single bond in the polymer. The variety of substituent groups leads to a wide range of properties.

The reaction to form polypropene is very similar to the reaction that forms polyethene. You could think of propene molecules as ethene molecules with a methyl group as a substituent. The polymer formed from propene looks just like that of polyethene, except that it contains methyl groups on every other carbon atom in the long chain: one per monomer (**Figure 2**). These methyl groups give the polymer added strength.

LEARNING **TIP**

Shorthand for Polymers

Polymers might be thousands of carbon atoms long. So far, we have represented polymer molecules as long chains of repeating units that end in a line at each end. This implies that the molecule continues indefinitely in each direction. We can show the structure of a polymer in a condensed form by writing the repeating monomer in parentheses with an "*n*" subscript to indicate the number of repeating units.



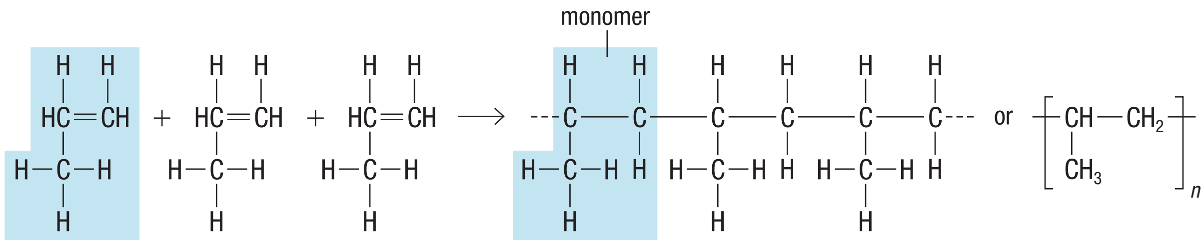
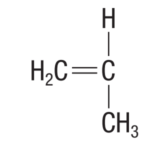
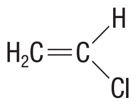
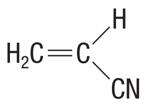
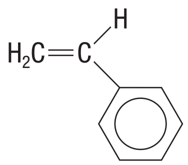
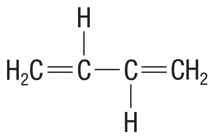
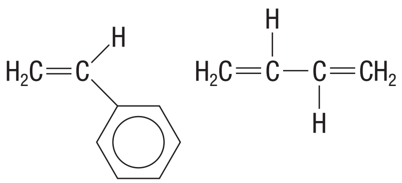


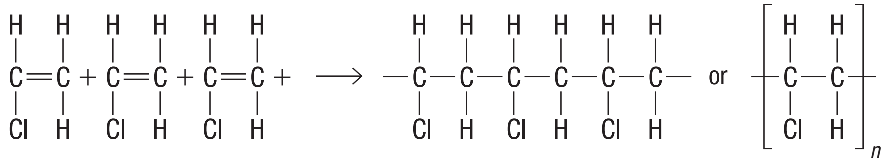
Figure 2 The polymerization of propene produces polypropene. Note how the structures of the reactant molecules are drawn so that their carbon–carbon double bonds are all aligned but the single bonds are above and below.

Table 1 Familiar Addition Polymers

Monomer		Polymer	
Name	**Formula**	**Name**	**Uses**
ethene	$H_2C{=}CH_2$	polyethene (polyethylene)	plastic bottles and pipes, insulation on electric wires, toys
propene		polypropene (polypropylene)	rope, packaging film, carpet fibres, toys 
chloroethene (vinyl chloride)		polyvinyl chloride (PVC)	pipes, construction materials, floor tile, clothing, reusable bags 
cyanoethene (acrylonitrile)		polyacrylonitrile (PAN)	carpet fibres, synthetic fabrics
tetrafluoroethene	$F_2C{=}CF_2$	polytetrafluoroethene (Teflon)	non-stick cookware, electrical insulation, ball bearings
vinylbenzene (styrene)		polystyrene	food and beverage containers, insulation, toys 
butane-1,3-diene (butadiene)		polybutadiene	tires, industrial coatings
vinylbenzene (styrene) and butane-1,3-diene (butadiene)		styrene–butadiene rubber (a copolymer)	synthetic rubber

Just as propene is similar to ethene with a methyl substituent group, other monomers are also similar to ethene with other substituents. These substituents could be chlorine, an alkyl group, or a benzene ring. These compounds also can undergo addition polymerization to produce a range of polymers, as Table 1 shows.

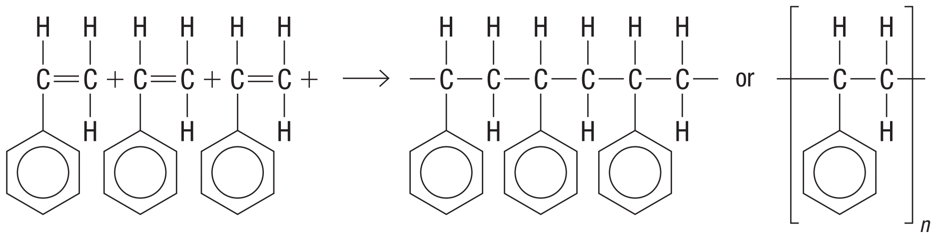
For example, polyvinyl chloride (PVC) is a polymer of the chloroethene monomer (also called vinyl chloride) (**Figure 3**).



vinyl chloride monomers polyvinyl chloride (PVC)

Figure 3 The formation of polyvinyl chloride (PVC)

If the substituent in ethene is a benzene ring, the compound is ethylbenzene (also known as styrene). The addition reaction of ethylbenzene molecules produces the polymer polystyrene (**Figure 4**). Polystyrene is used to make heat-resistant disposable drinking cups and it is used in many plastic toys.



styrene monomers polystyrene

Figure 4 Styrene monomers react to produce polystyrene, which is the polymer in familiar Styrofoam products.

Tutorial 1 Drawing Addition Polymers and Their Monomers

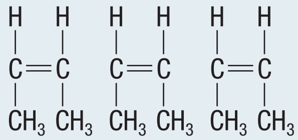
In this tutorial you will learn how to draw an addition polymer given the name of its monomer, and how to draw the monomer given the structure of the polymer.

Sample Problem 1: Drawing a Polymer

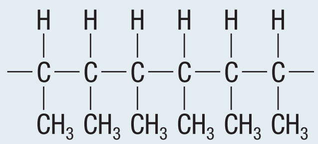
Draw a structural diagram showing three repeating units of the addition polymer formed from cis-but-2-ene.

Solution

First, draw three structural diagrams of cis-but-2-ene, $CH_3CH{=}CHCH_3$. Show each molecule with the double-bonded carbon atoms all in a line, and place other atoms below or above that line.

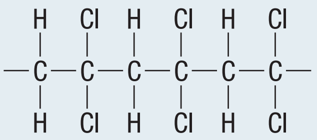


Next, connect the monomers with single bonds to form a chain. Remove the double bonds within the monomer, replacing them with single bonds so that each carbon atom has exactly four bonds. Add lines at each end to indicate that this is just one segment of the longer polymer molecule.



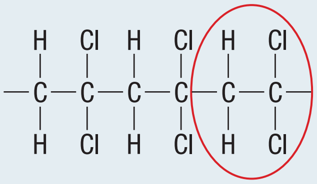
Sample Problem 2: Drawing a Monomer from a Polymer Structure

Draw a structural diagram of the monomer used to make Saran, shown below. Name the monomer.

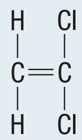


Solution

First, identify the repeating unit. In this case, the repeating unit in the polymer is CH_2–CCl_2, circled below. (Note that it would also be correct to identify the repeating unit as CCl_2–CH_2.)



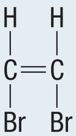
Next, draw the monomer, replacing the single bond between the 2 carbon atoms with a double bond. (Remember that, during an addition reaction, double bonds between carbon atoms in a monomer become single bonds between carbon atoms in the polymer.)



The name of this compound is 1,1-dichloroethene.

Practice

1. Draw and name the polymers that would be produced from each of the following monomers. Circle the repeating unit. K/U C

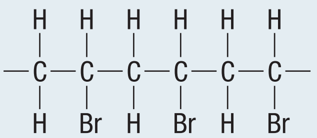
(a) 

(b) $CH_3—CH_2—CH=CH—CH_2—CH_3$

(c) $CHCl=CH—CH_3$

2. Draw a section of the addition polymer polyacrylonitrile, showing 3 monomers. (See Table 1). K/U C

3. Draw and name the monomer used to produce the following polymer: K/U C



Plastics

plastic a synthetic substance that can be moulded (often under heat and pressure) and that then retains its given shape

A **plastic** is a synthetic polymer that can be moulded into shape (often under heat and pressure) and will then retain its shape when cooled. There are many kinds of plastics, including polymers of substituted ethene monomers: polystyrene, polyvinyl chloride, nylon, polyesters, rubber, polyethene, and polypropene. We see products made from plastics all around us: tires, DVDs, automobile trim, packaging materials, and eyeglass lenses. Plastics are usually manufactured from petrochemicals. Not all polymers are plastic, but all plastics are polymers.

Research This

Paying with Plastic

Skills: Researching, Analyzing, Evaluating, Communicating — SKILLS HANDBOOK A5.1

In 2011, Canada joined the small number of countries that manufacture banknotes from synthetic polymers (**Figure 5**). The polymer is a biaxially oriented polypropene (BOPP) and is replacing the traditional cotton fibre. BOPP is made by stretching polypropene uniformly in two directions. The resulting synthetic polymer makes the bills more durable, more resistant to dirt and water, and more difficult to counterfeit. The new $100 bill feels smoother than the traditional paper bill, but the size remains unchanged. The Bank of Canada plans to replace all bills with polymer bills.

Figure 5 The new $100 bill has two see-through sections and a smooth surface.

1. Research anti-counterfeit technology that is incorporated into Canadian polymer bills. Choose one type and explore how successful this technology is at preventing counterfeiting.
2. Research to find out what properties of BOPP influenced the Bank of Canada to choose it as a material for making notes.
3. Research the advantages and disadvantages of using polymer-based bills compared to traditional cotton-paper bills.

A. List the advantages and disadvantages of using polymer-based bills and cotton-paper bills. T/I

B. How are the polymer bills designed to foil counterfeiters? T/I A

C. How successful are anti-counterfeiting technologies? Do you think this technology could be applied to coins? T/I A

WEB LINK

Properties of Plastics

Most plastics are chemically unreactive. This can be explained by their structure: they are held together by stable single bonds. Because these single carbon–carbon bonds are very strong and less reactive than double bonds, the resulting polymer molecules tend to be very stable chemically. The fact that plastics resist breakage makes them a good replacement for glass in containers for food, water-based liquids, some solvents, and many other chemicals. Some plastics, however, are weakened or even dissolved by non-polar organic solvents. Not all plastics are suitable for all uses.

Plastics are moulded to give them the required shape. Many plastics, such as those used in plastic bags and upholstery foam, are flexible and can be bent and folded. Others, such as those used in car fenders and plastic water bottles, retain their shapes during normal use. What holds the polymer chains together so effectively? Polymer molecules, like all molecules, are attracted to one another by van der Waals forces. Although these intermolecular forces are generally weak on an individual basis, polymer chains are often thousands of carbon atoms long and the attractive forces are additive. Certain substituent groups may also cause electrostatic attractions between molecules.

Most plastics become softer and more flexible when they are heated because heat increases molecular motion. This motion disrupts the intermolecular forces briefly. The polymer chains slide past each other and the plastic becomes stretchy and flexible (**Figure 6**). This allows heated plastics to be shaped.

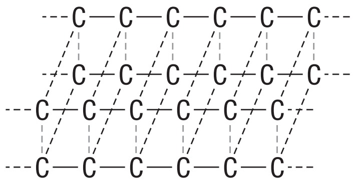


Figure 6 Weak forces between carbon atoms allow the plastic to flex and stretch.

Polyethene plastics are classified according to their density. The most common forms are low-density polyethene (LDPE) and high-density polyethene (HDPE). LDPE is made by adding a small amount of compounds, such as butadiene, that have two or more double bonds. The butadiene results in branches in the polymer chains. These branches prevent the molecules from packing as tightly as those in HDPE, which consist of mostly straight-chain molecules. The branched polymer therefore has a lower density.

LDPE is mostly used for packaging materials (**Figure 7(a)**). The major use of HDPE is for blow-moulded products. These are products in which a bubble of molten HDPE is blown into a mould of the desired shape. Examples of blow-moulded products are milk jugs and bottles for consumer products (**Figure 7(b)**).

Because polypropene has more carbon atoms per monomer than polyethene, it tends to be harder and less flexible. Much of the polypropene that is produced is used for moulded parts, such as bottle caps, parts for appliances and electronics, and plastic toys. The strength of polypropene fibres also makes them useful for manufacturing rope, twine, and carpeting.

Polystyrene flows easily when it is hot, but becomes hard when it cools. Pure polystyrene is hard and colourless, so it is used to make disposable cutlery, DVD cases, and plastic models. When air or nitrogen is injected into the molten polystyrene, it expands into a light, foamy plastic. Expanded polystyrene is used to make cups for hot drinks and building insulation.

Polyvinyl chloride (PVC) also becomes hard when it is cooled. Because it is strong and relatively inexpensive, PVC is widely used in building construction. Door and window frames, water and sewage pipes, and siding are examples of products formed from PVC. Additives make PVC softer and more flexible, so that it can be used as insulation for electrical wires, a waterproof coating for shoes and clothes, and even imitation leather upholstery. PVC is a somewhat controversial material. During its

UNIT TASK BOOKMARK

In the Unit Task, described on page 116, you will consider how solvents interact with other materials.

(a)

(b)

Figure 7 (a) Plastic bags are generally made from LDPE. (b) Plastic bottles with the recycling code “2” are made from HDPE.

use, and especially during incineration after the useful life of an object is over, PVC may release persistent toxic compounds into the environment. These compounds may be harmful to humans and other organisms.

Since having a high molecular mass is associated with a very strong, durable plastic, one might think that polymer chemists' goal would be to produce polymers with chains that are as long as possible. However, this is not necessarily the case. Polymers become much more difficult to process as the molecular mass increases. Molten polymer must be able to flow through pipes as it is processed. As the chain lengths increase, viscosity also increases. The flow requirements of the manufacturing process usually set the upper limit of molecular weight.

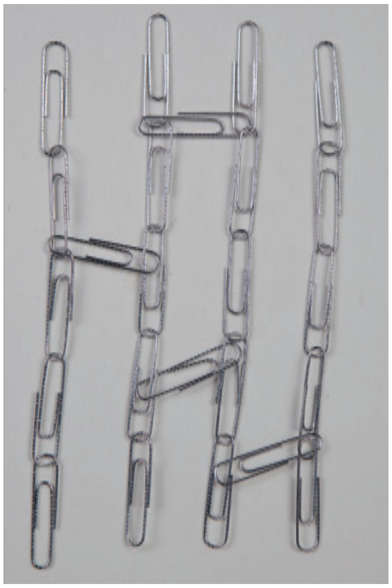


Figure 8 The more paper clips running between the vertical rows, the stronger the structure will be. These are just like cross-links in a polymer.

Plasticizers

In addition to the polymer itself, many plastic products include plasticizers. Plasticizers are substances added to increase flexibility, making the plastics easier to produce and shape into useful objects. Plasticizer molecules are inserted between polymer chains, keeping the chains spaced apart. This slightly weakens the forces that hold the molecules rigidly in place. However, some plasticizers, such as phthalates, have been linked to negative health effects. You will learn more about phthalates in Section 2.3.

Polymer Cross-Linking

All of the polymers illustrated above form long chains by joining monomers. Depending on other functional groups attached to the monomers, individual chains of some polymers can link together. Chemical bonds can form between separate polymer strands in a process called cross-linking. Cross-linking binds multiple polymer chains together to form networks (**Figure 8**). These networks may be two-dimensional or three-dimensional structures.

The properties of a polymer depend on a number of factors including the functional groups present, the number of monomers in the polymer molecule, and the degree of cross-linking that occurs. In general, the more cross-links there are, the more tightly the chains are held together and the more rigid and inflexible the polymer (**Figure 9**).

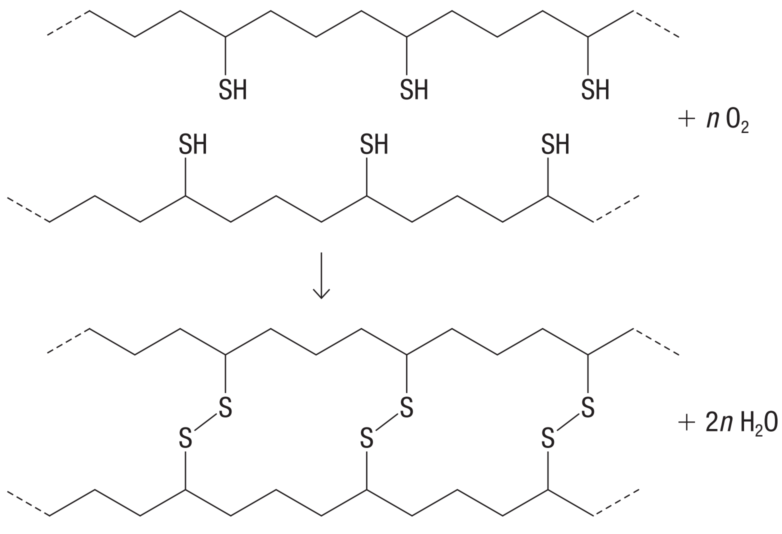


Figure 9 Two polymers with —SH groups can form sulfur–sulfur cross-links.

Dienes are alkenes with two carbon–carbon double bonds. Incorporated into polymer molecules, dienes form strong cross-links from one chain to another. The more dienes that are added to a polymer chain, the more cross-linking will occur. The number of diene monomers added controls the rigidity of the polymer. As cross-links are added, the density of the polymer increases as well. Plastics can be made soft or hard depending on the degree of cross-linking. A hard, dense, inflexible garbage bag would not be that useful nor would a soft, flexible fencepost.

A diene used for cross-linking polymers is 1,4-diethenylbenzene, also called divinylbenzene or DVB. Incorporated into polystyrene, 1,4-diethenylbenzene makes the resulting plastic stronger (**Figure 10**).

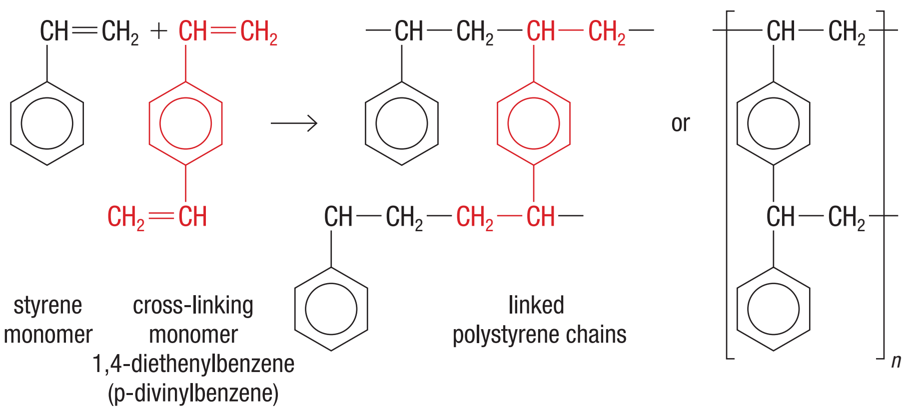


Figure 10 The addition of 1,4-diethylbenzene to polystyrene allows cross-links to form between adjacent polymer chains.

Some cross-linking agents are inorganic. As Figure 9 shows, sulfur is able to form two covalent bonds to connect two different polymer chains. Natural latex from rubber trees is very soft and gooey. The diene monomer in latex, 2-methylbutadiene, forms partially unsaturated polymer chains. This polymerization results in a soft, reactive rubber (**Figure 11(a)**). When sulfur is added to latex and the mixture is heated, the sulfur forms cross-links that make the polymer much tougher and stiffer (**Figure 11(b)**). This process was named "vulcanization" for Vulcan, the Roman god of fire. The cross-links bring the polymer chains back to their original position after the rubber is stretched. The elasticity of rubber makes it suitable for tires, providing a comfortable, bump-less car ride.

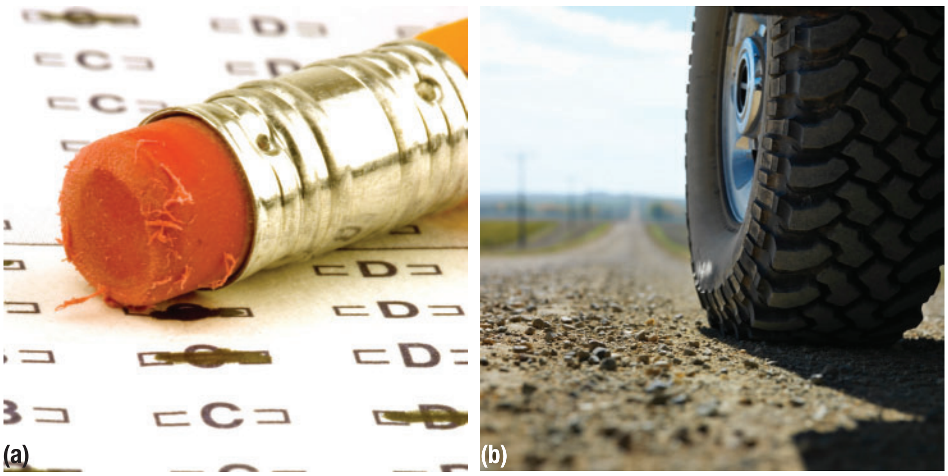


Figure 11 (a) Rubber monomers undergo addition reactions to form a soft rubber polymer. (b) Vulcanization adds sulfur cross-links to the rubber polymer.

Some plastics can withstand more heat than others. This heat tolerance determines how products made from the plastics can be manufactured and used. Some plastics will melt or soften when heated and hold their shape when cooled. These plastics are called thermoplastics and they can be moulded. Thermoplastic polymers do not contain many cross-links. Highly cross-linked plastics will not soften at high temperatures because the cross-links, which are strong covalent bonds, are not overcome by heating. These plastics are called thermoset polymers.

Elastomers are as they sound—elastic. They are polymers with a limited amount of cross-linking, which allows them to stretch and then snap back to their original shape. The polymer chains in an elastomer at rest are condensed and tightly wound up but, when stretched, the chains straighten out. Most elastomers are carbon-based, such as neoprene and rubber. Silly Putty is a type of silicone-based elastomer. It is bouncy and stretchy, and it floats.

Mini **Investigation**

Guar Gum Slime

Skills: Performing, Observing, Analyzing

SKILLS HANDBOOK A1

Guar gum is a natural substance produced by the guar plant. When guar gum is heated in water, it forms polymers that cause the solution to become more solid. Many processed foods include guar gum as a thickener, much like soluble cornstarch that thickens gravy. Oil drillers also mix guar gum into the slurry that they pump into oil wells.

Sodium borate (borax) is a cleaning agent often used for laundry. It is a hydrated ionic compound made up of sodium and polyatomic borate ions: $Na_2B_4O_7 \cdot 10\ H_2O(s)$. In solution the borate ions react with certain organic compounds to form cross-linked polymers. In this investigation, the borate ions link with –OH groups in the guar gum molecules to form a cross-linked substance with interesting physical properties.

Equipment and Materials: lab apron; chemical safety goggles; 250 mL beaker; wooden stir stick; 100 mL measuring cylinder; electronic balance; 100 mL beaker; aluminum pie plate; 110 mL warm distilled water; food colouring (optional); 1.0 g guar gum powder; 0.4 g sodium borate, $Na_2B_4O_7(s)$

Sodium borate is an irritant. Avoid skin and eye contact. If the solution splashes onto your skin or into your eyes, wash the affected area for 15 min with plenty of cool water and inform your teacher. Wash your hands at the end of the investigation.

Do not consume anything in the laboratory or remove anything from the laboratory to consume later.

1. Put on your lab apron and chemical safety goggles.
2. Add 100 mL of warm water to the 250 mL beaker. Add food colouring (optional). Slowly add the guar gum powder, stirring constantly with the stir stick to dissolve the powder.
3. Add 10 mL of warm water to the 100 mL beaker. Add the sodium borate crystals to the water.
4. Add the sodium borate solution to the guar gum solution. Immediately begin stirring the mixture with the stir stick. Within a couple of minutes, a slimy substance will form.
5. Lift some of the "slime" out with the stir stick and place it on the aluminum pie plate. The mixture is safe to touch. Use your hands to manipulate the slime. Try stretching, poking, and slapping it. Move it quickly and slowly. Record your observations.

A. What happened when you first started stirring the mixture? K/U T/I
B. What happened after stirring for a few minutes? K/U T/I
C. Describe the appearance and properties of the slime. Are the properties constant, or do they vary? K/U T/I
D. Describe how cross-linking gives this mixture its properties. K/U T/I
E. How might the use of guar gum by the oil-drilling industry affect the price of food? Comment on the implications of this. A

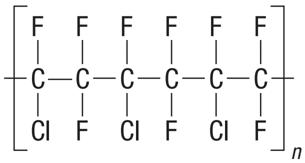
2.2 Review

Summary

- Addition polymers form when monomers link during addition reactions.
- The properties of addition polymers can be varied by selecting monomers with certain substituent atoms or groups, particularly by adding substances that can form cross-links between polymer chains.
- Plastics are synthetic substances that can be moulded, often under heat and pressure. Plastics that can be heated and formed in moulds are called thermoplastics. Those that cannot be heated and formed are called thermoset polymers. Elastomers are flexible polymers that return to their original shape after being stretched.

Questions

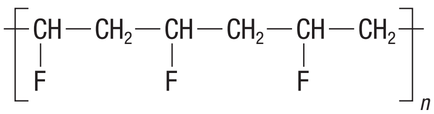
1. Kel-F is a polymer with the structure



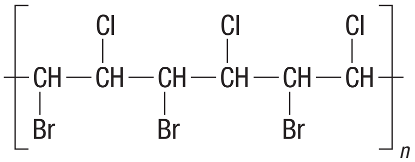
Name and draw the monomer for Kel-F. K/U C

2. Write the name and formula of the monomer that could be used to produce each of the following polymers: K/U C

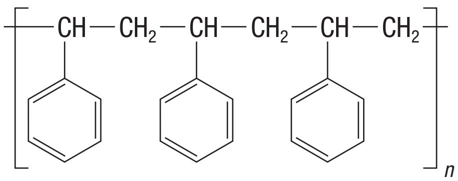
(a)



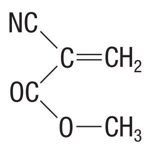
(b)



(c)



3. "Super glue" contains methyl cyanoacrylate.



When it is exposed to water or alcohols (for example, on two surfaces to be bonded), ethyl cyanoacrylate quickly polymerizes. Draw the structure of the polymer formed by methyl cyanoacrylate. K/U C

4. Explain how cross-linking occurs and what effects it has on the properties of a polymer. K/U T/I
5. Polystyrene can be made more rigid by copolymerizing styrene with p-divinylbenzene. K/U C
   (a) Draw the structure, and write the IUPAC name, of p-divinylbenzene.
   (b) How does p-divinylbenzene make the copolymer more rigid?
6. Scientists have developed polymers that can "heal" from scratches, much as skin heals. Research how these polymers repair themselves and where they might be used. Prepare an illustrated presentation or blog post to share your information with salespeople in the plastics industry. T/I C A
7. Recycling programs are in place in most parts of Ontario, but not all types of plastic can be recycled. T/I C A
   (a) What are the different classes of plastic? Summarize your findings in a table.
   (b) Find out what types of plastic cannot be recycled in your region, and why.
   (c) How long does it take for plastic garbage bags to decompose in a landfill site?
   (d) What can you do, personally, to reduce the environmental impact of plastics?
8. Polystyrene is a popular packaging material. T/I C A
   (a) What properties of polystyrene make it particularly useful for packaging?
   (b) What biodegradable materials can be used as an alternative packaging material?
   (c) In a graphic organizer, compare polystyrene and the alternative materials.
   (d) Decide which you feel is the better choice. Defend your decision.

WEB LINK