

* APPLICATION AND INVESTIGATION

- Investigation 1 Evaluate arguments for and against conserving fossil fuels only for the synthesis of useful chemical products.
- 2 a Explain the dual purposes of cracking higher boiling point fractions obtained from the distillation of crude oil.
b Describe the process of catalytic cracking.
c Distinguish between catalytic cracking and thermal cracking.
- 3 Construct a balanced chemical equation for the catalytic cracking of heptane (C_7H_{16}).
- Investigation 4 Research and identify how zeolite catalysts can be developed for particular purposes.
- 5 Explain why alkenes are susceptible to addition reactions.
- 6 Predict and name the products formed in the following reactions:
a propene with Cl_2
b 1-butene with HCl
c ethylene with H_2O in the presence of a catalyst.
- 7 Plan a method for the preparation of the following compounds:
a 2-chloropentane
b 1,2-dichloropentane
c 2-propanol.
- 8 Design an experiment to distinguish between samples of cyclohexane and cyclohexene. Justify your procedure by explaining the observations you would expect to make.
- Investigation 9 Gather and present information from secondary sources to identify whether ethylene is produced at an industrial plant in New South Wales. If so, identify:
a the method of production
b the major uses of the ethylene produced.

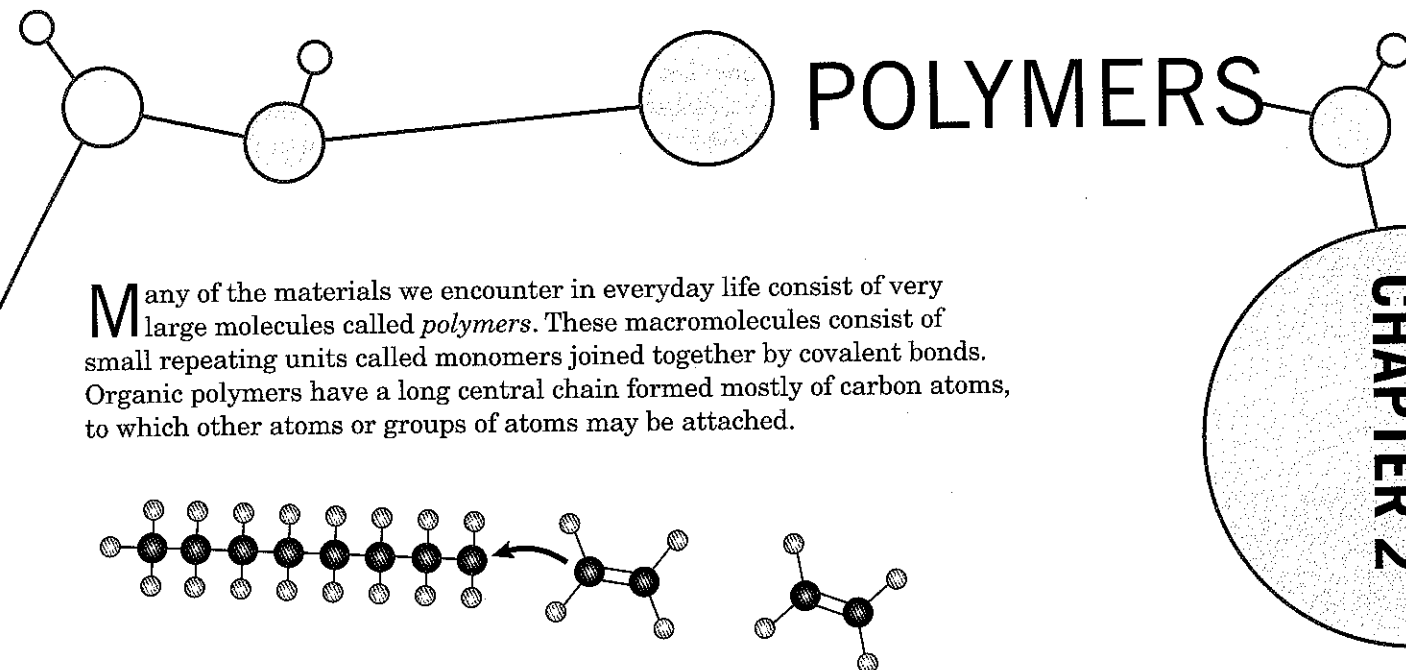
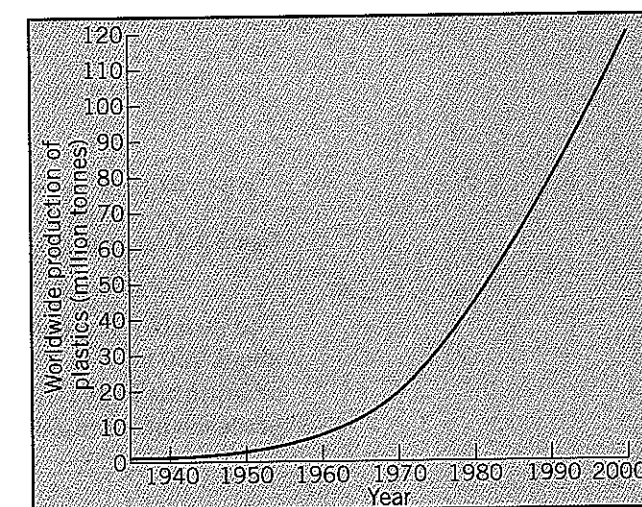


Figure 2.1 Polymers form by monomers joining together to form a chain.

For convenience we can divide polymers into two classes: natural and synthetic. Naturally occurring polymers such as rubber, cellulose, silk, wool and starch have been known and used by humans since ancient times. Over the past one hundred years, synthetic polymers have become increasingly important materials in our society. These synthetic polymers include polyethylene, PVC, PET, Teflon, polyester, nylon and rayon. Synthetic polymers in the form of plastics, films, fibres and synthetic rubber have replaced wood, paper, wool, cotton, natural rubber and other natural materials in many applications. Because they do not corrode, are lightweight and relatively cheap to produce, they are also replacing metals in many more. The packaging of our foods and goods, the buildings we live in, the cars we drive, the appliances we use, even the shoes and clothing we wear, have made use of synthetic polymers.

Synthetic polymers are, however, a fairly recent development. The first commercially produced plastic was celluloid, a modified form of the natural polymer cellulose. Celluloid could be moulded into a hard plastic or a thin film. It was used as a substitute for ivory to make such things as billiard balls, and at one stage was used to make movie film. A major problem with its use was its highly flammable nature. A number of movie theatres burned down as a result of heat from the projector causing the celluloid film to catch alight. When safer substitutes became available, celluloid was replaced in most applications. Today it is still used in the manufacture of ping-pong balls. The first truly synthetic polymer produced was Bakelite.

Figure 2.2 Worldwide production of plastics has increased dramatically over the past 70 years.



Developed by Leo H. Baekeland in 1907, Bakelite is a hard, strong plastic that was used to make telephones, electrical devices, gramophone records and cabinets. It was from this point that the plastics industry began to grow rapidly.

Today a huge variety of synthetic polymers with a wide range of properties are available. Many of these polymers have been designed for particular applications. For example, Kevlar, a polymer, is stronger than steel but much lighter. It is used in racing yacht sails, to reinforce some leisure boats, and in ballistic (bulletproof) vests.

2.1 Polymerisation reactions

The chemical reaction by which monomers become linked to form polymers is known as *polymerisation*. These monomers, many of which are synthesised from petroleum or coal, bond together to form large molecules of repeating units in the polymer.

For this process to occur, the monomers must have a structure that can change to accommodate the additional bond needed to join the repeating units together. There are two major types of polymerisation reactions: addition polymerisation and condensation polymerisation.

Addition polymerisation

In the process of *addition polymerisation*, the monomers simply add to the growing polymer chain in such a way that all the atoms present in the monomer are also present in the polymer. Addition reactions involve unsaturated monomers (containing a carbon-carbon double bond) joining together. In this reaction, one of the bonds in the C=C double bond is broken and the resulting molecules link up. This occurs because breaking the bond provides each carbon atom with extra bonding capacity, which it uses to form bonds between the monomers. This is illustrated in the equation for the polymerisation of ethylene in Figure 2.3.

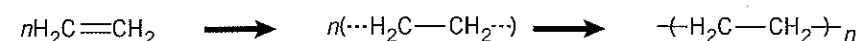
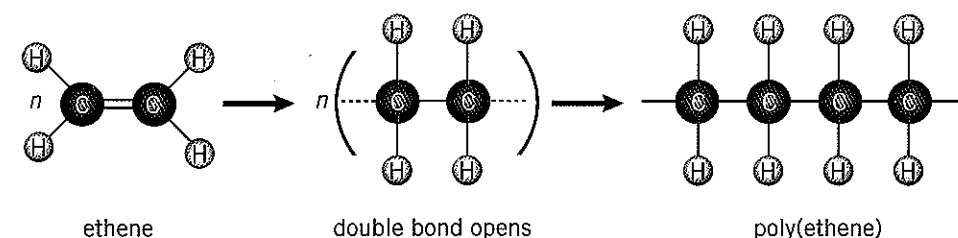


Figure 2.3 Addition polymerisation of ethylene

The number of monomer units that make up addition polymers ranges from about 100 to over 100 000. Addition polymerisation reactions require a catalyst or initiator to get the reaction started. Once it is under way, however, the reaction proceeds quite rapidly as addition polymerisation is a chain reaction.

Polyethylene, polyvinyl chloride (PVC), polystyrene and Teflon are well-known synthetic polymers formed by addition polymerisation. The production and uses of some of these important polymers are discussed in detail in Unit 2.2.

Condensation polymerisation

Condensation polymerisation involves a reaction between two different functional groups in which a molecule of water (or some other small molecule) is eliminated and the two functional groups become linked together. Condensation polymerisation usually involves a reaction between two different monomers, as shown in Figure 2.4, but can occur where a molecule contains two different functional groups (Figure 2.5). The most common type of condensation polymerisation occurs between monomers containing a carboxylic acid group (–COOH) and either an alcohol (–OH) or an amine group (–NH₂). Many natural polymers such as cellulose, starch, glycogen, silk, wool and proteins, and synthetic polymers such as nylon, polyethylene terephthalate (PET) and Kevlar, are formed by condensation polymerisation.

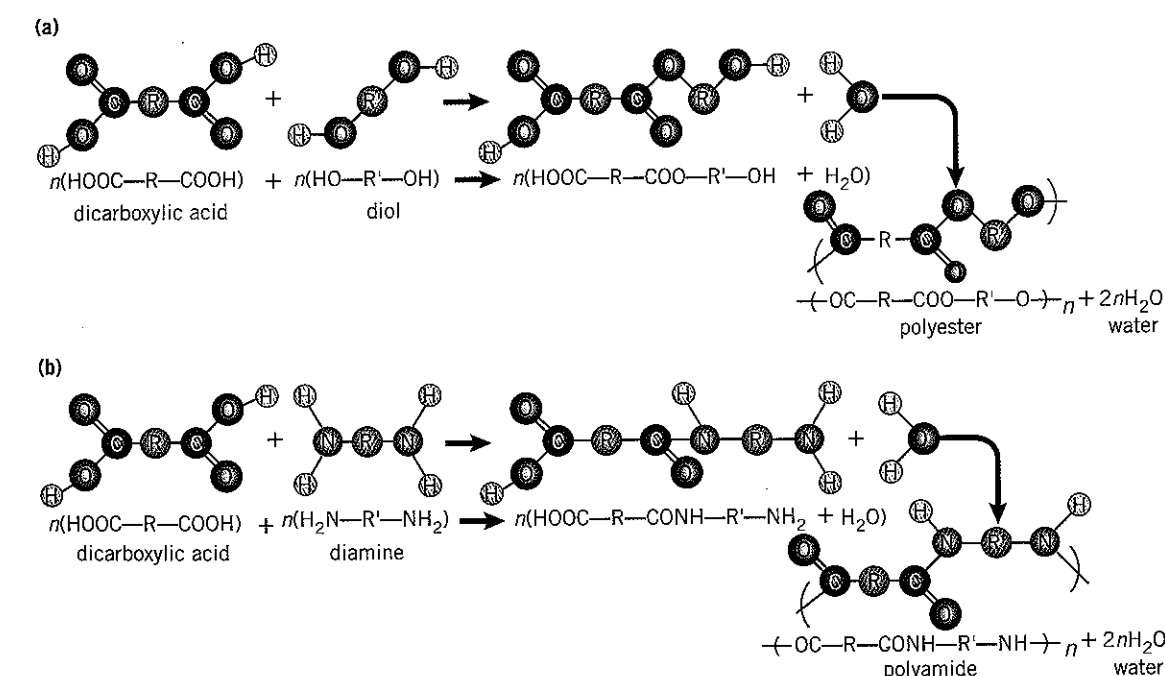


Figure 2.4 Formation of (a) polyesters and (b) polyamides by condensation polymerisation

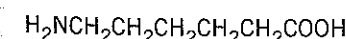
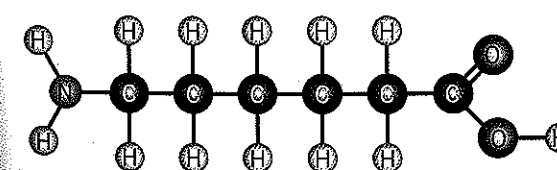


Figure 2.5 The structure of 6-aminohexanoic acid, which contains two different functional groups capable of undergoing condensation polymerisation

CHEMISTRY CONTEXT

* TWO IMPORTANT POLYMERS

Polytetrafluoroethene (Teflon): an addition polymer

Polytetrafluoroethene, better known by its trade name, Teflon®, is formed by the addition polymerisation of tetrafluoroethene, as shown in Figure 2.6. Teflon forms a tough, almost frictionless surface that is very resistant to heat and chemicals. This makes it ideal as a coating on non-stick frypans, greaseless bearings, chemically resistant liners and skis.

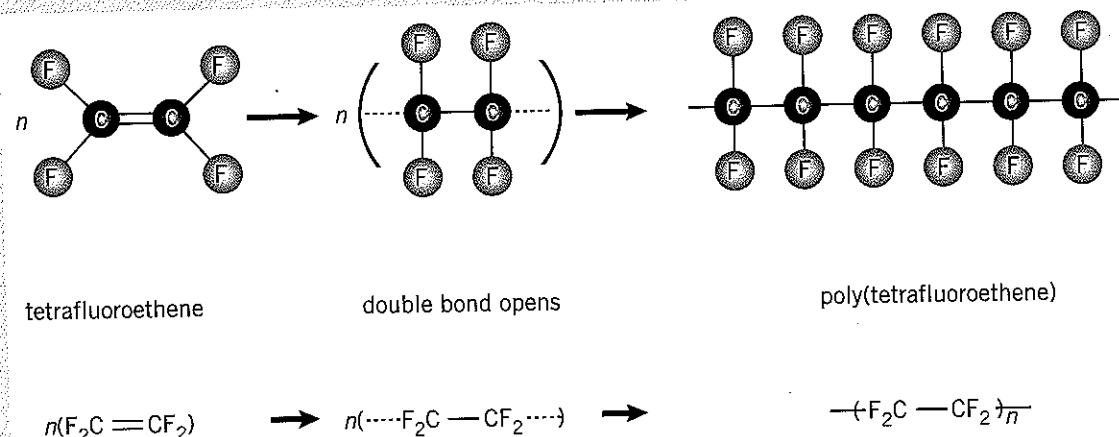


Figure 2.6 Equation for the polymerisation of tetrafluoroethene

Polyethylene terephthalate (PET): a condensation polymer

Polyethylene terephthalate, commonly referred to as PET, is a polyester formed by the condensation polymerisation of 1,2-ethanediol and terephthalic acid. It is used in drink bottles, food packaging, photographic film, audio and video tape, clothing fibres under trade names such as Dacron and Terylene, windsurfer sails, synthetic blood vessels and as a skin substitute for burn victims.

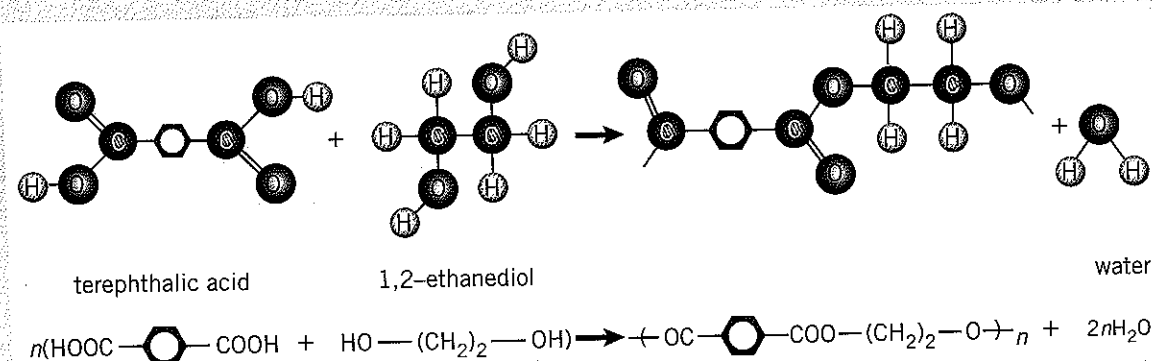


Figure 2.7 General equation for the condensation polymerisation of ethylene glycol and terephthalic acid

Factors affecting the properties of polymers

The properties of a polymer, including its strength and flexibility, are determined by a number of factors, including:

- **the length of the chain (the number of monomer units).** Plastics composed of longer polymer chains are stronger than those with shorter chains. This is because longer polymers have greater dispersion forces between them.
- **the arrangement of the chains with respect to each other.** When the molecules are lined up and closely packed, they form crystalline regions (Figure 2.8), resulting in a stronger, less flexible polymer. Amorphous regions, in which the polymer chains have a more random arrangement, produce weaker and softer plastics. Drawing polymer fibres through a small hole (called a *spinneret*) aligns them and gives the fibre greater strength (Figure 2.9).
- **the degree of branching from the chain.** More branching restricts the orderly packing arrangement and therefore reduces the density and hardness of the polymer but increases its flexibility. (See LDPE and HDPE in Unit 2.2.)
- **functional groups in the monomer units.** Polar functional groups on the monomers increase the intermolecular forces between polymer molecules. Hydroxyl ($-\text{OH}$) and amine ($-\text{NH}_2$) groups result in hydrogen bonding between polymer molecules. Increased intermolecular forces will increase the hardness of the plastic.
- **cross-linking between polymer chains.** Thermosetting plastics have covalent bonds linking polymer chains together (as shown in Figure 2.13 on p. 20). This makes the polymer very hard and difficult to melt. These covalent bonds cannot be broken by heat without decomposing the plastic. Thermoplastics, on the other hand, have no cross-linking. They tend to consist of many long chains with weaker intermolecular forces between the chains (as shown in Figure 2.11 on p. 19). Heating allows the chains to be rearranged. The special properties of elastomers result from the overlapping arrangement of the polymer chains and a lesser amount of cross-linking between chains than exists in thermosetting plastics (see Figure 2.15 on p. 21).
- **the inclusion of additives.** Very few polymers are used in their pure form. Most have additives, which are included to improve or extend the properties of the polymer. These additives include pigments to give the desired colour, plasticisers to soften the material, stabilisers to increase resistance to decomposition by heat and/or ultraviolet radiation, and flame retardants to reduce flammability.

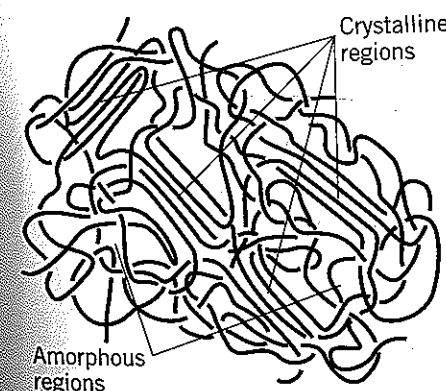


Figure 2.8 Crystalline and amorphous regions of a polymer

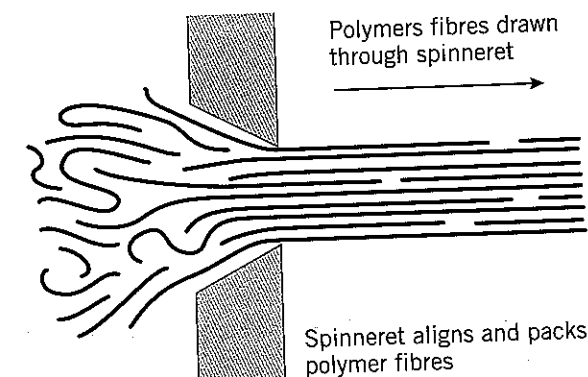
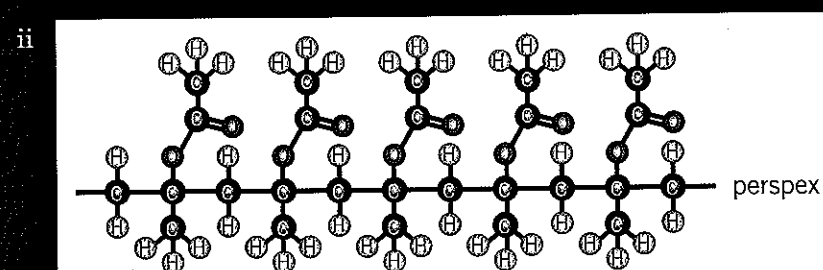
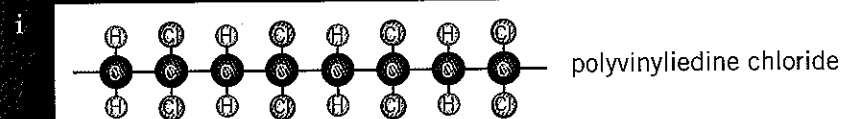


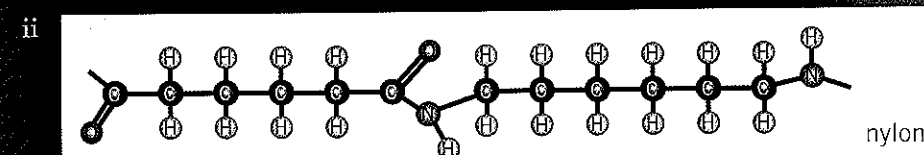
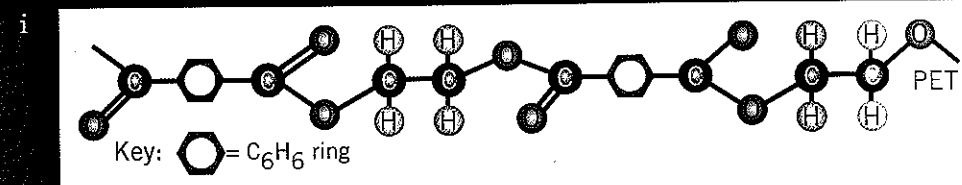
Figure 2.9 Drawing polymer fibres through a spinneret results in closer packing of the polymer chains and increased strength.

* Review exercise 2.1

- 1 Define polymerisation.
- 2 Distinguish between addition polymerisation and condensation polymerisation reactions.
- 3 Identify the structural features shared by monomers that undergo:
 - a addition polymerisation
 - b condensation polymerisation.
- 4 a Draw the structural formula of the monomer that forms each of the following addition polymers:



- b Draw the monomer(s) that form each of the following condensation polymers:



- 5 Propylene (propene) ($\text{CH}_2=\text{CH}-\text{CH}_3$) can undergo addition polymerisation. Construct an equation to indicate how polypropylene is formed from propylene.
- 6 The structure of the monomer 6-aminohexanoic acid is shown in Figure 2.5. Draw three repeating subunits to show how this condensation polymer forms.
- 7 Assess how the hardness of a polymer changes with the following factors:
 - a increased branching of polymer chains
 - b cross-linking between polymer chains
 - c decreasing the length of polymer chains
 - d increasing the orderly arrangement of polymer chains
 - e addition of a plasticiser to the polymer.

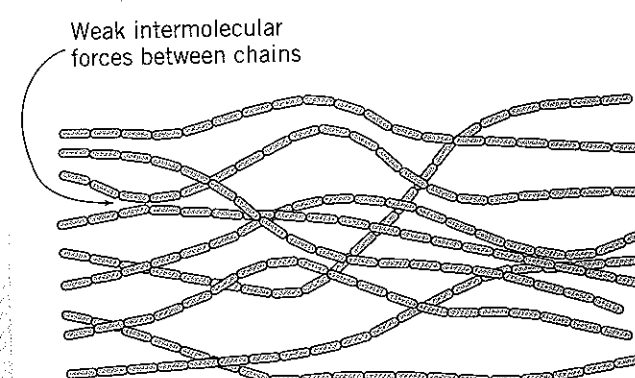
CHEMISTRY CONTEXT

* THERMOPLASTICS, THERMOSETTING PLASTICS AND ELASTOMERS

Polymers are often classified as thermoplastics, thermosetting plastics or elastomers. These different groups have specific properties.

Thermoplastics

Thermoplastics are plastics that become soft and flexible when heated but on cooling become harder again. As a consequence, these plastics are readily reshaped and remoulded. Various moulding processes are used to manufacture the large range of toys, containers, bottles, bins and films made from thermoplastic materials (Figure 2.11). Examples of thermoplastics are polyethylene, polystyrene, PVC, perspex and nylon. Thermoplastics tend to consist of many long chains with weak intermolecular forces between the chains, as shown in Figure 2.10. Heating allows the chains to be rearranged.



Thermoplastics

- Consist of many long chains with weak dispersion forces between chains.
- Chains can easily slide past each other when heated or stretched.

Figure 2.10 The structure of thermoplastics

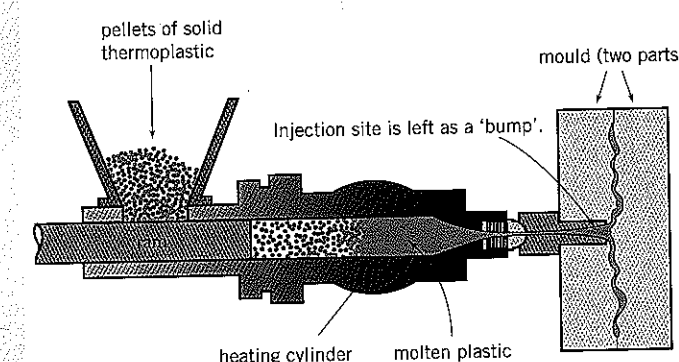
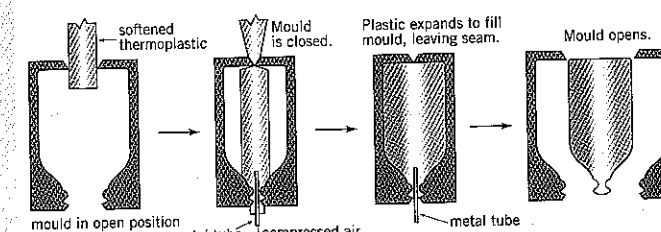
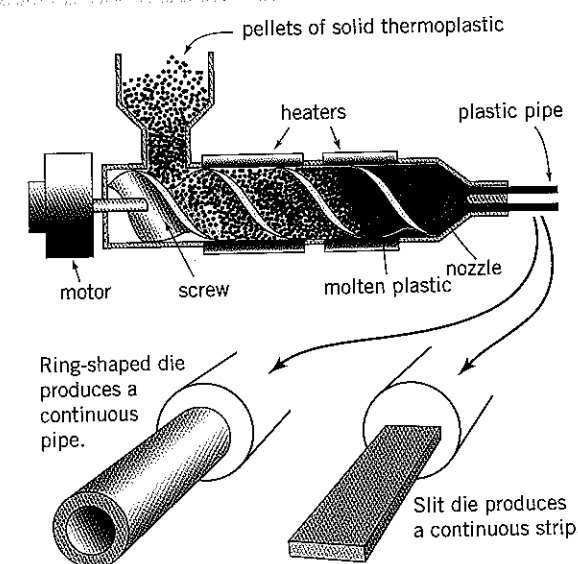


Figure 2.11 Various moulding processes are used to manufacture products from thermoplastics.

CHEMISTRY CONTEXT, cont.

Thermosetting plastics

Thermosetting plastics are hard plastics that cannot be softened by heating after the plastic has been formed. Urea-formaldehyde, phenol-formaldehyde (Bakelite), melamine-formaldehyde (Formica) and epoxy resins such as Araldite are examples of thermosetting plastics. These are used in electrical switches, heat-resistant handles and in laminates on kitchen and bathroom benches and cupboards (Figure 2.12). In these plastics there is a significant amount of cross-linking in the form of covalent bonds between the chains, as shown in Figure 2.13. These covalent bonds cannot be broken by heat without the plastic undergoing a change in its chemical structure.

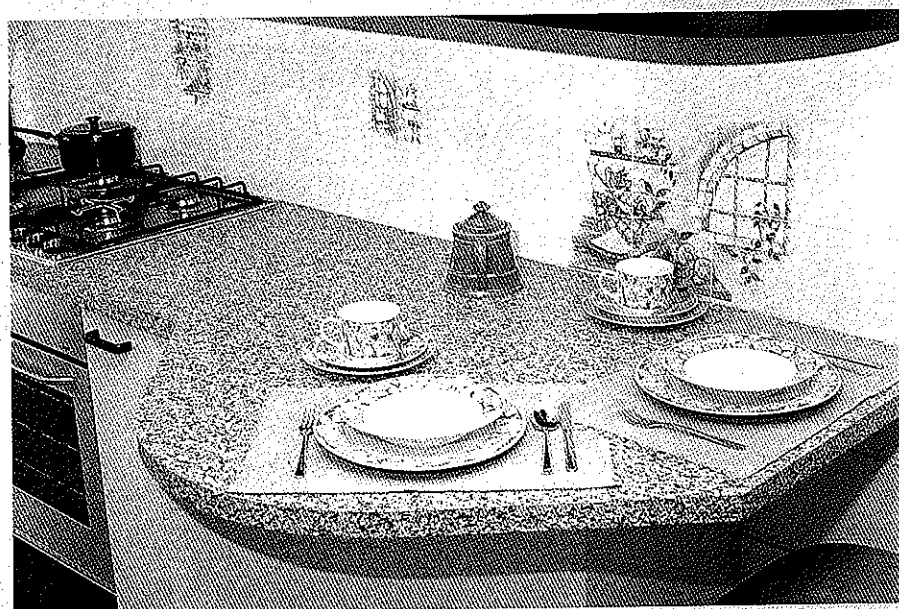
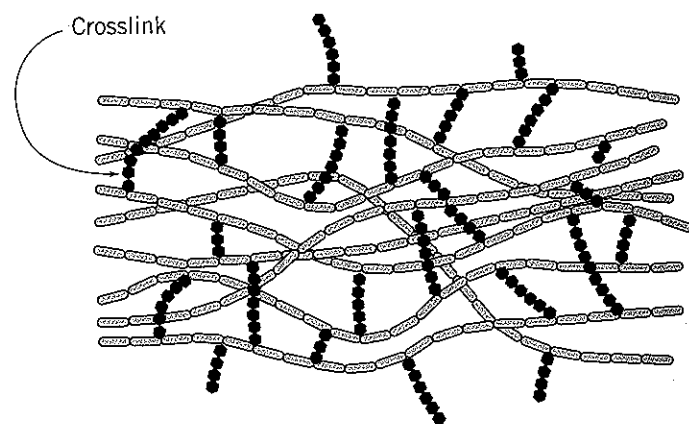


Figure 2.12 Kitchen laminate, an example of a thermosetting plastic



Thermosetting plastics

- Consist of long chains with many crosslinks between chains.
- Cannot be softened by heating.

Figure 2.13 The structure of thermosetting plastics

CHEMISTRY CONTEXT, cont.

Elastomers

Elastomers are polymers that can be stretched by applying some force but revert to their original shape when the distorting force is removed. Vulcanised natural rubber and synthetic rubbers are examples of elastomers (Figure 2.14). This capacity to revert to the original shape is due to the overlapping nature of the chains and a degree of cross-linking. This allows the chains to be stretched out but the cross-linking pulls the chains back into their overlapping arrangement when the distorting force is removed, as can be seen in Figure 2.15.

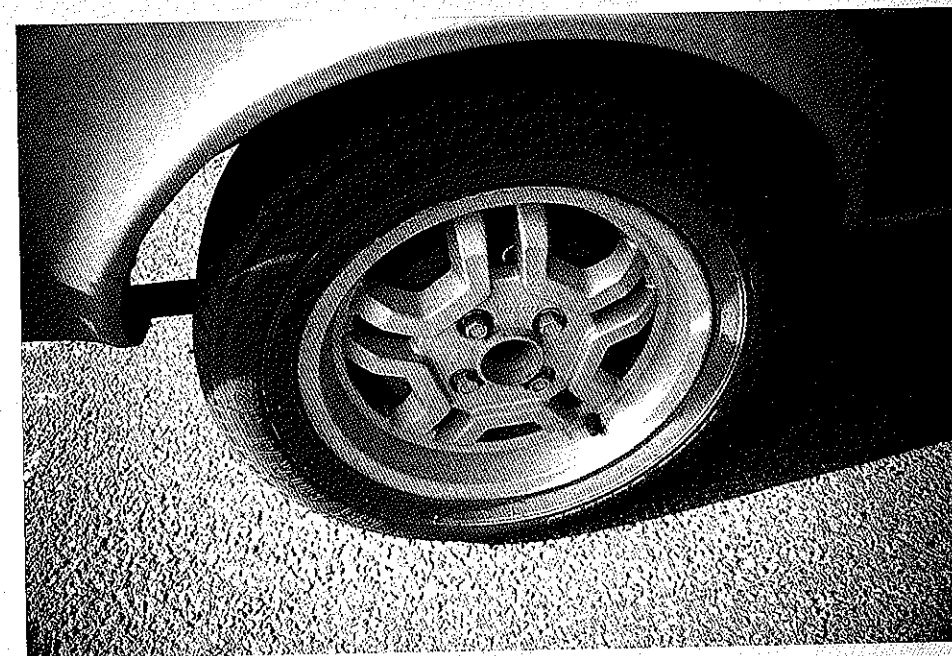


Figure 2.14 A rubber tyre, an example of an elastomer

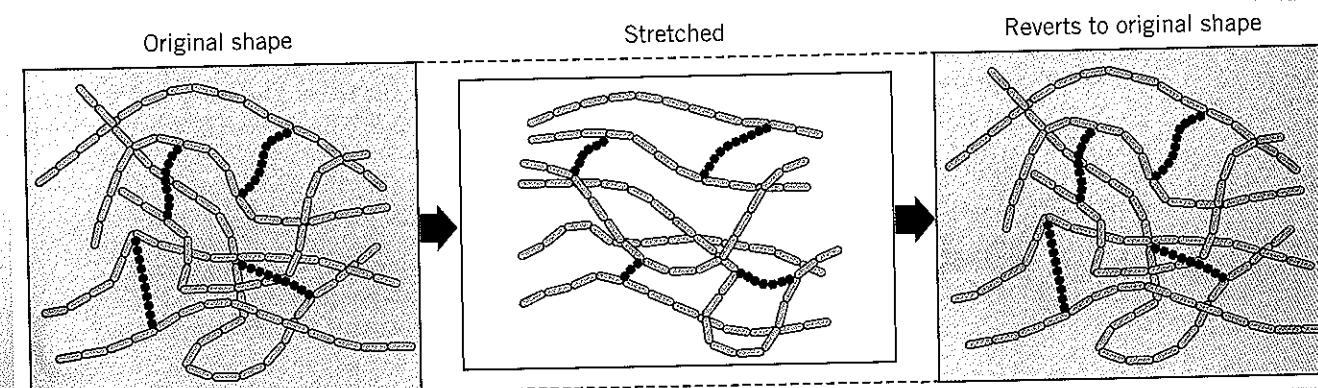


Figure 2.15 The structure of elastomers

Fibres

A *fibre* is a long, strong, threadlike structure made up of many polymer molecules. Natural fibres include wool, cellulose and silk, while synthetic fibres include nylon, polyester and acrylics. Fibres have a vast range of applications, including: the manufacture of thread, fishing lines, nets and ropes; nylon hosiery; fabrics for clothing of all types; and to strengthen tyres and many other composite materials. The properties of fibres depend on several factors, including the nature of the functional groups present in the polymer, the length of the polymer chains, the strength of the forces between the polymer chains, and the treatment of the fibre.

Elastomers

- Consist of partially coiled chains with some cross-linking.
- The chains can be stretched out but return to their original arrangement when the distorting force is removed.

2.2 Commercially and industrially important synthetic polymers

Ethylene and its derivatives are particularly useful starting materials for addition polymerisation reactions. These molecules possess a double bond and readily undergo addition polymerisation, as shown in Figure 2.16.

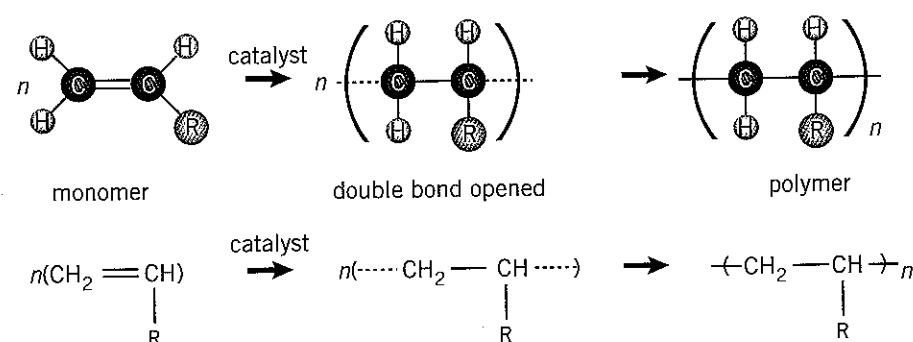


Figure 2.16 General equation for the addition polymerisation of monomers derived from ethylene

Ethylene, with the structure $\text{CH}_2=\text{CH}_2$, is the simplest monomer capable of undergoing addition polymerisation. Many other monomers can be produced by replacing one or more hydrogen atoms in ethylene with a different atom or group of atoms. Some important monomers are shown in Figure 2.17. The different atom or group attached to the ethylene molecule modifies the properties of the polymer it forms. Thus by substituting the hydrogen atoms of ethylene molecules with new groups, chemists can 'design' polymers for particular uses. The uses and properties of some important polymers derived from ethylene are described in the next section.

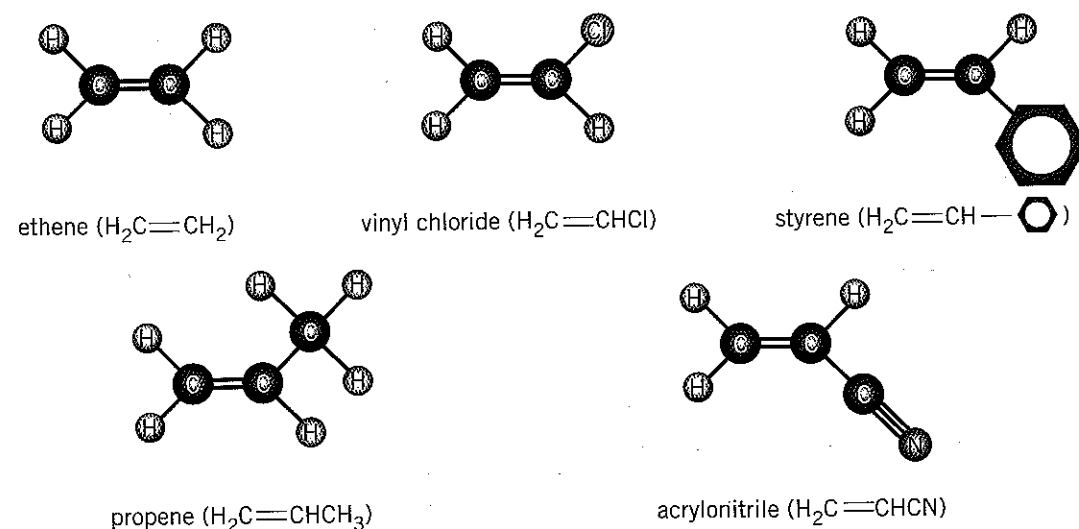


Figure 2.17 Some important monomers that undergo addition polymerisation reactions

Polyethylene: the number one synthetic polymer

Ethylene can be changed from a gas to a liquid by subjecting it to high pressure. If the liquid ethylene is then heated in the presence of a catalyst, the ethylene molecules join together to form a long chain or polymer called polyethylene, also known as polyethene and polythene, as shown in Figure 2.18.

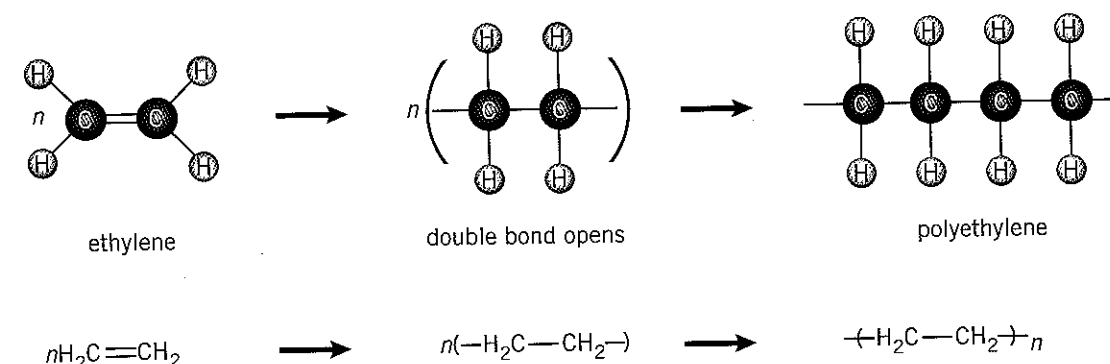


Figure 2.18 Equation for the polymerisation of ethylene

The number of monomer units (n) that make up a polyethylene molecule, and hence the length of the chain, varies greatly but is generally in the range of 1000 to 50 000 units. These chains are like strands of spaghetti. They may be tangled up to form an amorphous mass or they may be aligned in parallel strands. A more orderly arrangement of the polymer chains results in stronger dispersion forces between neighbouring molecules and thus greater hardness and strength. However, when the polymer chains are oriented randomly, the dispersion forces are weaker and the structure has less strength.

There are two forms of polyethylene: *low-density polyethylene (LDPE)* and *high-density polyethylene (HDPE)*. Both forms are thermoplastic, non-toxic, impermeable to water (waterproof), resistant to most chemicals and excellent insulators. The low-density form is less dense, softer and more flexible than the high-density form.

The differences in properties between these two forms are dependent on the degree of branching of the polymer chains. In LDPE, the degree of branching is much greater and this reduces the dispersion forces between the strands. This results in soft, flexible, low-density plastics with relatively low melting points. Figure 2.19 illustrates how LDPE has more branching than HDPE, which consists mostly of straight-chain molecules. The branching in LDPE means the polymer chains cannot pack as tightly together. Consequently, the density of the material is reduced. In HDPE, on the other hand, the polymer chains can pack more tightly due to the presence of fewer side branches. As a result, extensive dispersion forces exist between molecules. This gives HDPE strength and toughness but makes it less flexible than LDPE. The degree of branching, and hence the density of the polymer, is determined by the conditions and catalysts used in the manufacturing process.

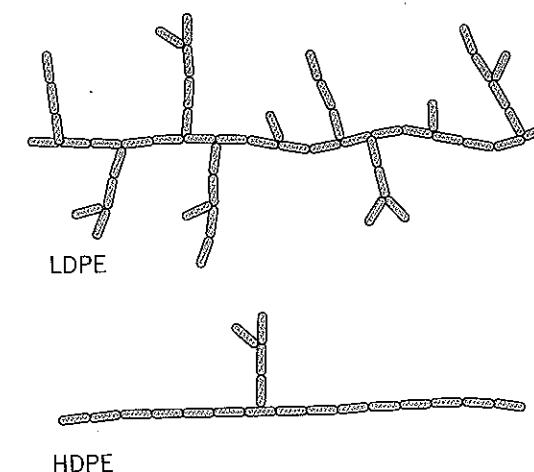
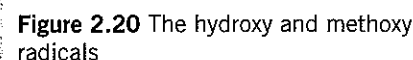
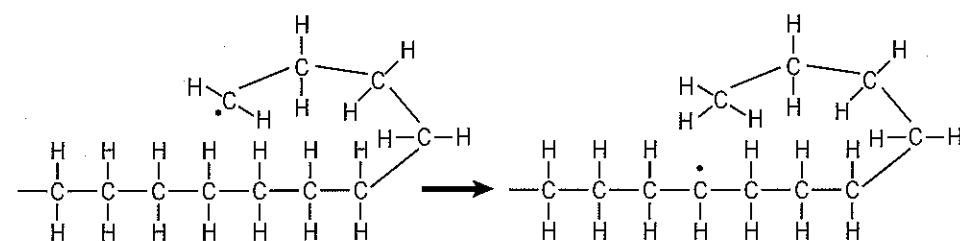


Figure 2.19 Branching in LDPE and HDPE



The polymerisation process consists of three stages: initiation, propagation and termination. During the production of LDPE, the reaction is initiated with a catalyst, usually an organic peroxide. These peroxides produce free radicals (molecules with at least one unpaired electron). The radical $R-O\bullet$, where R represents an alkyl group and \bullet represents an unpaired electron, is electron deficient and attacks the double bond in the ethylene. This causes one of the bonds between carbon atoms in the $CH_2=CH_2$ molecule to break, and a covalent bond is formed between one of the carbon atoms and the radical. The resulting molecule, $R-O-CH_2CH_2\bullet$, is itself a radical and will attack the double bond in another ethylene molecule, resulting in the 'addition' of another $-CH_2CH_2-$ group. This process continues and so the polymer chain rapidly grows. These reactions are referred to as *chain propagating reactions*.

At various times it is possible for two free radical polymers to react to form a covalent bond. This type of reaction is called a *chain terminating reaction* (Figure 2.22).



The radical is now in the middle of the chain from where a branch will grow.

Figure 2.21 'Backbiting' results in branched polymer chains.

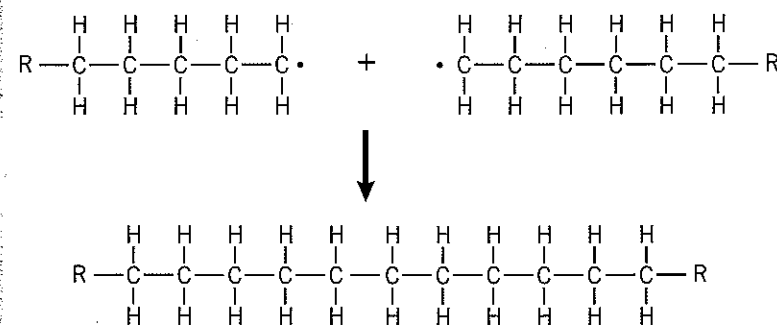


Figure 2.22 Chain terminating reactions are those in which two polymer radicals combine to form a covalent bond.

Production and uses of high-density polyethylene

HDPE is used in the manufacture of pipes to carry natural gas. Because of its chemical resistance it can be moulded into various containers to hold petrol, oil, detergents, acids and solvents. Its durability and toughness make it an ideal material for the manufacture of children's toys, plastic buckets, lunch boxes and playground equipment. HDPE can also be made into tough films such as freezer bags.

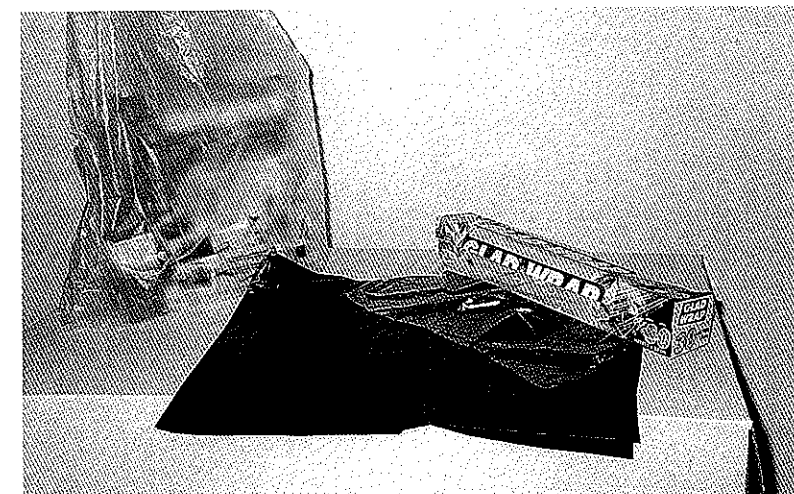


Figure 2.23 Some items made from low-density polyethylene

Polyvinyl chloride: versatile PVC

Pure PVC is not a particularly useful plastic, as it is hard, very brittle and tends to decompose when heated. However, the inclusion of various additives to improve its flexibility and thermal stability have so greatly extended its range of uses that the production of PVC is now only exceeded by that of LDPE and HDPE. Depending on the additives used, PVC can be rigid as in water pipes, or flexible like a garden hose. Rigid forms of PVC are widely used in the building industry for external cladding, guttering and down pipes, electrical conduit, waste water



Figure 2.24 Some items made from high-density polyethylene

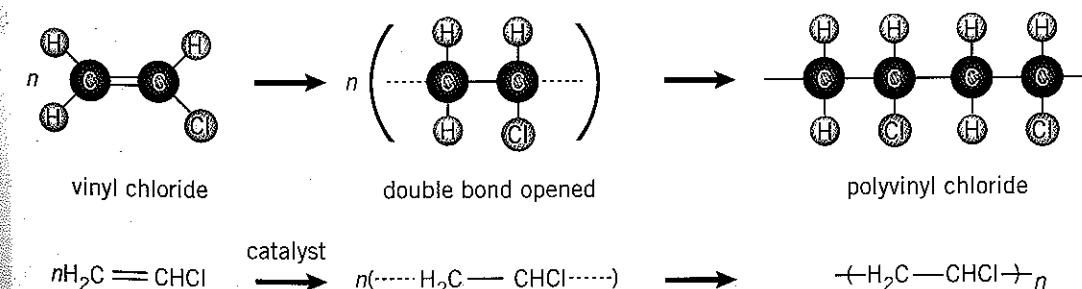


Figure 2.25 Equation for the polymerisation of vinyl chloride (chloroethylene)



Figure 2.26 Polyvinyl chloride (PVC) has many applications. These raincoats are made from PVC.

pipes, rigid panels and floor tiles. Kitchen utensils and credit cards are also made of PVC. More flexible forms of PVC are used as upholstery coverings for cars and furnishings, electrical insulation and garden hoses. Because it is impervious to oils and most organic materials, PVC is used to make bottles to hold these materials. There has been some debate in recent years that the plasticisers used to increase its flexibility can leak out of the plastic and may have health risks associated with their use, particularly when PVC is used in children's toys or food containers.

Polystyrene

Polystyrene or polyphenylethylene is another useful polymer. The phenyl group replaces one of the hydrogen atoms in the ethylene molecule forming the monomer phenylethylene (also known as ethenylbenzene), more commonly known as styrene. Polystyrene comes in many forms, the most familiar of which is polystyrene foam, sold under the trade name Styrofoam®. Styrofoam is produced by blowing gas through liquid polystyrene until it froths up into a foam, which is then allowed to cool and solidify. Until 1990, chlorofluorocarbons (CFCs) were used for this purpose but their role in the depletion of the ozone layer (see Unit 13.3) has resulted in hydrocarbon gases being used instead. The gases trapped in the foam make Styrofoam an excellent lightweight insulator. Therefore Styrofoam finds uses as

disposable insulating cups, ice boxes, fast food containers and packing material. Its low density has also resulted in its use in body boards and as the core of surfboards.

Polystyrene can also be produced as a hard, clear, brittle plastic. This form is used in the manufacture of audio cassette and CD cases and clear plastic drinking glasses. With different production techniques and additives, including colouring agents, this tough form of polystyrene can also be used to make many other products including computer and television cabinets, wall tiles and sturdy furniture.

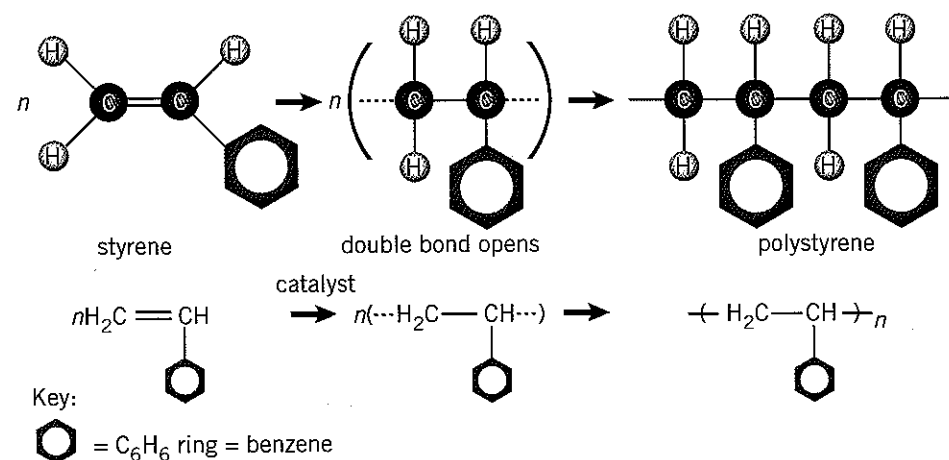


Figure 2.27 Equation for the polymerisation of styrene (phenylethylene)

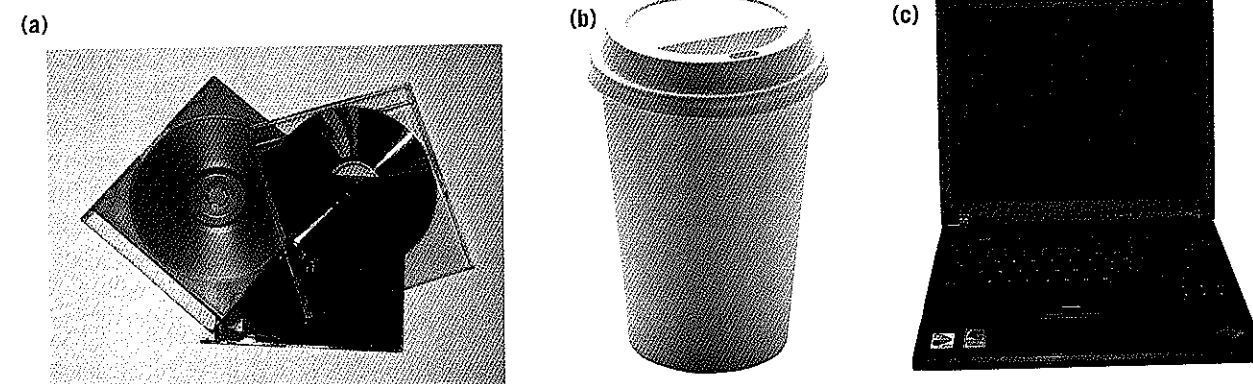


Figure 2.28 Some items made from polystyrene (polyphenylethylene) (a) CD cases (b) Styrofoam® cup (c) Computer casing

* Review exercise 2.2

- Construct** equations to represent the formation of the following addition polymers:
 - polyethylene
 - polystyrene
 - polyvinyl chloride
- Identify** the systematic names of the following monomers:
 - vinyl chloride
 - styrene
- Account** for the difference in the properties of LDPE and HDPE, in terms of their structure.
- If a sample of PVC has polymer chains containing, on average, 15 000 monomer units, **calculate** its molar mass.
- Identify** a suitable polymer(s) for each of the following uses, and **explain** why the polymer would be suited to the application.
 - disposable coffee cup
 - squeezable container for washing-up detergent
 - rope
 - shopping bag
 - freezer bag
 - toolbox
 - non-stick frypan coating
 - cool drink bottle

2.3 Polymers from biomass

Most of the synthetic polymers produced today are derived from fossil fuels. In theory, however, any carbon-containing substance could provide the starting material for the synthesis of polymers. Until recently, petroleum fractions have been the most convenient and economical raw material. However, as our supplies of petroleum and natural gas are being used up, scientists from around the world have begun looking not only for alternative sources of energy but for renewable supplies of materials from which to produce synthetic polymers. One of the most promising sources of such raw material is biomass. *Biomass* is organic material derived from living organisms. It includes plant and animal material such as crops

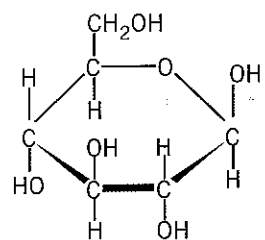
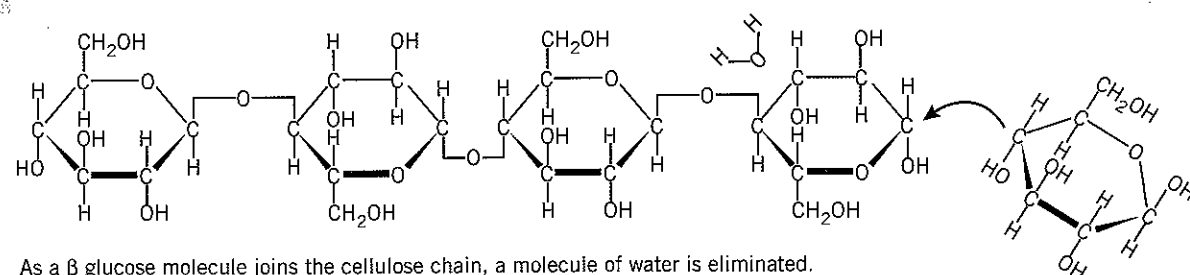


Figure 2.29 A glucose molecule

and trees, animal dung, and domestic and industrial organic waste. All living organisms produce natural polymers called *biopolymers*. Polysaccharides (such as cellulose and starch), proteins (including wool, hair and silk) and nucleic acids (DNA and RNA) are all biopolymers. It has been suggested that plant material such as cellulose, starch and gluten, which contain the basic carbon chain structures required by the plastics industry, would be an ideal source of raw material for the petrochemical industry. After all, petroleum, which currently provides the petrochemical industry with feedstock, is derived from ancient plants and animals. The advantage of using biomass, particularly plant material, rather than petroleum fractions is that, unlike fossil fuels, biomass is a renewable resource.

Before examining how materials extracted from biomass could be used to produce synthetic polymers, it is necessary to examine the structure of some of these biopolymers.

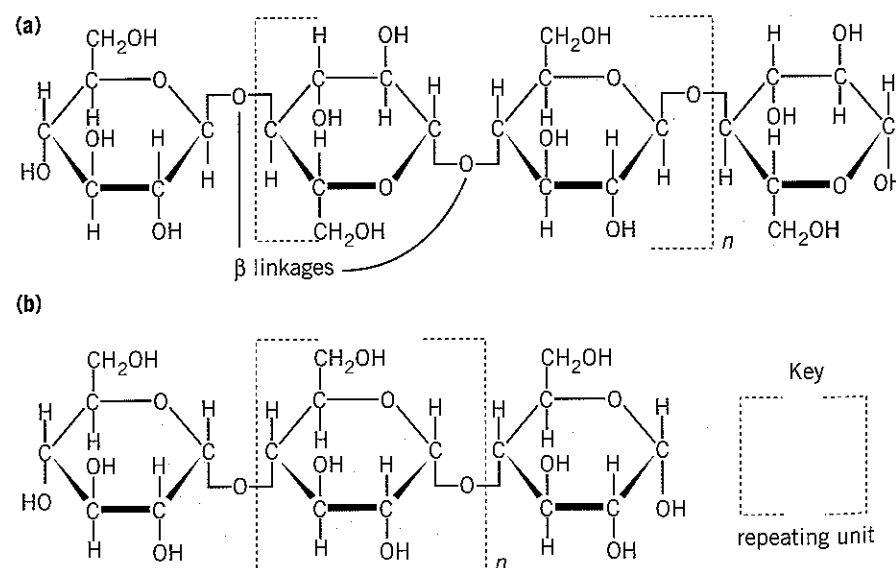
Polysaccharides such as cellulose and starch consist of many glucose units linked together. They are condensation polymers, because when glucose molecules (see Figure 2.29) join together, a molecule of water is eliminated from the reactive functional groups, as shown in Figure 2.30. Although cellulose and starch both consist entirely of linked glucose monomers, the linking between the monomers is different. A consequence of this difference is that the digestive enzymes of humans can digest starch but not cellulose. However, certain bacteria in the soil, the gut of termites and some herbivorous mammals, such as rabbits, cows and sheep, produce enzymes called *cellulases*, which can break down cellulose molecules into glucose. Cellulose is therefore a food source for cows and sheep, but for humans it is mainly a source of fibre or roughage.



As a β glucose molecule joins the cellulose chain, a molecule of water is eliminated.

Figure 2.30 Formation of cellulose. As a β glucose molecule joins the cellulose chain, a molecule of water is eliminated.

Figure 2.31 Structure of (a) cellulose and (b) starch



Cellulose: the most abundant polymer on earth

A large proportion of the world's biomass is in the form of cellulose. In fact, it is the most abundant single polymer in the biosphere. Cellulose is the main constituent of plant cell walls and the major structural component of woody plants and natural fibres such as cotton, flax and hemp (wood is about 50% cellulose, and cotton fibres are over 90% cellulose). A typical cellulose molecule is made up of thousands of glucose monomers. The arrangement of glucose monomers in cellulose and starch is shown in Figure 2.31. The β -linkages found in cellulose result in the formation of flat, ribbon-like strands. The close packing of these ribbons and the strong hydrogen bonds between them give cellulose its great strength and rigid structure.

Polymers from cellulose

The use of plant material as a source of raw material for the plastics industry could be achieved in two ways. The existing biopolymer chains in the plant material could be modified to meet specific applications. Celluloid and rayon are polymers derived from modified cellulose. Alternatively, the biopolymers could be broken down into smaller molecules which would be used to build new synthetic polymers. The breakdown of these biopolymers could be achieved using bacteria that possess the cellulase enzyme or by pyrolysis.

Polymers made from cellulose are not recent developments. In fact, the first commercially produced plastic, cellulose acetate or celluloid, is a modified form of cellulose. In cellulose acetate, some of the $-\text{OH}$ groups in cellulose are converted into ester groups by reaction with ethanoic (acetic) acid. This is illustrated in Figure 2.32.

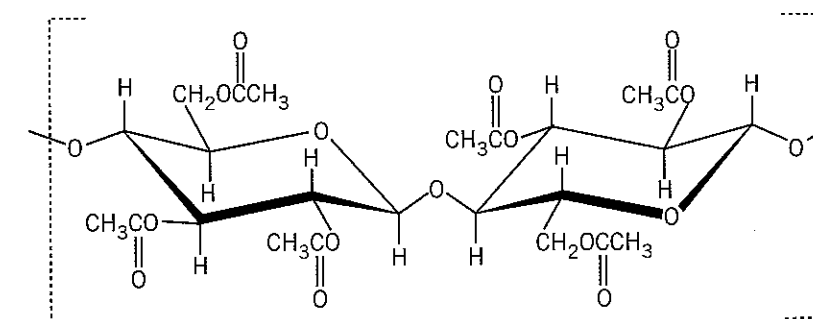


Figure 2.32 Structure of cellulose acetate

Rayon, another synthetic polymer derived from cellulose, was one of the first synthetic polymers to be mass-produced. It is made from regenerated cellulose fibres usually derived from wood pulp. These fibres are chemically treated with sodium hydroxide and carbon disulfide to soften them and break them down into smaller units. The resultant syrupy substance, called viscose, is then extruded into a solution of sulfuric acid through a nozzle with numerous small holes, called a spinneret. The fine threads of rayon polymer harden and may then be spun into fibres or combined with other fibres and woven into fabric.

Until recently, only the long cellulose fibres found in wood pulp could be used to make rayon. However, the production of rayon from shorter cellulose fibres, typically found in waste paper, straw and the husks from wheat and corn, is now possible. This new single-step process uses zinc chloride to combine cellulose chains by forming complexes with them. The advantage of this process is that the raw materials required are often waste products and are cheaper than wood pulp.

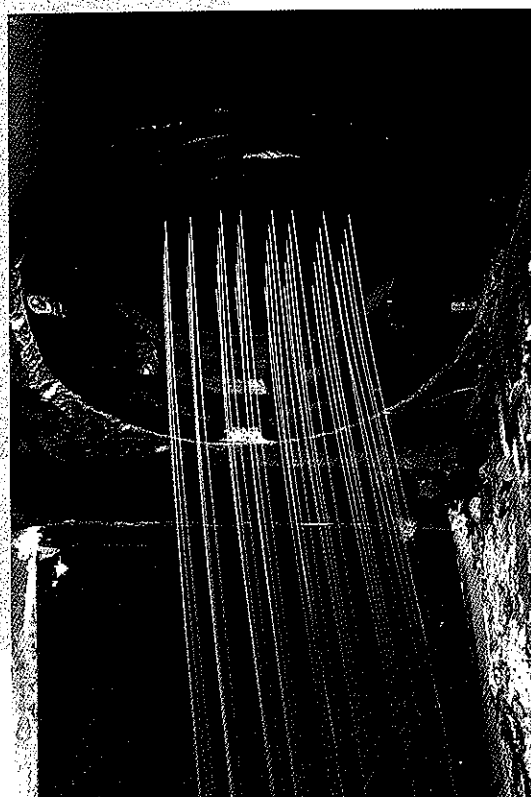


Figure 2.33 Extrusion of rayon through a spinneret

Cellulose can also be broken down into its constituent sugars. The first step in this process involves thermochemical (steam/acid) pretreatment of the cellulose followed by hydrolysis using the enzyme cellulase. The sugars that are produced may then be converted into chemicals which can be used as monomers for the polymerisation process.

Plastics and fibres made of biopolymers are biodegradable because the bonds within the molecule can be broken down by bacteria and fungi. This is an advantage in some applications but a disadvantage in others.

Plastics designed to be used only once, such as food wrappers and disposable containers, could be made of starch or cellulose-based plastics. A number of products made from such materials have appeared on the market in recent years. Packaging material has traditionally consisted of shredded paper or styrofoam 'peanuts'. A United States company has developed a range of packaging products made from corn starch. This loosefill has properties similar to polystyrene foam but with the advantages that it is biodegradable and is made from a renewable resource.

* Review exercise 2.3

- 1 **Discuss** the need for alternative sources of raw materials for the petrochemical industry.
- 2 **Identify** examples of biomass.
- 3 **Describe** the structure of cellulose.
- 4 **Explain** why cellulose is classified as a condensation polymer. **Draw** a diagram to support your answer.
- 5 Both cellulose and starch are polymers made from glucose monomers. **Compare** their structures.
- 6 **Discuss** why cellulose is considered a possible source of raw material for the production of synthetic polymers.

CHEMISTRY CONTEXT

* DISPOSAL OF PLASTICS

Modern societies generate huge quantities of waste, of which plastics make up a considerable proportion. Plastic wastes are unattractive and can be harmful to wildlife, particularly birds and aquatic life. Because plastics are so durable, they remain in the environment for very long periods. This is because most common plastics have structures that are different from materials found in the

natural world. Nature's decomposers, bacteria and fungi, generally lack the enzymes required to break the bonds within these synthetic polymer molecules.

Such molecules are said to be *non-biodegradable*. They cannot readily be decomposed into simpler compounds that can be returned to the environment and used by other organisms. This presents the problem of how society should dispose of its plastic waste. At present, much of the plastic we produce ends up as landfill. Around 20% by volume of the waste that arrives at the local tip is made of plastic. The problem is that landfill sites around major population centres are filling rapidly. Therefore many local councils now actively encourage their residents and local industries to recycle plastics.

Other than using less plastic, the issue of plastic waste disposal is most commonly addressed through recycling, incineration and the possible use of biodegradable plastics.

Recycling plastics

The main problem associated with recycling is separating plastics into their various types. This process is time consuming and adds to the cost of recycling. To make this easier, plastics manufacturers use a recycling number code, as shown in Figure 2.35. Unfortunately, the low cost of manufacturing plastics means it is often cheaper to make new plastics rather than recycle existing ones.



Figure 2.34 Plastics account for about 20% by volume of landfill.

Symbol			
	PETE	HDPE	V
Type of plastic	Poly(ethylene terephthalate) PET	High Density Polyethylene HDPE	Unplasticised Poly(vinyl chloride) UPVC
Symbol			
	LDPE	PP	PS
Type of plastic	Low Density Polyethylene LDPE	Polypropylene PP	Poly(styrene) PS

Figure 2.35 Synthetic polymers and their recycling number codes

CHEMISTRY CONTEXT, cont.

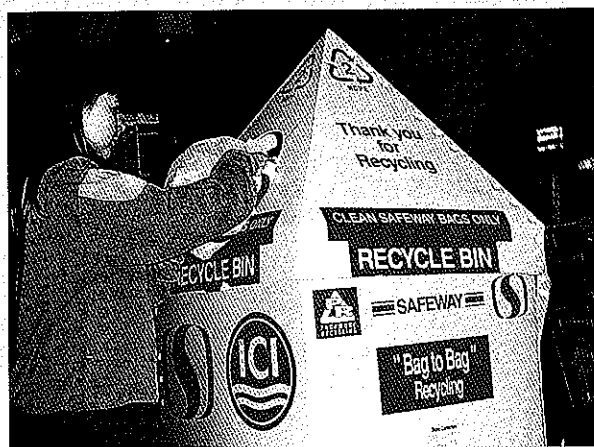


Figure 2.36 Recycling symbol on a collection container

Incineration

Another method for disposing of plastics is incineration. Normal incineration produces carbon dioxide and water and releases significant quantities of heat, which can be used as a source of energy. Unfortunately, some plastics such as PVC and acrylics also release toxic gases, HCl and HCN respectively, that can cause additional environmental and health concerns. In fact, toxic fumes produced by burning synthetic polymers found in furniture and furnishings are a serious concern in house, hotel, train and aeroplane fires.

However, if incineration is carried out at about 700°C in the absence of oxygen, a process called pyrolysis, the plastics are reduced to simple petrochemical raw materials such as methane, ethylene, propylene and benzene. These can be separated by fractional distillation and used as starting materials for the petrochemical industry. Another useful by-product of this process is energy, which can be used to produce electricity. At present this method for disposing of plastics is very expensive, but it may become more economical in the future.

Degradable plastics

In recent years there has been a great deal of interest in the development of degradable polymers, especially biodegradable and photodegradable plastics. Degradation involves breaking bonds within the polymer molecule to form smaller molecules that can be used by organisms within the environment. One method involves the inclusion of certain bonds or groups within the polymer that make it more susceptible to biological and UV-induced degradation. Another approach has been to incorporate naturally biodegradable biopolymers such as starch within the plastic. These initiatives have met with mixed success and there remains the problem of determining the impact of the smaller polymer chain fragments in the environment. Much more research is needed in this area. Current developments in the production of biopolymers are discussed in Unit 2.4.

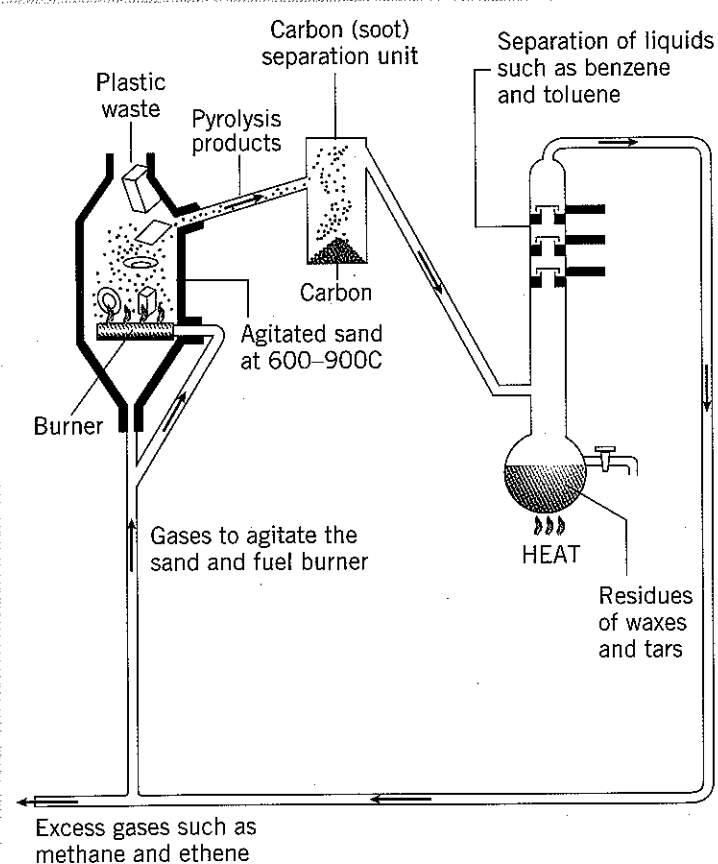


Figure 2.37 Schematic diagram of a pyrolysis plant

2.4 Current developments in the use of biopolymers

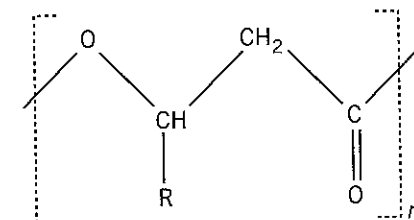
A biopolymer is a naturally occurring polymer produced by living organisms including plants, animals and micro-organisms. Many biopolymers have been used by humans since ancient times. These include rubber, flax, starch, silk, wool and hair. But there is increasing interest in developing new biopolymers with special properties and which have the benefit of being both biodegradable and renewable. The biodegradability of biopolymers makes their use advantageous in certain applications and will greatly reduce the amount of plastic waste in our landfill (see Chemistry Context, opposite).

Many new biopolymers have been developed in the past few decades, and of these, some have shown great potential for use in certain applications, including:

- polyhydroxyalkanoates (PHA) such as polyhydroxybutyrate (PHB)
- polylactic acid (PLA)
- cyclodextrins (CD).

Plastics produced by bacteria

A number of types of bacteria have been discovered that produce biopolymers. These 'natural plastics', known as polyhydroxyalkanoates or PHAs, have similar properties to common synthetic plastics currently in use, such as polypropene.



R = *n*-alkyl side chain of variable length

Figure 2.38 Chemical structure of PHAs

PHAs can be melted, moulded and shaped into various forms but, unlike synthetic plastics, they are biodegradable. ICI (Imperial Chemical Industries), one of the largest manufacturers of petrochemicals, has set up a pilot plant in Billingham, England, to manufacture these biopolymers. The plastic-producing bacteria (*Alcaligenes eutrophus*) are grown in fermentation vats and fed on molasses (a by-product of sugar production) or methanol. Extraction of the plastic from the bacteria involves breaking down the bacteria's cell walls and separating this from the cell debris. In the future, as petroleum reserves decline and prices rise, the production of plastic by bacteria may become economically viable.

Bacteria are not the only organisms capable of producing biodegradable plastics. Researchers have genetically modified plants to produce PHAs. By inserting bacterial genes into plants such as sugar cane and oilseed crops it could be possible to produce the raw materials needed for the manufacture of nylon, certain plastics, glues and lubricants.

Waste from crops such as potatoes, corn and maize contains starch, which can be broken down into simple sugars by enzymes. These simple sugars include lactose, which can then be fermented by lactic bacteria to produce lactic acid (Figure 2.39). Lactic acid can then undergo condensation polymerisation to form polylactic acid (PLA). This synthetic biopolymer is a polyester and has properties similar to polyethylene terephthalate, PET (see Chemistry Context, p 16). PLA is very strong but is biodegradable, making it ideal for uses such as food packaging, plant pots, disposable plates and cutlery.

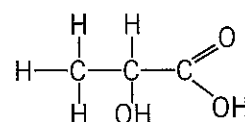


Figure 2.39
Chemical structure of lactic acid

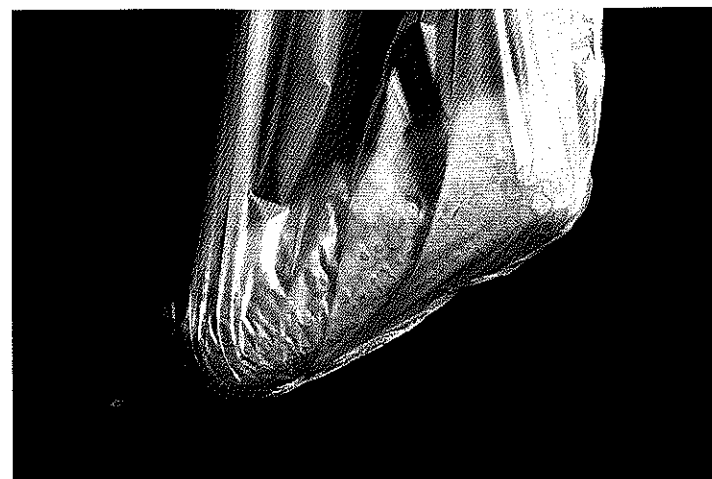


Figure 2.40
The biodegradable plastic bag containing this sweet corn cob is itself made from maize (sweet corn) starch.

* Review exercise 2.4

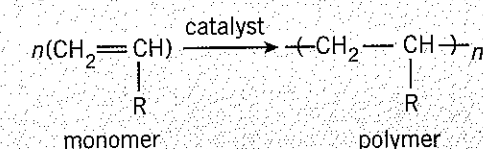
- 1 Biopolymers have the potential to be:
 - used in their natural form
 - used in some chemically modified form
 - broken down to form the base units required to manufacture conventional synthetic polymers.

Identify a named biopolymer produced by each of these methods.

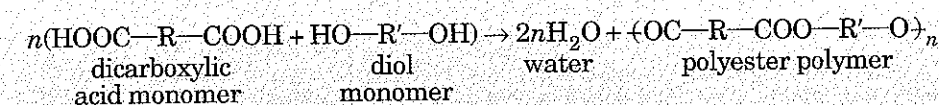
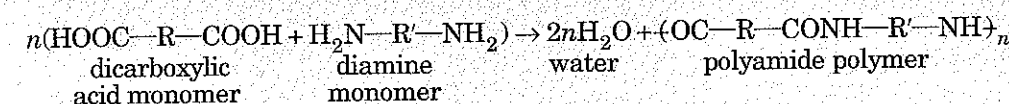
- 2 **Discuss** the advantages and disadvantages of using biopolymers.
- 3 a **Describe** an industrial process currently used to produce a named biopolymer.
 b **Identify** the specific organism or enzyme used in the process described in part a.
 c **Relate** the structure and properties to the uses of the biopolymer concerned.

*KEY POINTS

- Polymers are large molecules made up of small repeating units called monomers.
- There are two major types of polymerisation processes:
 - 1 Addition polymerisation occurs when small molecules with a C=C double bond join together.



- 2 Condensation polymerisation occurs when two monomers link together, with the accompanying elimination of a small molecule such as water. Often one monomer is a dicarboxylic acid and the other monomer is a diamine or a diol.



- The properties of a polymer are determined by a number of factors, including:
 - 1 the length of the chain (the number of monomer units)
 - 2 the arrangement of the chains with respect to each other
 - 3 the degree of branching from the chain
 - 4 functional groups in the monomer units
 - 5 cross-linking between polymer chains
 - 6 the inclusion of additives.
- The monomers and uses of some synthetic polymers are shown in Table 2.1.

TABLE 2.1

Monomer	Polymer	Use
ethylene	polyethylene	moulded plastics: containers, toys, bags, bottles, wrapping materials
vinyl chloride (chloroethylene)	polyvinyl chloride (PVC)	pipes, rigid panels, floor tiles, electrical insulation, records, kitchen utensils
styrene (phenylethylene)	polystyrene polyphenylethylene	surfboards, cups, insulating material
tetrafluoroethane	Teflon	greaseless bearings, chemically resistant liners, non-stick liners
terephthalic acid and 1,2 ethanediol	polyethylene terephthalate (PET)	clothing fibres, bottles, film, audio/video tape, synthetic blood vessels and skin

- Biomass is organic material derived from living organisms including plant and animal material.

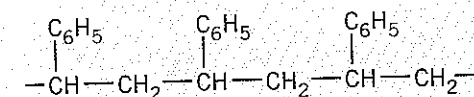
- The extraction of materials from biomass, particularly cellulose, is being investigated to decrease our dependence on fossil fuels.
- Cellulose is a condensation polymer consisting of glucose subunits (monomers).
- Biopolymers are produced by living organisms and include:
 - 1 polysaccharides (e.g. cellulose and starch)
 - 2 proteins (e.g. wool, hair and silk)
 - 3 nucleic acids (e.g. DNA and RNA)
 - 4 rubber.
- Many plastics are non-biodegradable and this presents problems with their disposal.
- Many new biodegradable biopolymers have been developed or are under investigation, including PHA and PLA.

* APPLICATION AND INVESTIGATION

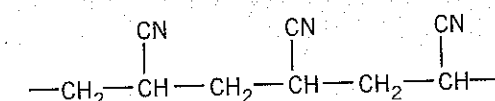
- Investigation
- 1 **Define**, with examples, the terms 'monomer', 'polymer' and 'polymerisation'.
 - 2 Carbon is the crucial element in the formation of the polymers discussed in this chapter.
 - a Carbon is particularly suited to the formation of polymers. **Account** for this with reference to the bonding of carbon.
 - b **Identify** another element that might be expected to form polymers.
 - c **Investigate** whether the element identified in part b does in fact form polymers.
 - 3 **Account** for the use of polyethylene in so many different and diverse applications.
 - 4 A sample of polyethylene has an average molar mass of 84 500. **Calculate** the average number of monomer units in the polyethylene sample.
 - 5 Conduct a first-hand investigation to **identify** the use of: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyvinyl chloride (PVC) and polystyrene in the following locations:
 - a bathroom
 - b kitchen
 - c lounge room
 - d bedroom
 - e car.
 - 6 Relate the specific properties of each plastic in Question 5 to its suitability for that application.

7 **Deduce** the structure of the monomers used to prepare the following polymers.

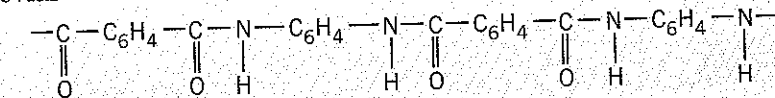
a polystyrene



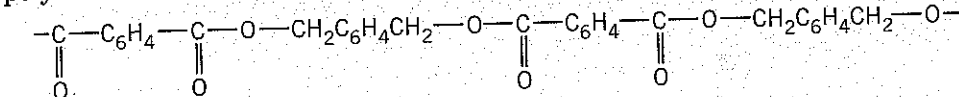
b Orlon



c Kevlar



d a polyester



8 Gather and present information from secondary sources on the industrial production of a synthetic plastic derived from biomass. Your report should include:

Investigation

- the source of the biomass material (e.g. waste sugar cane stalks)
- the material(s) extracted from the biomass
- details of the industrial process
- uses of the synthetic plastic.

9 Gather and present information from secondary sources on the success of plastic recycling in New South Wales. In your report you should:

Investigation

- **compare** the recycling rates for different plastics
- **describe** what happens to recycled plastics after they are collected until they are modified to form useful products
- **identify** products manufactured from recycled plastics.

10 Gather and present information from secondary sources on the production of biopolymers (natural plastics) by bacteria. Your report should include:

Investigation

- the name and chemical structure of the biopolymer
- the scientific name of the specific bacteria
- details of the industrial process, including the extraction of the biopolymer from the bacteria
- applications of the biopolymer
- advantages and disadvantages of its use.