

Polymers offer an almost limitless variety of properties, enabling them to be used for many different purposes. Synthetic, carbon-based polymers are often called plastics.

In this chapter, you will learn about the formation of addition and condensation polymers. The characteristics of the molecules used to make these very large molecules will be considered, as will the unique properties of the different polymers they form.

Using several common polymers as examples, you will also learn how the properties of polymers can be modified for different applications.

Science understanding

- Addition reactions can be used to produce polymers, including polyethene and polytetrafluoroethene
- The structure of an addition polymer can be predicted from its monomer and the structure of an addition polymer can be used to predict the monomer from which it was derived
- Condensation reactions can be used to produce polymers, including polyamides and polyesters
- The structure of a condensation polymer can be predicted from its monomer(s) and the structure of a condensation polymer can be used to predict the monomer(s) from which it was derived
- Industry produces a vast range of plastics including addition polymers (polyethene, polytetrafluoroethene) and condensation polymers (nylon and polyethylene terephthalate (PET)), which have different properties and uses

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15.1 Polymers: a diverse class of materials



FIGURE 15.1.1 (a) The polymer used to make the toy soccer players in this game was selected for its strength and because it is easy to mould. (b) The polymer bank notes used in Australia are strong and flexible. (c) The polymers in the helmet, gloves and bottle are similar, but structural differences have given them very different properties.



FIGURE 15.1.3 Darwin's bark spider (*Caerostris darwini*) is an orb-weaving spider whose web is made of one of the toughest natural polymers ever studied.

Polymers are an incredibly diverse range of materials. Natural polymers such as proteins, starch, cellulose and DNA play essential roles within living systems and have also been used and modified by humans for many other applications. In the last century, many wholly synthetic polymers have been developed and are one of the most successful and useful classes of materials. Synthetic polymers are used for everyday plastic bags, containers and clothing fibres, and in advanced medical applications such as drug delivery systems. In Figure 15.1.1, you can see a range of familiar polymers. The polymers that make up these objects were selected for their strength or flexibility. In this chapter, you will examine a range of polymers and learn how their properties are related to their structure.

POLYMER STRUCTURE

Polymers are covalent molecular substances composed of many small molecules joined together to form a long chain of atoms. The word 'polymer' comes from the Greek *poly*, meaning 'many', and *mer*, meaning 'part'. Polymers are formed by joining together thousands of smaller molecules, called **monomers** (*mono* means 'one') through a process called **polymerisation**, as shown in Figure 15.1.2. Polymer chains are made up of identical segments that are repeated along the length of the molecule. Each of these segments is called a repeating unit.

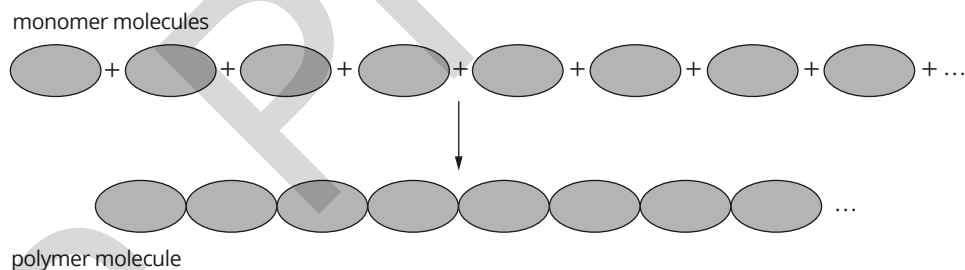


FIGURE 15.1.2 Monomers join to each other to form polymers.

NATURAL POLYMERS

Many polymers are found in nature. For example, carbohydrates are polymers made from sugar monomers, principally glucose and fructose. Proteins, as discussed in Chapters 17 and 18, are also polymers made from amino acid monomers. Many natural polymers are used in a range of applications. For example, silk and cotton are natural fibres used in the textile industry. Silk is a protein produced by the mulberry silkworm (*Bombyx mori*). Cotton is the seed hair of plants of the genus *Gossypium* and is primarily composed of the carbohydrate cellulose. Latex, used to make rubber, is also a polymer harvested from rubber trees.

The web of a Darwin's bark spider (*Caerostris darwini*) is the toughest natural polymer ever studied (Figure 15.1.3). The web is composed of proteins and amino acids that polymerise upon contact with air. The web has a similar tensile strength to high-grade steel and is of similar strength to Kevlar—the polymer used to make bulletproof jackets.

SYNTHETIC POLYMERS

The first synthetic polymer, Bakelite, was created in 1907 by Leo Baekeland, who called it 'the material of a thousand uses'. Bakelite is a hard, brittle plastic used to make cases for things such as telephones and electric guitars. Bakelite is not widely used any more, but other synthetic polymers are used for hundreds of thousands of different purposes (Figure 15.1.4).

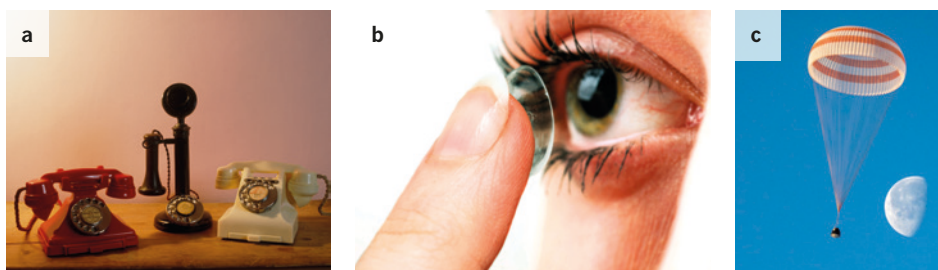


FIGURE 15.1.4 (a) The first synthetic polymer Bakelite was used to make telephone and radio casings. (b) Contact lenses are made of a flexible oxygen-permeable polymer. (c) A space shuttle falling back to Earth. The parachute is made of the synthetic polymers nylon and Kevlar. Many other synthetic polymers are used in the construction of the space shuttle itself, particularly its heat-resistant coatings.

Synthetic polymers can have very different properties from those of materials found in nature, such as metals or wood. These properties can be tailored to meet specific applications. As a result, polymers are used widely. Polymers can be made stronger, harder or more flexible than wood and are resistant to moisture and insects. Like metals, polymers can be hard, strong, malleable and ductile. However, polymers are much lighter than metals and are insulators of heat and electricity. Synthetic polymers can also be cheap to produce in large quantities because they can be produced from chemicals that are readily available.

CHEMISTRY IN ACTION

Synthetic polymers in medicine

Biological polymers such as silk, horn, hair and cellulose have been used by humans for hundreds of years for a range of different purposes, including in medicine. The use of sutures (stitches used to heal wounds) made from plant material or animal intestines can be traced back to the Ancient Egyptians and the process of mummification. Synthetic polymers have also recently become widespread in medicine because their properties are tailored to specific applications. Synthetic polymers are used in contact lenses, drug delivery systems, dentistry, joint replacements, dressings and grafts, as well as in a range of containers and tubings used to store and deliver fluids and drugs.

Some medicinal polymers are materials also commonly used outside the body. For example, polytetrafluoroethene (Teflon) and polyethene terephthalate (PET) are non-biodegradable and are used widely to make synthetic veins for bypass operations as alternatives to using

transplanted veins from other parts of the body. Similarly, joint replacements and prosthetic limbs often consist of a metal such as titanium paired with ultra-high molecular weight polyethene. Often antioxidants such as vitamin E are added to the polyethene to prevent oxidative damage caused by the biological environment.

An exciting emerging application for synthetic polymers in medicine is as drug delivery agents. Drugs or other particles are coated in polymers and form small microspheres or nanospheres. These polymers can be designed to degrade under specific environmental conditions, such as particular pH, enzyme concentrations or light irradiation, only releasing the drugs at the desired destination within the body. A common polymer used in these applications is poly lactic glycolic acid, a biodegradable copolymer that breaks down to produce two naturally occurring molecules.

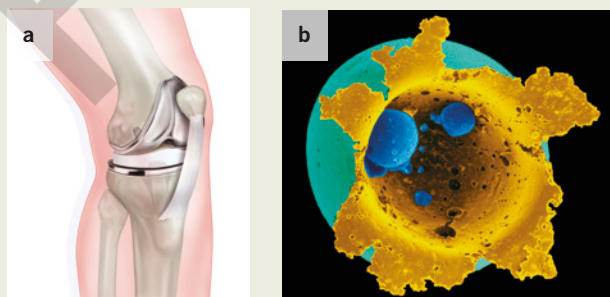


FIGURE 15.1.5 (a) A knee prosthesis consisting of titanium and polyethene. The prosthesis is designed so that the titanium is always bordered with the polyethene, to allow smoother movement. (b) A coloured scanning electron micrograph of a polymer-coated drug-delivery capsule. Some drugs work best when delivered to a specific site in the body. The polymer capsule is designed to burst in a particular biological environment, releasing the molecules held inside.

STRUCTURAL PROPERTIES OF POLYMERS

The properties of a polymer are determined primarily by the type of monomers used to produce it. However, other structural features also affect the properties of the polymer. These factors affect the strength of the intermolecular forces between the polymer chains and include:

- the length of the polymer molecules
- branching of the polymer chains
- cross-linking between polymer chains.

Length

As a polymer chain get longer, the strength of the dispersion forces between neighbouring polymer chains increases. This means that the resulting polymer is a harder and more rigid material. For example, ultra-high molecular weight polyethene (UHMWPE) consists of extremely long polymer molecules. This makes UHMWPE such a tough polymer that it can be used to make artificial hip joints, safety helmets and even bulletproof vests.

Branching

When polymers are formed, monomers can join together in a linear fashion or with a degree of branching. Branched polymers are formed when some monomers react with sites on the side of the polymer chain instead of at the end of the polymer chain. When a monomer joins to the side of the polymer chain, it begins a new chain growing in a different direction. The difference between straight-chain and branched-polymers is illustrated in Figure 15.1.6.

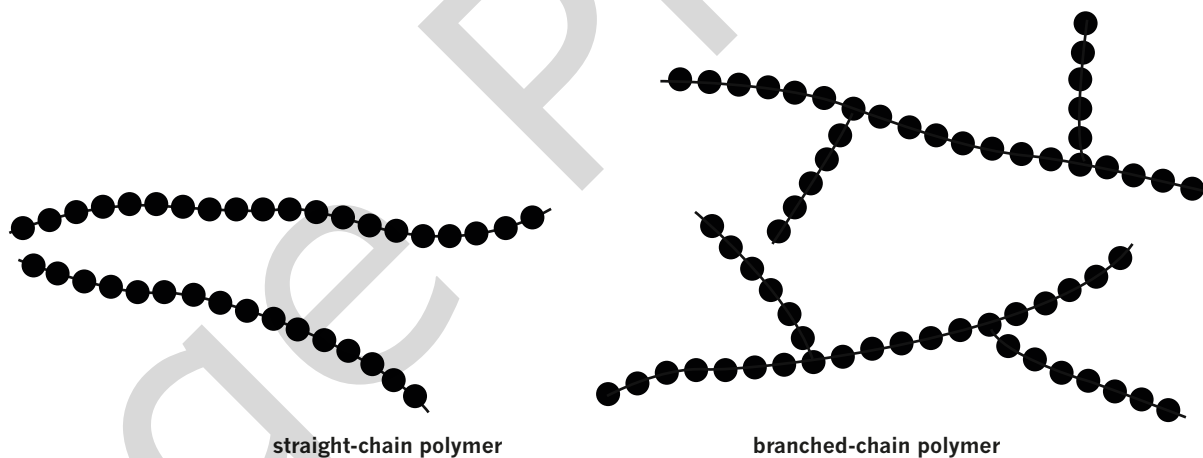


FIGURE 15.1.6 Straight-chain polymers have linear molecules. Branched-chain polymers have shorter polymer chains branching off in different directions from the main polymer.

Polymer branching changes the properties of the polymer significantly depending on the nature and extent of the branching. Branching can cause the polymer molecules to be spaced further apart, resulting in a less dense material. With a greater distance between the polymer chains, the intermolecular attraction between neighbouring chains is weakened, increasing the flexibility of the material. The effect of branching on the properties of polyethene is discussed in greater depth in section 15.2.

Both straight-chain and branched-chain polymers exist as **thermoplastic** polymers, as long as there are no covalent **cross-links** between polymer chains. For chemists, the term '**plastic**' describes a property of a material, rather than the material itself. A substance is described as plastic if it can be easily moulded. Thermoplastic polymers soften when heated, which means they can be remoulded or recycled. Polymers are only thermoplastic if the bonds between the long polymer chains are hydrogen bonds, dipole–dipole bonds or weak dispersion forces, rather than covalent bonds. When heated, the molecules in thermoplastic materials have enough energy to overcome the intermolecular forces and become free to move and slip past one another (Figure 15.1.7). If the polymer can be remoulded, then it can probably be recycled easily—a desirable property.

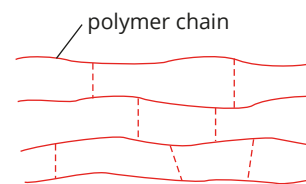
Cross-linking

In cross-linked polymers, the polymer branches are covalently bonded to neighbouring polymer chains. This bonding creates a polymer network as shown in Figure 15.1.8. Polymers of this type cannot be liquids because the polymer chains are held in place by the cross-linking and are unable to flow.

Cross-linked polymers typically exist as thermosetting polymers. **Thermosetting** polymers decompose or burn when heated, rather than melting, and are hard and rigid. They do not soften because the bonds between the chains are very strong. If the temperature is high enough to break the covalent bonds, the bonds may break at any point, causing the polymer to decompose. They are used to make items such as saucepan handles, bowling balls and shatterproof crockery. It is difficult to recycle thermosetting polymers as they cannot be remoulded into new shapes.

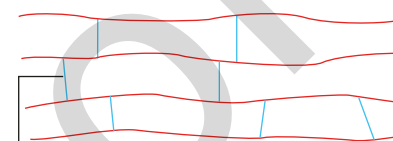
Elastomers

Elastomers are formed when only occasional cross-links are present. The chains in these polymers can still move past each other when stretched but the cross-links return the chains to their original positions once the force causing the stretching is released. Elastic bands and other rubber items are made of elastomers. The cross-links stop elastomers from completely melting when heated and makes recycling difficult. For example, the sulfur cross-links in the polymer in car tyres (Figure 15.1.9) make the tyres non-recyclable.



Heat causes the molecules to move enough to overcome the weak forces between molecules.

FIGURE 15.1.7 A thermoplastic polymer has weak bonds between the chains.



The heat required to break the cross-links is also sufficient to break the bonds within the molecules themselves.

FIGURE 15.1.8 A thermosetting polymer has strong covalent bonds between the chains.

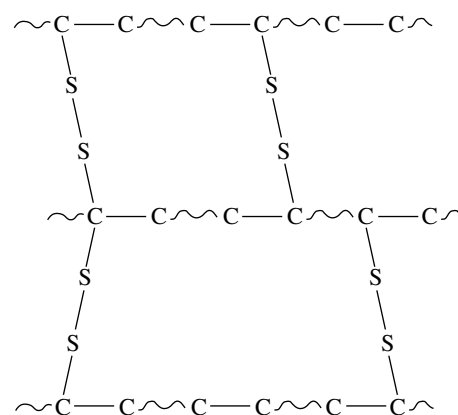


FIGURE 15.1.9 The elastomer chains in rubber car tyres are cross-linked by sulfur atoms.

15.1 Review

SUMMARY

- Polymers are a class of natural and synthetic materials with a wide range of properties and uses.
- Polymers are synthesised by forming covalent bonds between smaller molecules (monomers), which form a long chain.
- There are three main types of polymer structures: straight-chain polymers, branched polymers and cross-linked polymers.
- Straight-chain and branched polymers without covalent cross-links are known as thermoplastic polymers. They will soften when heated and can be reshaped.
- Polymers with covalent bonds, or cross-links, between chains are hard and rigid and are known as thermosetting polymers. They do not melt and instead either burn or decompose when heated.
- Elastomers are polymers with occasional cross-links that allow them to stretch and return to their original position.

KEY QUESTIONS

- 1 Define:
 - a polymer
 - b monomer
 - c repeating unit.
- 2 Explain the difference between a thermosetting and thermoplastic polymer.
- 3 Two polymers A and B are composed of the same monomers, but polymer B has a much higher degree of branching. Which material, A or B, would you expect to have stronger dispersion forces between polymer chains? Explain your answer.
- 4 To what degree would you expect the polymer chains in natural rubber to be cross-linked? Suggest a reason for your answer.

15.2 Addition polymerisation

As you learnt in Year 11, addition reactions can involve the reaction of an alkene with another molecule. All of the atoms of both molecules are present in the final product. Under some conditions, alkenes undergo an addition reaction with themselves to produce long chains, known as **addition polymers**. The reaction of the monomer ethene with itself to form polyethene, shown in Figure 15.2.1, is the simplest example of the **addition polymerisation** process. Several thousand ethene monomers usually react to make one molecule of polyethene.

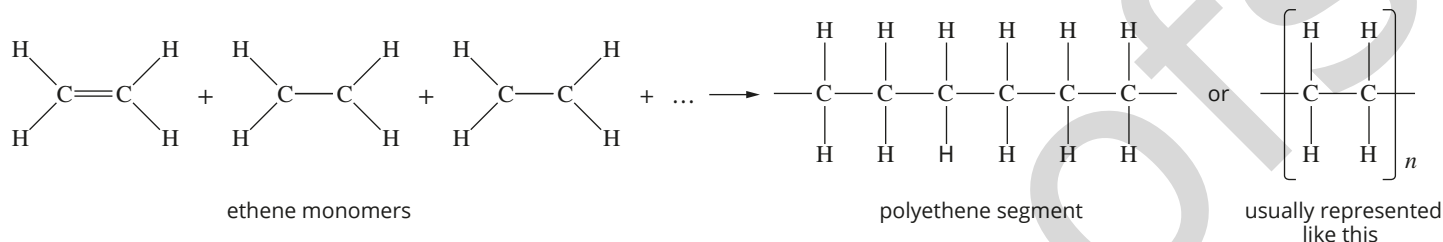


FIGURE 15.2.1 Thousands of ethene monomers join together to make one chain of polyethene. The standard notation shown simplifies the drawing of such a large chain.

Large square brackets and the subscript n are used to simplify the drawing of long polymer molecules. The value of n may vary within each polymer molecule, but the average molecular chain formed might contain as many as 20 000 carbon atoms. Polymers really are very large molecules!

Because all the atoms of the monomers are present in an addition polymer, the empirical formula of the monomer is the same as that of the polymer. Figure 15.2.2 provides an alternative representation of a polyethene chain segment, called a ball-and-stick model.

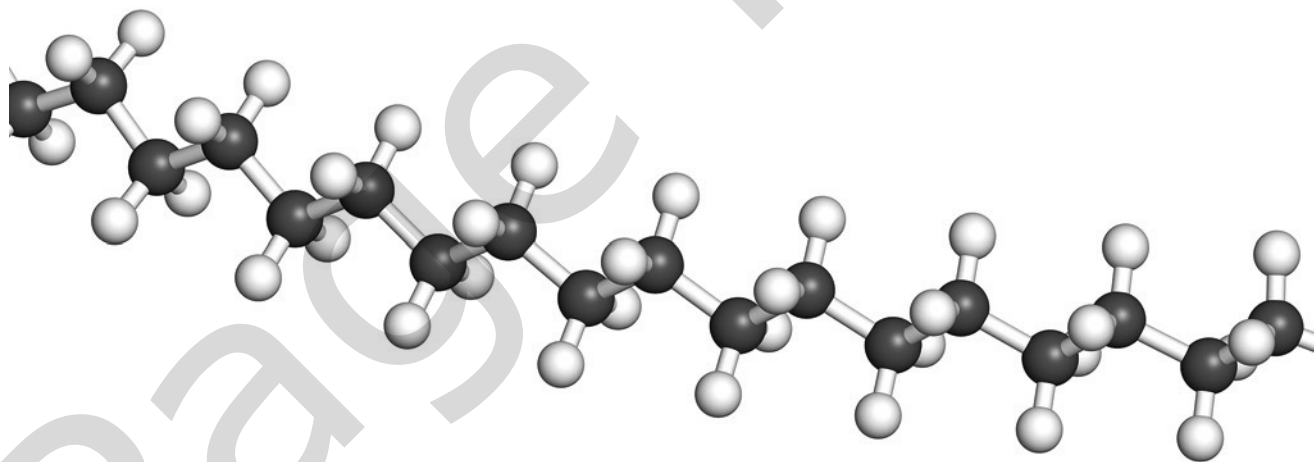


FIGURE 15.2.2 A ball-and-stick representation of a segment of polyethene

Ethene is an unsaturated molecule because it contains a carbon–carbon double bond. When ethene polymerises, the double bonds break and new covalent bonds are formed between carbon atoms on nearby monomers. The polyethene formed does not contain any double bonds and is therefore a saturated molecule.

i Addition polymerisation requires monomers that are unsaturated (contain a double or triple carbon–carbon covalent bond). During the polymerisation process, the double or triple bond is broken and single C–C bonds are formed between monomers.

The name of a polymer formed through addition polymerisation often includes the monomer that was used to make it. The names of four common addition polymers and their monomers are listed in Table 15.2.1.

TABLE 15.2.1 Monomer and polymer names

Monomer	Polymer
Ethene	Polyethene
Propene	Polypropene
Tetrafluoroethene	Polytetrafluoroethene (PTFE)
Chloroethene (vinyl chloride)	Polychloroethene, or polyvinylchloride (PVC)

It is possible to predict the structure of an addition polymer from the monomers. Read through the steps in Worked Example 15.2.1 to predict the structure of an addition polymer.

Worked example 15.2.1

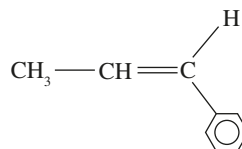
ADDITION POLYMERS: FORMING POLYMERS

Draw the addition polymer that has $\text{CH}_3\text{-CH=CH-CH}_3$ as its monomer.	
Thinking	Working
Write the chemical formula for the monomer so that the double bond is horizontal and the bonds to all other groups are perpendicular to the carbon centres.	$\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{CH}_3 \quad \text{H} \end{array}$
Repeat this several times so that the C=C double bonds of neighbouring monomers are adjacent to one another.	$\begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 \\ & & & & & & & & & \\ \text{C} = & \text{C} & \text{C} = & \text{C} & \text{C} = & \text{C} & \text{C} = & \text{C} & \text{C} = & \text{C} \\ & & & & & & & & & \\ \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} \end{array}$
Remove the double bonds and connect all carbon centres with single bonds. This gives you the structure of the polymer.	$\begin{array}{cccccccccccc} \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 \\ & & & & & & & & & & & \\ -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}- \\ & & & & & & & & & & & \\ \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} \end{array}$

Worked example: Try yourself 15.2.1

ADDITION POLYMERS: FORMING POLYMERS

Draw the addition polymer produced from the following monomer. Include at least three repeating units.



It is also possible to identify the monomers of an addition polymer from the polymer molecule. Read through the steps in Worked Example 15.2.2 to see how to identify the monomers of an addition polymer.

Worked example 15.2.2

ADDITION POLYMERS: DETERMINING THE MONOMER UNIT

Draw the structure of the monomer that produces the following polymer.

Thinking	Working
Identify the repeating unit of the polymer. It will contain just two adjacent carbon atoms from the polymer backbone.	
Remove every second single bond along the length of the chain and form the double bond between the two carbon atoms of the monomer. This gives you the structure of the monomer.	

Worked example: Try yourself 15.2.2

ADDITION POLYMERS: DETERMINING THE MONOMER UNIT

Draw the structure of the monomer that produces the following polymer.

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POLYETHENE

As described above, polyethene is the simplest example of an addition polymer, consisting of a long C–C chain. It is better known by its common names, polythene or polyethylene. Because it is essentially an extremely long alkane, it is a non-polar molecule and exhibits only dispersion forces between adjacent long polymer chains (Figure 15.2.3). These dispersion forces are sufficiently strong to cause polyethene to be a solid at room temperature.

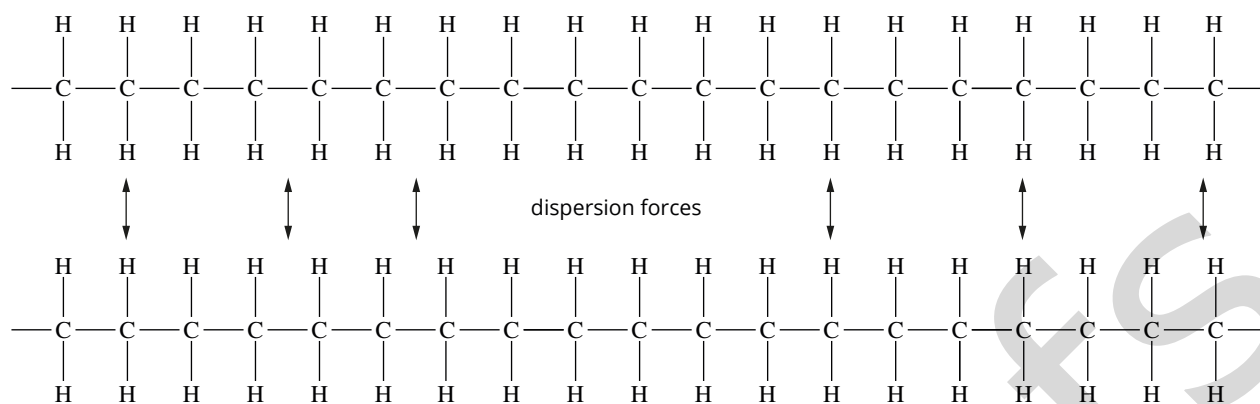


FIGURE 15.2.3 Dispersion forces between polyethene molecules are strong enough to make polyethene a solid at room temperature.

Polyethene can exist in two different structural forms depending on how it is manufactured. The manufacturing process affects the degree of branching on the polyethene chain and hence the strength of the dispersion forces between neighbouring chains. This makes the polymer suitable for different uses.

Low-density polyethene (LDPE)

The earliest method of producing polyethene involved high temperatures (around 300°C) and extremely high pressures. Under these harsh conditions, the polymer is formed rapidly by a process called free-radical polymerisation. Free radicals are highly reactive atoms, molecules or ions with an unpaired electron. The free radicals break the double bonds in the ethane monomers to start the polymerisation reaction. However, the free radicals also attack the sides of the polymer chain, resulting in significant branching. Figure 15.2.4 shows that the product contains many small branches off the main polymer.

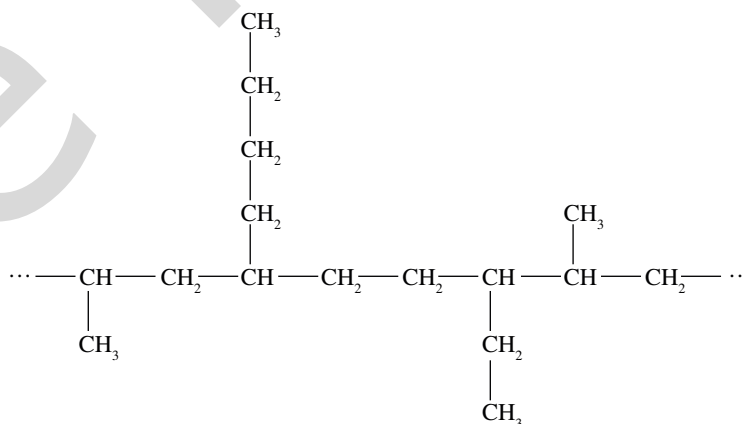


FIGURE 15.2.4 Polyethene made under high pressure and at high temperatures has short branches off the main chain.

The presence of these branches affects the properties of the polymer because the molecules cannot pack closely together. The dispersion forces between molecules are weaker when the molecules are further apart. The arrangement of the polymer molecules can be described as disordered or non-crystalline. This form of polyethene is known as **low-density polyethene** or LDPE, a low-density material that is soft and flexible. Its structure and properties are described in Figure 15.2.5. LDPE is used in plastic bags, flexible containers and the waterproof layer in juice and milk cartons.

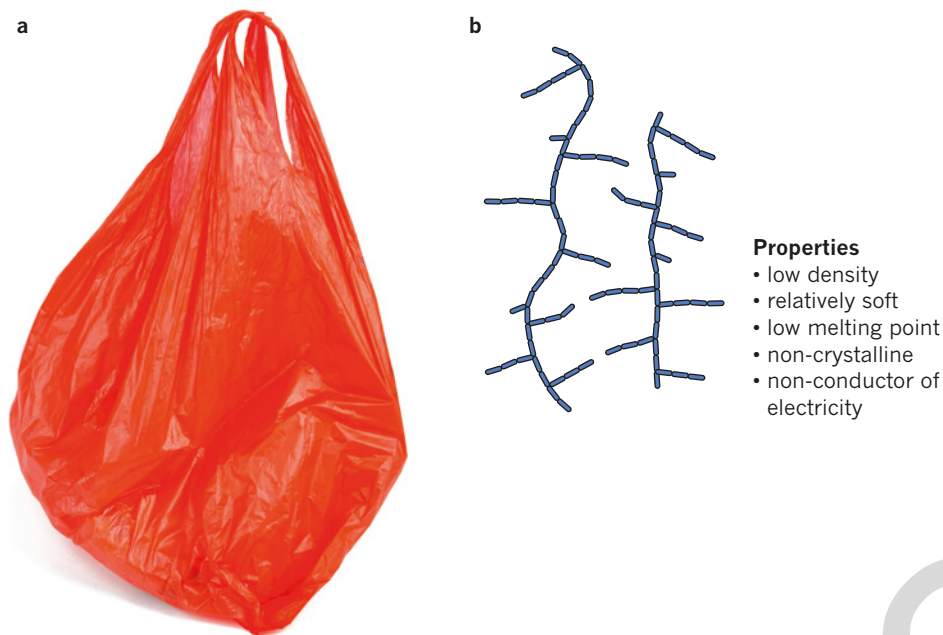


FIGURE 15.2.5 Properties and structure of low-density polyethene: (a) a bottle made from LDPE; (b) LDPE has a branched structure.

High-density polyethene (HDPE)

A low-pressure method of producing polyethene was developed by Union Carbide in the late 1960s. Highly specialised transition metal catalysts are used to avoid the need for high pressures. The polymer molecules are produced under much milder conditions and have very few branches.

The lack of branches allows the molecules to pack together tightly, increasing the density and the hardness of the polymer formed. The arrangement of the polymer molecules is more ordered, resulting in crystalline sections. This form of polyethene is known as **high-density polyethene** or HDPE. Its structure and properties are summarised in Figure 15.2.6. HDPE is used in plastic bottles, food storage containers, water pipes and fuel tanks.

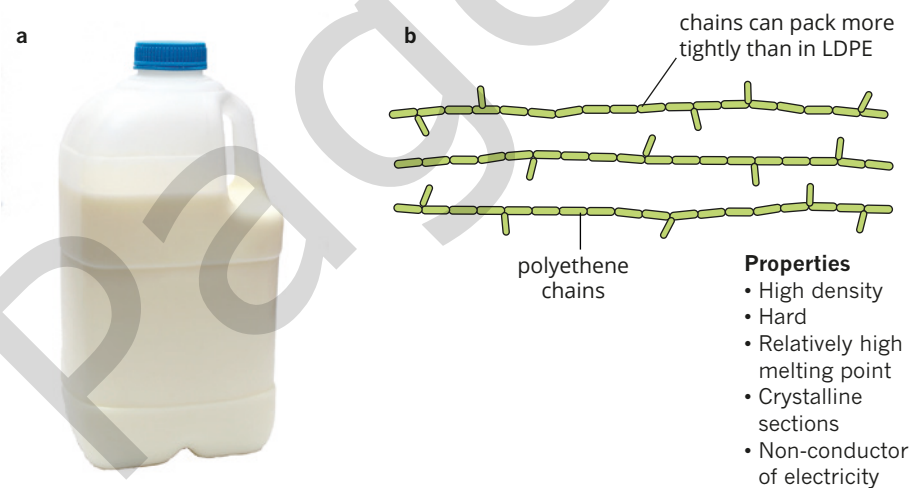


FIGURE 15.2.6 Properties and structure of high-density polyethene: (a) a bottle made from HDPE; (b) HDPE structure

CHEMFILE

The discovery of polyethene

The first practical method for the synthesis of polyethene was discovered by accident in 1933 in the laboratory of Imperial Chemical Industries (ICI) in Cheshire, England, when some oxygen was accidentally added to a container of ethene. The oxygen initiated the polymerisation reaction between the ethene molecules.

‘When it first happened, it was a fluke’, recalled Frank Bebbington, a young laboratory assistant who was involved in the discovery. He assembled a reaction vessel to produce the polymer, only to watch the pressure slowly fall. ‘We thought there was a small leak in the system. I felt embarrassed’, he said.

Frank’s colleagues went to lunch and he continued to top up the reaction vessel with more ethene. After his colleagues returned, the vessel was opened and they found that they had indeed made the new plastic. It took until 1938 for ICI to develop the industrial process that allowed them to produce their first commercial batch of polyethene.

Commercial use of the polymer flourished during World War II, when it was used to replace much heavier components in planes and ships.

POLYTETRAFLUOROETHENE (PTFE)

Many applications require polymers with more specialised properties than polyethene. Polytetrafluoroethene (PTFE) has the structure $[-CF_2-CF_2-]_n$ and is formed from the monomer tetrafluoroethene $CF_2=CF_2$ (Figure 15.2.7). It is more commonly known by the brand name Teflon. Its many properties are summarised in Table 15.2.2 and have led to its use in a wide range of applications, including plumber's tape, non-stick cookware, artificial hips and vocal cords, and machinery parts that require lubrication and pipes or containers designed to hold reactive or corrosive liquids.

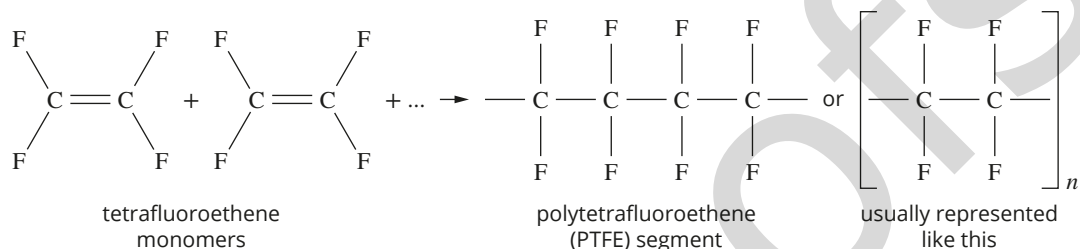


FIGURE 15.2.7 Tetrafluoroethene monomers react together to form polytetrafluoroethene (PTFE), also known as Teflon.

TABLE 15.2.2 The properties of Polytetrafluoroethene (PTFE), also known as Teflon

Property	Applications
Non-stick	Teflon repels all other substances, both hydrophobic (oil, fat) and hydrophilic (water and aqueous solutions).
Heat resistance	The melting point of Teflon is 335°C and its upper operating temperature is 260°C.
Chemical resistance	Because of the strength of the C–F bonds, Teflon is extremely resistant to all known chemicals. It is not attacked by strong acids and alkalis and is inert to all organic solvents.
Good mechanical properties	Teflon is strong and durable.
Low friction coefficient	Teflon is slippery to the touch. The friction coefficient between two pieces of Teflon is very low.
Flame resistance	Teflon is non-flammable.

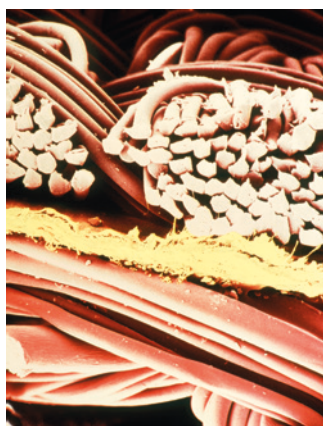


FIGURE 15.2.8 Scanning electron micrograph of Gore-Tex fabric. The small yellow and white particles are Teflon. The small holes between these particles allow vapour to pass through the fabric but not liquid.

Another innovative application of Teflon is in Gore-Tex[®] (Figure 15.2.8). Gore-Tex is a fabric that 'breathes'. Liquid water from rain cannot penetrate a Gore-Tex raincoat, but water vapour from sweat can escape through it. High-quality camping clothing is often made from Gore-Tex.

POLYVINYLCHLORIDE (PVC)

Ethene and tetrafluoroethene molecules are non-polar, meaning that the intermolecular forces present between polyethene and Teflon molecules are weak dispersion forces. When a polymer is made from polar monomers, the chains will be held together by stronger polar attractions, such as dipole–dipole interactions or hydrogen bonds.

Polyvinyl chloride (PVC) is made from the polymerisation of chloroethene ($\text{CHCl}=\text{CH}_2$) as shown in Figure 15.2.9.

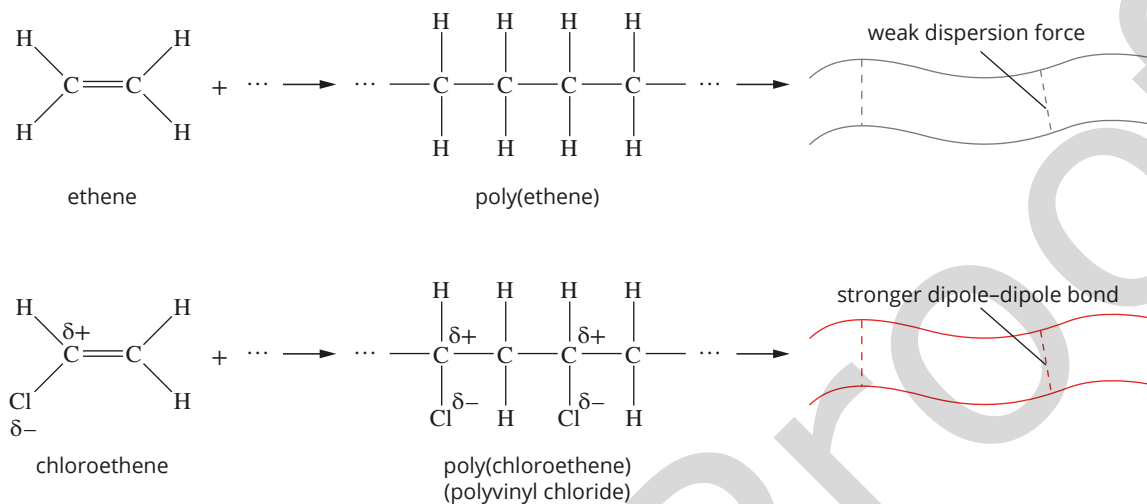








FIGURE 15.2.9 Polyvinyl chloride is formed from polymerisation of polar chloroethene monomers, and has dipole–dipole attractions between chains.

The carbon–chlorine bonds in a PVC molecule are polar and allow dipole–dipole attractions to form between polymer chains. Because of this, PVC is harder and more rigid than polyethene and Teflon. One of the main applications of PVC is in drain pipes. Incorporating additives such as plasticisers, as discussed in section 15.4, allows even more widespread use of PVC.

OTHER ADDITION POLYMERS

There are many examples of commercial addition polymers. Table 15.2.3 shows polymers that may be familiar to you. Each of these polymers offers a unique property or properties that make them of commercial interest.

TABLE 15.2.3 Commercial addition polymers

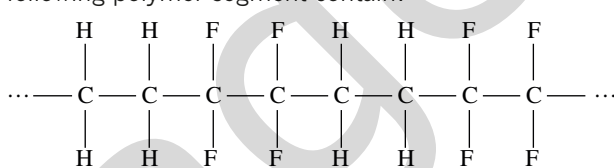
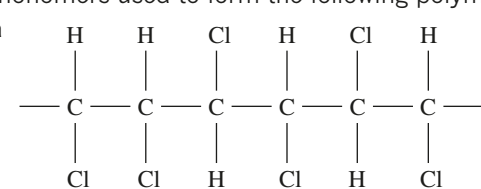
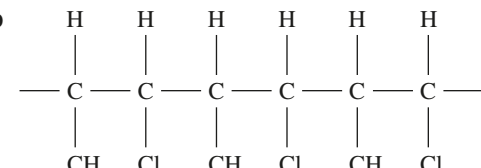
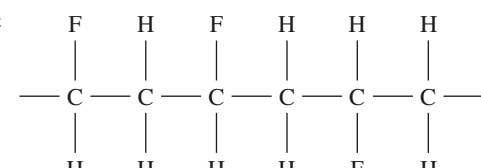
Monomer	Polymer	Properties	Examples	Application	
Propene	Polypropene (polypropylene)	Durable, cheap	Artificial grass, dishwasher-safe plastic, ice-cream containers, rope	propene	polypropene 
Dichloroethene	Polyvinylidene chloride (PVDC)	Sticks to self, transparent, stretchy	Food wrap	dichloroethene	polyvinylidene chloride (PVDC) 
Propenenitrile	Polypropenenitrile (acrylic)	Strong, able to form fibres	Acrylic fibres, fabrics	propenenitrile	polypropenenitrile (acrylic) 
Phenylethene (styrene)	Polyphenylethene (polystyrene)	Hard, brittle, low melting point	Toys, packaging, expanded foams	phenylethene (styrene)	polyphenylethene (polystyrene) 
Methylcyanoacrylate	Polymethylcyanoacrylate	Polymerises on contact with water	Super glue	methyl cyanoacrylate	polymethyl cyanoacrylate (superglue) 
Methyl-2-methylpropenoate	Polymethyl methacrylate (Perspex)	Transparent, strong	Perspex (a glass substitute)	methyl-2-methyl propenoate	polymethyl methacrylate (Perspex) 

15.2 Review

SUMMARY

- Addition polymers are formed from the reactions of monomers containing carbon–carbon double (or triple) bonds.
- During addition polymerisation, the double (or triple) carbon–carbon bond is broken and new single bonds are formed between the monomers.
- The most common polymer used is polyethene ($-\text{CH}_2-\text{CH}_2-$), formed from the addition polymerisation of ethene monomers ($\text{CH}_2=\text{CH}_2$). It can be manufactured in two different ways to make two different products: high-density polyethene (HDPE) and low-density polyethene (LDPE).
- High-density polyethene (HDPE) has a low degree of branching and hence has relatively strong dispersion forces between polymer chains. This makes it harder, denser and more rigid than LDPE.
- Low-density polyethene (LDPE) has a high degree of branching and hence has weaker dispersion forces between polymer chains. This makes it less dense than HDPE and more flexible.
- Polytetrafluoroethene (PTFE), also known as Teflon and used in Gore-Tex, is a polymer with the formula ($-\text{CF}_2-\text{CF}_2-$), formed by the addition polymerisation of tetrafluoroethene monomers ($\text{CF}_2=\text{CF}_2$).
- The polarity and size of side groups in the polymer affect the strength of the attractions between polymer chains.

KEY QUESTIONS

- 1 Which one of the following is an important feature of a monomer if it is to undergo addition polymerisation?
A Single carbon–carbon bonds
B Functional groups on the end of each molecule
C A C=O double bond
D A carbon–carbon double or triple bond
- 2 How many repeating monomer units does the following polymer segment contain?

- 3 Draw a section of the addition polymers formed from the following monomers. For each, draw at least two repeating units.
 - a Bromoethene ($\text{CH}_2=\text{CHBr}$)
 - b Propene ($\text{CH}_2=\text{CHCH}_3$)
 - c Acrylonitrile ($\text{CH}_2=\text{CHCN}$)
- 4 Identify and draw the structural formulas of the monomers used to form the following polymers.
 - a 
 - b 
 - c 
- 5
 - a In terms of their structures, explain the difference in properties between HDPE and LDPE.
 - b Which of these two forms would be a suitable material for:
 - i a soft, flexible plastic wrap?
 - ii a 2-litre drink container?
 - iii wrapping material for frozen food?

15.3 Condensation polymerisation

Addition polymerisation is limited to the use of unsaturated monomers. To obtain an even broader range of polymers, chemists use a second technique, known as **condensation polymerisation**. For condensation polymerisation to occur, the monomers must have two functional groups, one on each end of the monomer. These functional groups react chemically with the functional groups on neighbouring monomers. The reaction links the monomers into long polymer chains, as shown in Figure 15.3.1.

Another feature of condensation reactions is that small molecules are also produced during the reaction. In the two **condensation polymers** we will examine in detail, polyamides and polyesters, a molecule of water (H_2O) is produced during each reaction between the two functional groups.

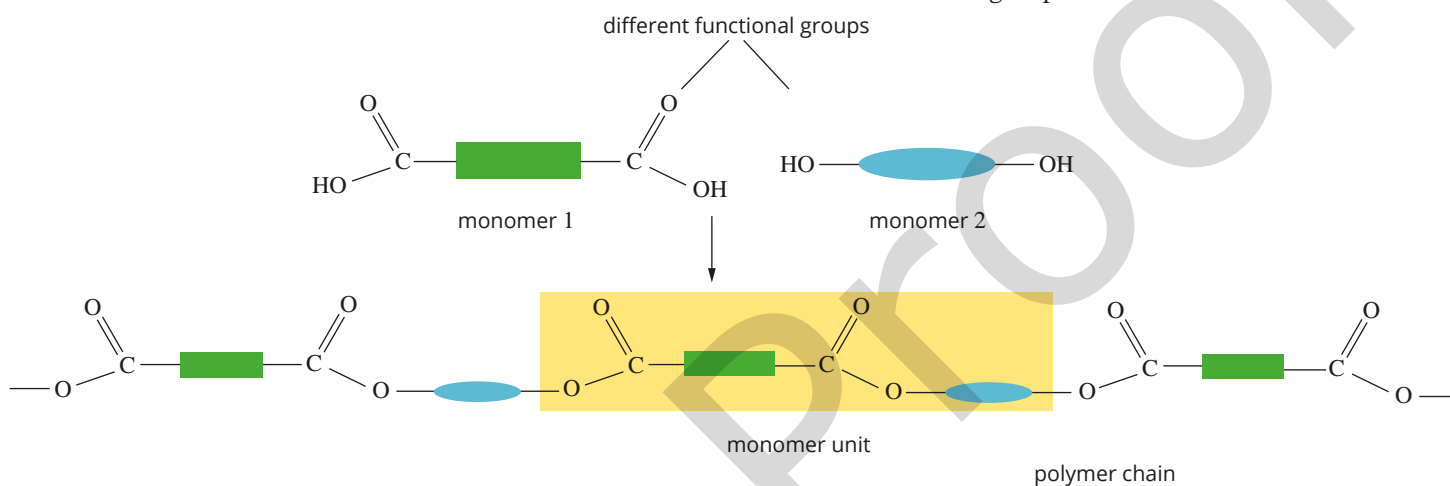


FIGURE 15.3.1 Condensation reactions require that the monomers have functional groups at each end of the molecule. These functional groups react together to form the polymer chain. As a result, an additional product is formed. In this case, the alcohol and carboxylic acid groups react to form an ester and water is produced.

The differences between addition and condensation polymers are summarised in Table 15.3.1.

TABLE 15.3.1 Comparison of addition and condensation polymers

Addition polymers	Condensation polymers
Monomers must be unsaturated, containing a double or triple carbon-carbon bond.	Monomers must contain two functional groups that can react with those on neighbouring molecules.
No by-products are produced during the reaction.	Small molecules, often water, are produced during the reaction.
The polymer backbone is a long C-C chain.	The polymer backbone contains functional groups; for example, amides or esters.

POLYESTERS

The term 'polyester' is commonly used to refer to a synthetic clothing material. However, in chemistry, **polyesters** are a class of polymers that are formed through the process of condensation polymerisation. Polyesters are formed by combining monomers that contain carboxyl and hydroxyl functional groups. Typically, they are formed by reacting a dicarboxylic acid monomer with a diol monomer (Figure 15.3.2). However, they can also be formed between monomers that contain both a carboxyl and an hydroxyl functional group within the same monomer.

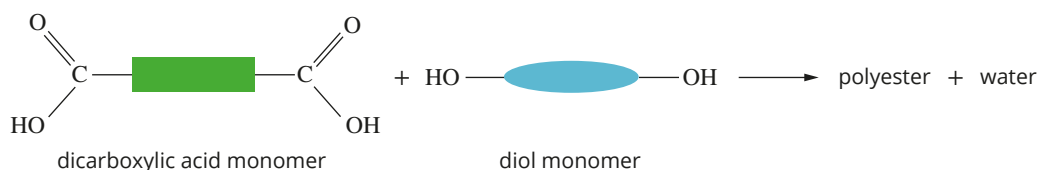


FIGURE 15.3.2 Dicarboxylic acid and diol monomers undergo condensation polymerisation to produce a polyester monomer and water.

i Polyesters are typically formed by combining a dicarboxylic acid monomer with a diol monomer in a condensation polymerisation reaction. Water molecules are also produced during the polymerisation reaction.

Polyethylene terephthalate (PET)

The polymer most often used to make polyester fabric is polyethylene terephthalate, or PET (or sometimes PETE). In addition to being used in fabrics, it has a range of uses including recyclable drink bottles and food packaging (Figure 15.3.3). PET is synthesised by reacting 1,4-benzenedicarboxylic acid monomers with ethane-1,2-diol monomers, as shown in Figure 15.3.4. PET is a strong material because the ester groups are polar and therefore PET exhibits dipole-dipole attractions between polymer chains.

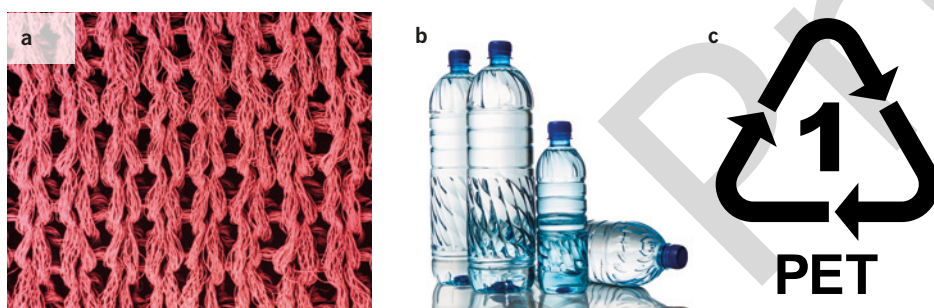


FIGURE 15.3.3 Polyethylene terephthalate (PET) has many uses. (a) A scanning electron micrograph showing knitted polyester fibres used in clothing. (b) PET is commonly used to make plastic bottles. (c) Bottles made of PET have the recycling code 01.

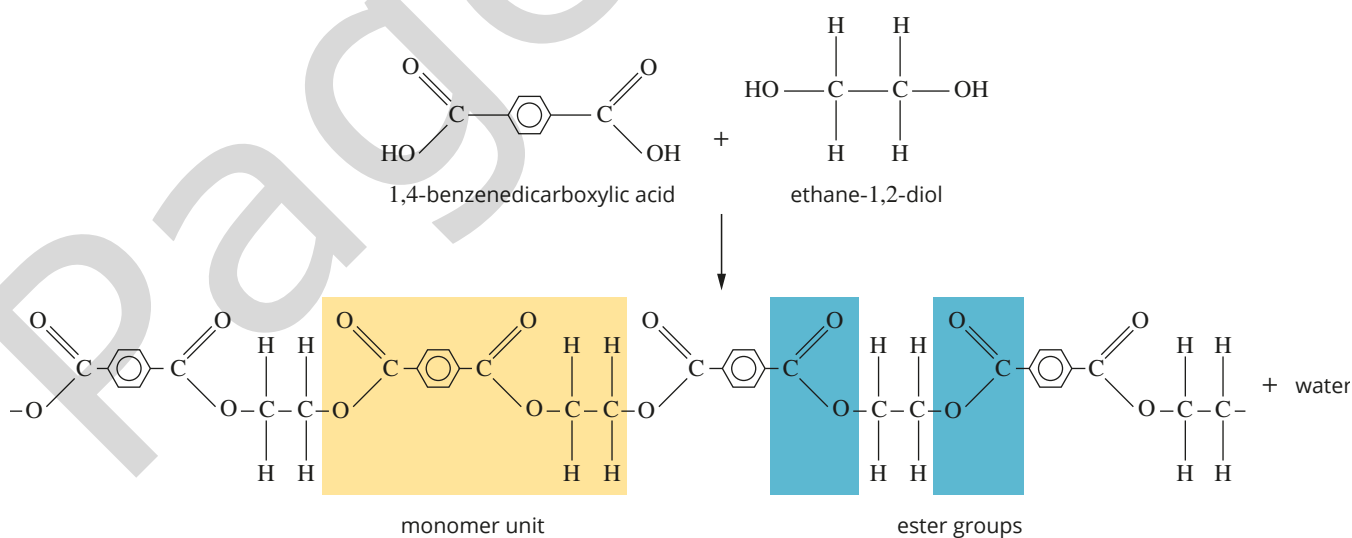


FIGURE 15.3.4 Polyethylene terephthalate (PET) is formed when 1,4-benzenedicarboxylic acid reacts with ethane-1,2-diol. Water is also produced. The PET is linked by ester groups, which is why it is part of the polyester family of polymers.

CHEMFILE

Bisphenol A (BPA)

Bisphenol A (BPA) is an organic compound containing two hydroxyl functional groups as shown in Figure 15.3.5.

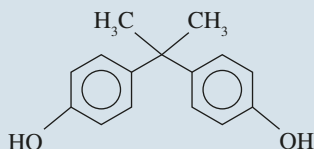


FIGURE 15.3.5 Bisphenol A (BPA) undergoes condensation polymerisation.

BPA is often used to produce condensation polymers. It can be combined with a dicarboxylic acid molecule to produce a polyester. More commonly, it is combined with phosgene (COCl_2) to produce polycarbonate plastic. In this condensation reaction, HCl is released rather than H_2O . Polycarbonate plastic is used to produce water bottles, sports equipment, medical devices, CDs and DVDs and the lining of water pipes.

There have been health concerns about the use of BPA in recent years. In particular, its use in baby bottles is of concern because BPA has been shown to mimic the action of the hormone oestrogen. Governments and health regulatory bodies have responded in various ways. In recent years, both the US Food and Drug Administration and European Food Safety Authority have concluded that BPA poses no risk to consumers of any age. Regardless, many products in the food industry are now advertised as 'BPA free'.

POLYAMIDES

Polyamides are another class of condensation polymer. Polyamides typically form when dicarboxylic acid molecules react with diamine molecules, as shown in Figure 15.3.6. They can also form between monomers that contain both a carboxyl and amino functional group within the same molecule. Polyamides tend to be stronger than polyesters of similar structure. This is because hydrogen bonds can form between the amide groups on neighbouring polymer chains. In polyesters, ester groups can only form dipole-dipole interactions with each other.

Nylon and Kevlar are two examples of commonly used synthetic polyamides. Proteins, as discussed in Chapter 17 and 18, are examples of biological polyamides.

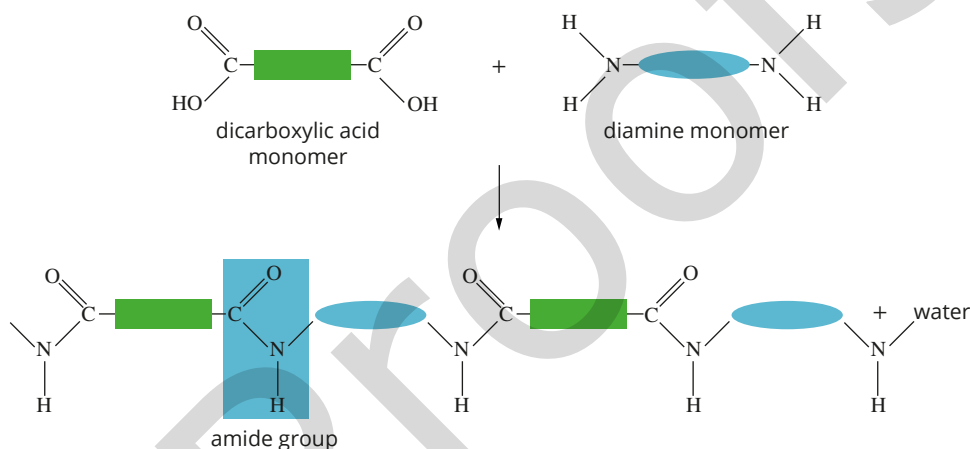


FIGURE 15.3.6 Dicarboxylic acid and diamine monomers undergo a condensation polymerisation reaction to produce a polyamide and water.

i Polyamides are typically formed by combining a dicarboxylic acid monomer with a diamine monomer in a condensation polymerisation reaction. Water is also produced during the condensation reaction.

Nylon

Nylon is a common example of a polyamide. It can be easily drawn into fibres with a high tensile strength. These fibres are often used to produce strong, lightweight materials for clothes, parachutes, ropes, fishing line and even guitar strings. However, nylon can also be used to make hard, rigid plastics that can be used in pipes and machinery.

The term 'nylon' refers to a group of polyamides in which the monomers contain linear carbon chains. A common example is nylon-6,6, which is so named because the dicarboxylic acid monomer has a chain of six carbons and the diamine monomer also has a chain of six carbon atoms, as shown in Figure 15.3.7.

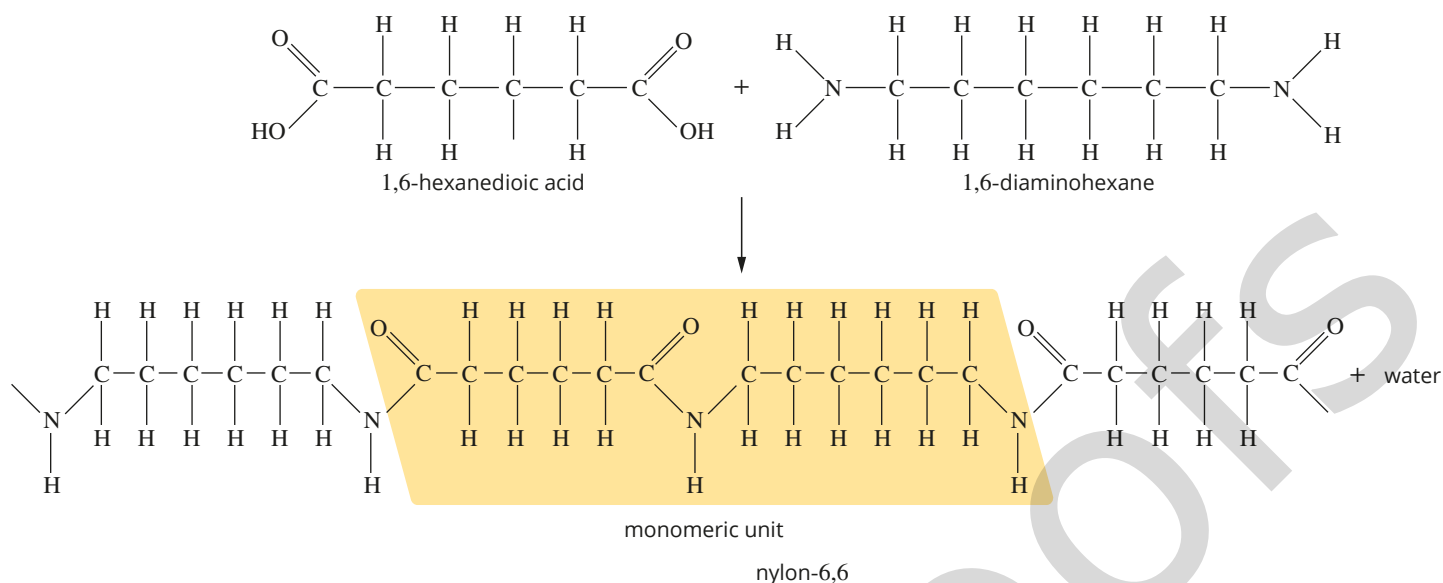


FIGURE 15.3.7 Nylon-6,6 is a polyamide formed when 1,6-hexanedioic acid reacts with 1,6-diaminohexane. Water is also produced.

Kevlar

Replacing the carbon chains in nylon with benzene rings produces the polymer known as Kevlar (Figure 15.3.8). Kevlar is an extremely strong material that is also very lightweight. This makes Kevlar particularly useful in a range of applications where extreme strength is required, such as bulletproof vests and anchor cables.

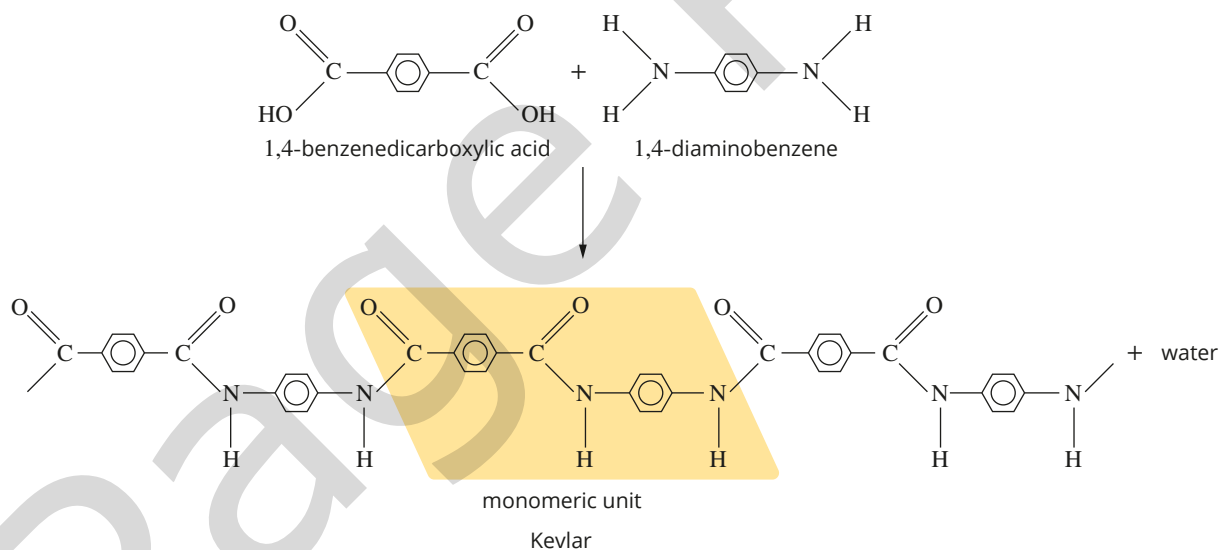


FIGURE 15.3.8 Kevlar is a polyamide molecule formed when 1,4-benzenedicarboxylic acid reacts with 1,4-diaminobenzene. Water is also produced.

The unique strength of Kevlar is due to its molecular structure. The benzene rings make the polymer chains rigid. It also allows the molecules to align closely together. As a result, there is strong hydrogen bonding between the amide groups in these molecules.

It is possible to predict the structure of a condensation polymer from the monomers. Read through the steps in Worked Example 15.3.1 to predict the structure of a condensation polymer.

Worked example 15.3.1

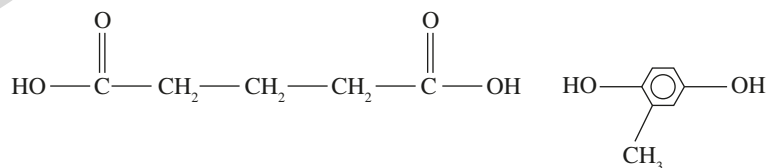
CONDENSATION POLYMERISATION: FORMING POLYMERS

Draw the condensation polymer produced from the following monomers. Include at least two repeating units.	
$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \quad \text{HO}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{OH}$	
Thinking	Working
Examine the functional groups on the monomer(s) and determine whether a polyamide or polyester will be formed. Remember an alcohol and carboxylic acid condense to form an ester, and an amine and carboxylic acid condense to form an amide.	The monomers are a diol and a dicarboxylic acid. Therefore, they will react to form a polyester.
To form the ester group in the polymer, remove the hydroxyl groups from the dicarboxylic acid and the hydrogen atoms from the hydroxyl groups of the diol.	$\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}- \quad \text{---O---CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{O---}$
Construct the repeating unit by joining the two halves.	$\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{O---}$
Write the repeating unit inside square brackets with a subscript n to indicate it is a polymer.	$\left[\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{O} \right]_n$

Worked example: Try yourself 15.3.1

CONDENSATION POLYMERISATION: FORMING POLYMERS

Draw the condensation polymer produced from the following monomers. Include at least two repeating units.



It is also possible to identify the monomers of a condensation polymer from the polymer molecule. Read through the steps in Worked Example 15.3.2 to see how to identify the monomers of a condensation polymer.

Worked example 15.3.2

CONDENSATION POLYMERISATION: DETERMINING THE MONOMER UNITS

<p>Draw the structure of the monomer(s) used to produce the following polymer.</p>	
<p>Thinking</p> <p>Determine whether the polymer is a polyamide or a polyester and circle the amide or ester linkages.</p>	<p>Working</p> <p>The polymer is a polyamide, due to the presence of the amide ($-\text{CONH}-$) groups.</p>
<p>Identify the repeating unit. Note that this may be composed of 1 or 2 separate monomers.</p>	
<p>Within the repeating unit, split the amide group at the C-N bond.</p>	
<p>Draw the two monomers individually, adding the H and OH groups to re-form the hydroxyl, carboxyl or amino functional groups on the monomer(s).</p>	

Worked example: Try yourself 15.3.2

CONDENSATION POLYMERISATION: DETERMINING THE MONOMER UNITS

<p>Draw the structure of the monomer(s) used to produce the following polymer.</p>
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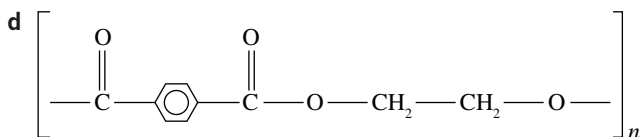
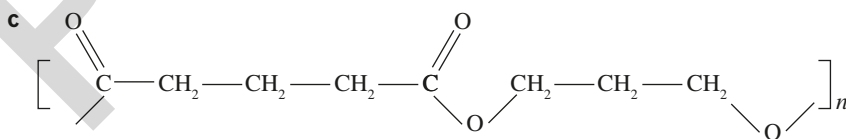
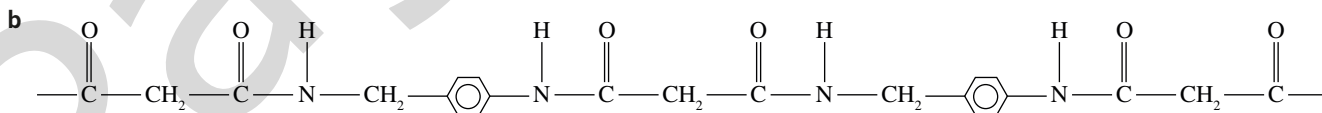
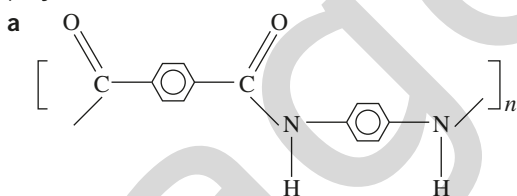
15.3 Review

SUMMARY

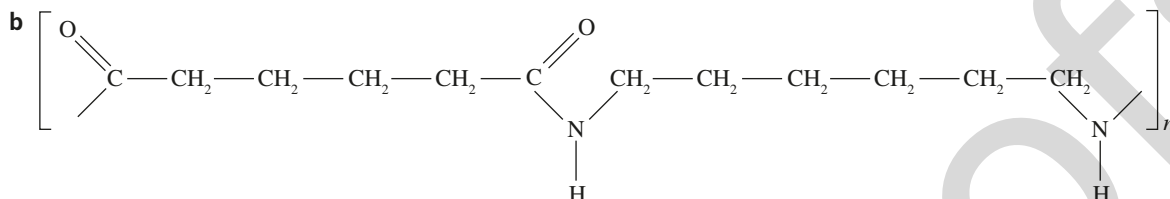
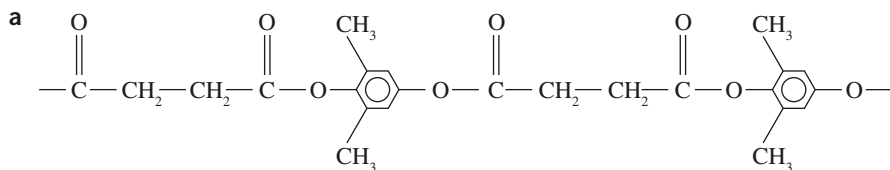
- Condensation polymerisation is a method for synthesising polymers.
- In condensation polymerisation, the monomers are joined via a covalent bond that is created by reacting two functional groups on each of the molecules.
- During a condensation reaction, smaller molecules are also produced. These are usually water molecules but can also be other small molecules such as hydrogen chloride (HCl), depending on the functional groups.
- Polyesters are formed by condensation polymerisation of dicarboxylic acid monomers and diol monomers.
- Polyethylene terephthalate (PET) is an example of a polyester.
- Polyamide polymers are formed by the condensation polymerisation of dicarboxylic acid monomers and diamine monomers.
- Nylon, Kevlar and proteins are examples of polyamides.
- Polyamides have hydrogen bonding between the amide groups on neighbouring chains, making polyamides tougher polymers than similar polyesters.
- The structure of condensation polymers can be predicted from their monomers. Likewise, the monomers can be derived from the structure of a condensation polymer.

KEY QUESTIONS

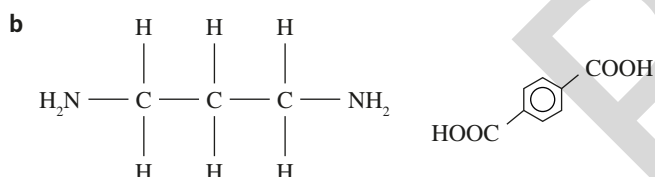
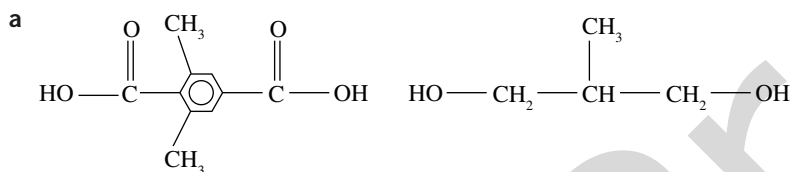
- 1 Which one of the following pairs of compounds could form a condensation polymer?
A Ethene and a dicarboxylic acid
B Two diol molecules
C A diamine and a dicarboxylic acid
D A diol and a diamine
- 2 When a condensation reaction is used to create a polyester molecule, name the other substance that is also produced.
- 3 Classify the following polymers as polyesters or polyamides.



4 Draw the monomers that make up the following polymers.



5 Draw the polymer that would be formed from the following two reactants.



6 In the name of nylon-6,6, the first 6 refers to the number of carbons in the diamine. The second 6 refers to the number of carbons in the dicarboxylic chain. Given this, deduce the structure of nylon-4,6.

15.4 Designing polymers for a purpose

The development of new polymers has been motivated by the need to replace existing materials that are in short supply and to produce materials with improved physical and chemical properties. The widespread use of polymers brings many advantages, as well as challenges. A very important issue is reducing polymer waste, through either **biodegradable** polymers or recyclable polymers. In section 15.1, you learnt how the length of polymer chains and the amount of branching can affect polymer properties. In this section, you will explore how changes in monomer structure and the addition of other substances to the polymer can modify polymer properties.

COPOLYMERS

In recent years, a new generation of versatile materials has been developed by combining two or more monomers into one polymer. A **copolymer** is a polymer made from at least two different monomers. Both addition and condensation polymers can be copolymers.

The Water Cube Stadium built for the 2008 Beijing Olympic Games (Figure 15.4.1) was made with a copolymer of ethene ($\text{CH}_2=\text{CH}_2$) and tetrafluoroethene ($\text{CF}_2=\text{CF}_2$) monomers. The copolymer is known as ethene tetrafluoroethene (ETFE). The stadium has over 100 000 m^2 of very thin ETFE 'bubble walls'. The walls allow more light and heat to penetrate than traditional glass does, lowering energy costs. ETFE weighs only 1% the weight of glass and is a better thermal insulator. It was designed by a consortium including two Australian companies, PTW Architects and Arup engineers.



FIGURE 15.4.1 The outer shell of the Water Cube Stadium in Beijing, China, is made of ETFE, a new copolymer building material.

Another copolymer called styrene–butadiene rubber (SBR) (Figure 15.4.2) is formed from styrene ($\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)$) and butadiene ($\text{CH}_2=\text{CHCH}=\text{CH}_2$). Pure polybutadiene is an elastomer used in the production of synthetic rubbers for applications such as tyres and golf balls.

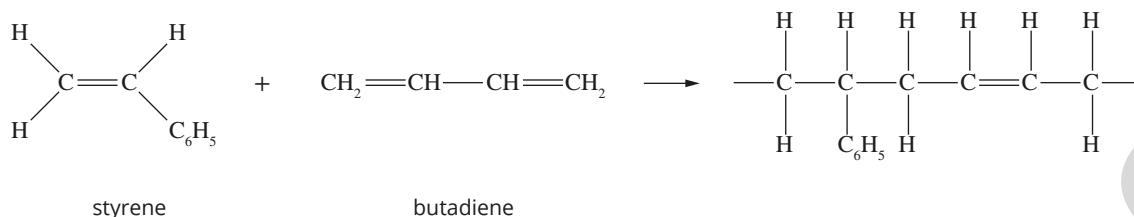


FIGURE 15.4.2 Formation of the SBR copolymer chain from two monomers.

A variety of polymers with different properties can be produced simply by altering the ratio of the monomers in styrene–butadiene rubber. For example, an elastomer similar to natural rubber is produced when the two monomers are present in close to equal amounts. Increasing the concentration of styrene monomers increases the abrasion resistance of the polymer and makes it suited for use in car tyres, its main application.

Addition of a third monomer, acrylonitrile ($\text{CH}_2=\text{CHC}\equiv\text{N}$), produces the polymer acrylonitrile–butadiene–styrene (ABS), which is used to make Lego[®] blocks. This polymer is rigid and strong, but can be melted easily. These properties have made this thermoplastic polymer very popular for use in 3D printing. In Figure 15.4.3, a 3D printer melts a thin cord of ABS, called a filament. The molten ABS is built up in layers, where it sets to make the solid object.

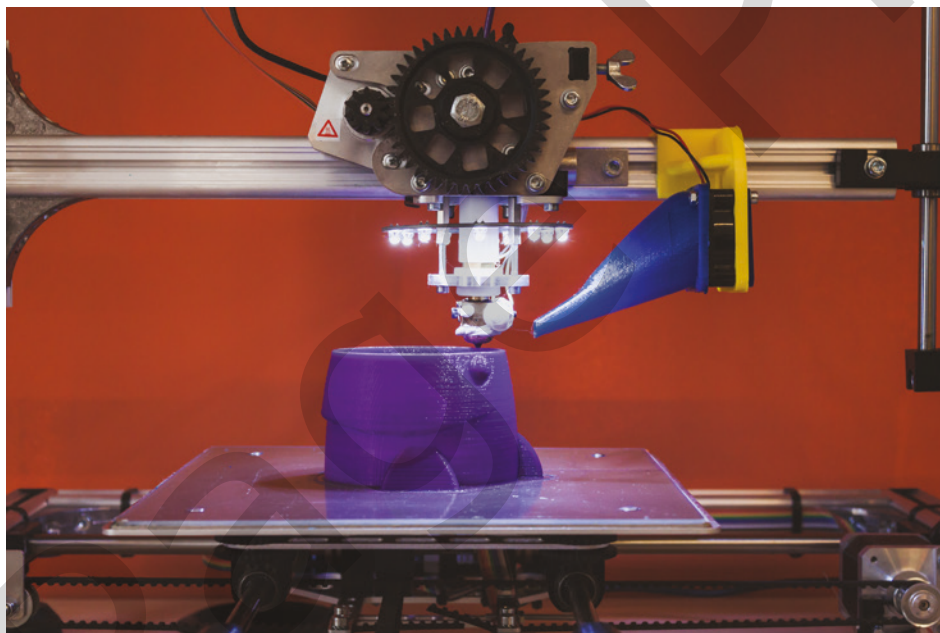


FIGURE 15.4.3 This 3D printer uses an ABS copolymer filament to make an object.

CHEMFILE

Conducting polymers

Polymers are usually known for their insulating properties. In 2000, the Nobel Prize in Chemistry was awarded to Alan MacDiarmid (born in New Zealand), Hideki Shirakawa (Japan) and Alan Heeger (USA) for the discovery of electrically conducting polymers. These groundbreaking **conductive polymers** have opened the way to lighter, polymer-based circuits that are being used now in biosensors.

The way in which a polymer can become electrically conducting is beyond the scope of this course, although the starting point is polymers with alternating double and single bonds such as polyethyne (Figure 15.4.4). When ethyne ($\text{CH}\equiv\text{CH}$) polymerises, one of the carbon–carbon bonds is rearranged to bond to neighbouring monomers. Each repeating monomer unit in polyethyne retains a carbon–carbon double bond.

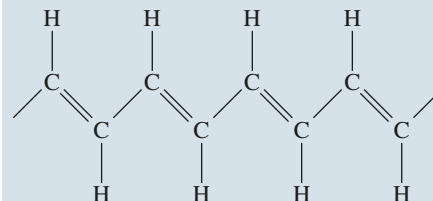


FIGURE 15.4.4 Polyethyne is a polymer that becomes conductive under some conditions.

The alternating double and single bonds in the polymer chain is called a conjugated system. Two of the electrons in the double bond are delocalised and able to move within the polymer chain.

crystalline

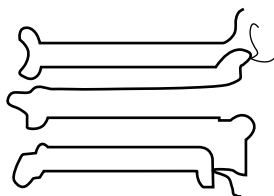


FIGURE 15.4.5 A crystalline region of a polymer material forms where the polymer chains are arranged in an ordered fashion.

amorphous

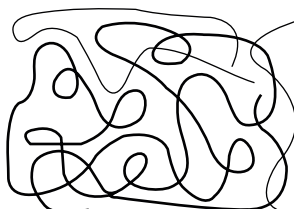


FIGURE 15.4.6 An amorphous region forms when polymer chains are disordered.

CRYSTALLINITY

Materials made from polymers consist of many long chains that twist around each other, with intermolecular forces from one chain to another. Many polymeric materials contain both **crystalline regions** and **amorphous regions**.

Where the chains are lined up in a regular arrangement, they create crystalline regions, as shown in the ordered section of the polymer in Figure 15.4.5.

Being regularly arranged brings the polymer chains closer together. The intermolecular forces between the closely packed chains are stronger and the presence of crystalline regions strengthens the material overall. Crystalline regions in a polymer prevent the transmission of light through the material, making it appear opaque (cloudy), so that light does not pass directly through it.

An amorphous region is where the polymer chains are randomly tangled and unable to pack very closely. The polymer chains shown in Figure 15.4.6 are amorphous because they have no orderly arrangement.

In some polymer materials, the entire solid is amorphous. Amorphous polymers are usually less rigid and weaker and are often transparent (see-through).

The percentage of the polymer that is crystalline, rather than being amorphous, influences the properties of the polymer. Increasing the percentage crystallinity of a material makes it stronger and less flexible. This also makes the material less transparent because the crystalline regions scatter light.

BRANCHING

As discussed in section 15.1, the degree of branching in a polymer chain has a large effect upon the density of the polymer material and strength of the intermolecular forces that exist between polymer chains. When extensive branching is present, polymer chains are unable to pack together as closely when solid, resulting in a less dense and more flexible material with far fewer crystalline regions. As discussed in section 15.2, HDPE can have a percentage crystallinity of up to 95% whereas LDPE is more amorphous with a percentage crystallinity as low as 65%.

ADDITIVES

Very few polymers are used in their pure form. Most include additives that improve or extend the properties of the polymer. These additives include pigments (to add colour), UV stabilisers (to prevent deterioration in sunlight), flame retardants and plasticisers.

PLASTICISERS

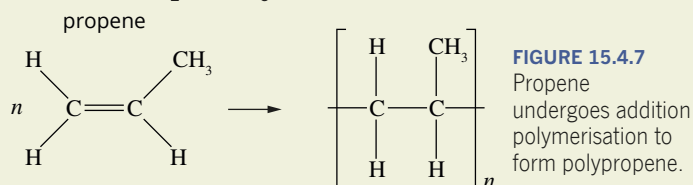
Plasticisers are small molecules that can be added to polymers during their manufacture. The polymer molecules are forced slightly further apart, weakening the forces between the chains and making the material softer and more flexible.

EXTENSION

Arrangement of side chains

The way that side chains are arranged within the polymer chain also has a significant effect upon the properties of a polymer material, such as polypropene (PP).

PP is an addition polymer made from the monomer propene ($\text{CH}_2=\text{CHCH}_3$), as shown in Figure 15.4.7.



The way the methyl **side groups** ($-\text{CH}_3$) are arranged along the polymer chain has a significant effect on the properties and uses of this polymer. Figure 15.4.8 shows the three different structural forms of PP.

- Isotactic PP has all the side groups on one side of the polymer chain and syndiotactic PP has the side groups on regularly alternating sides of the polymer chain. These two arrangements allow crystalline regions to form, and significant attractive forces exist between the chains. Isotactic PP is used in many applications. For example, it is used to make babies' bottles that can be sterilised in boiling water without softening, Australian banknotes, very strong fibres and ropes, thermal underwear and fleece jackets.
- Atactic PP has the side groups randomly distributed. This prevents the chains from stacking together well and forming crystalline regions. Atactic PP is very soft and has limited usefulness.

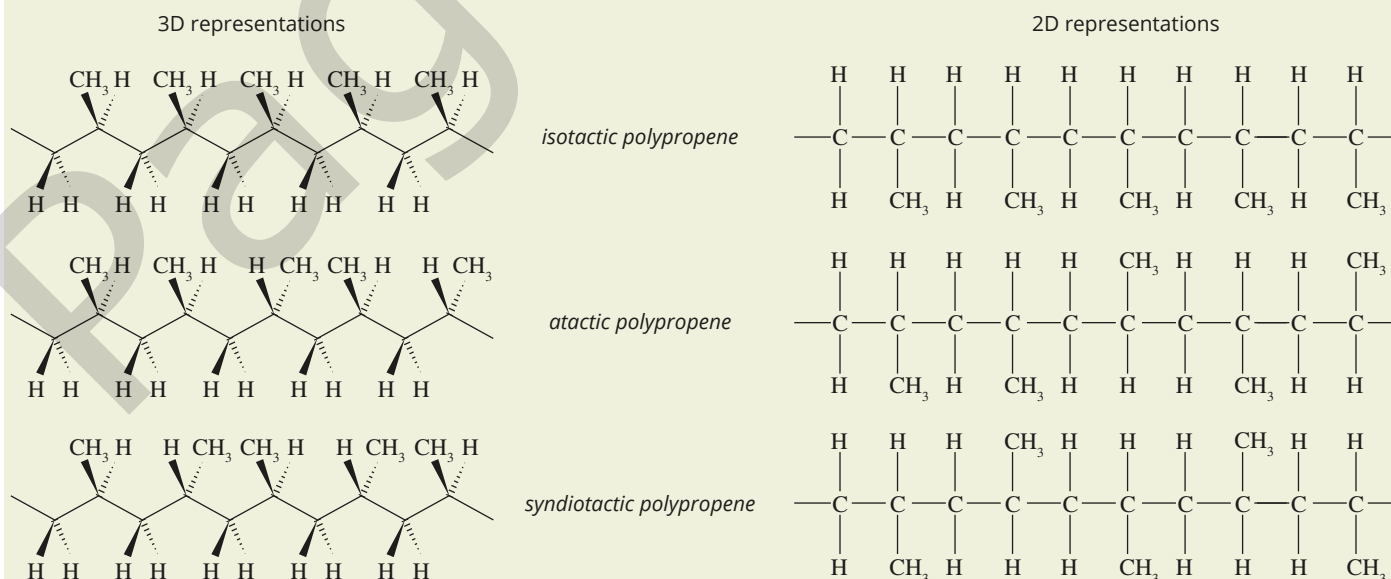


FIGURE 15.4.8 Sections of three different structural forms of polypropene

Size of side group on monomer

Bulky side groups in polymer chains make it difficult for the chains to slide over one another or stack closely together. This prevents the formation of crystalline regions that refract light. As a result, an amorphous material is produced that is often transparent, making it a useful substitute for applications where glass had been traditionally used.

Polystyrene is an example of an addition polymer that is formed from a polar monomer called styrene or phenylethene (Figure 15.4.9). The styrene molecule contains a benzene ring as a bulky side chain.

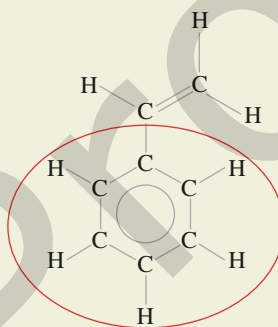


FIGURE 15.4.9 The styrene monomer contains a bulky benzene ring side group (circled in red).

In polystyrene, benzene rings are covalently bonded to every second carbon atom in the polymer chain. The bulky benzene side chain makes it quite difficult for the chains to slide over each other or to stack closely together. This causes polystyrene to be a hard but quite brittle plastic with a low density. It is used to make food containers, picnic sets, refrigerator parts and CD and DVD cases.

CHEMFILE

Hydrogels

Hydrogels are networks of polar polymer chains that are highly absorbent, containing up to 90% water. Hydrogels can be both natural and synthetic and are used in a range of applications. Because of their high water content, most hydrogel structures are biocompatible, and they are used in biomedical applications such as contact lenses, breast implants, dressings for burns and scaffolds for tissue engineering. Hydrogels are also commonly used outside the body in disposable nappies and as water-saving granules for the garden. They are also used to plug leaks in dams and ponds, and to control water flow in the mining industry. For example, if suitable hydrogels are added to a leaky dam, they will absorb water and be forced down into the cracks and holes in the dam floor by the water pressure. The hydrogels will continue to expand, sealing the surface.

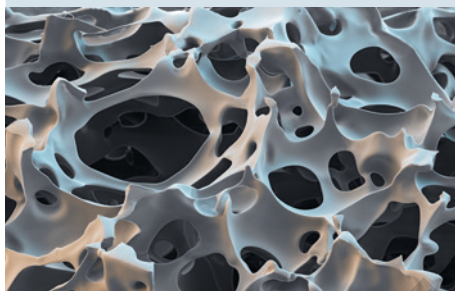


FIGURE 15.4.12 A scanning electron micrograph of a polymer hydrogel formed from the polymerisation of acrylic acid. It can hold many times its own weight in water.

Because of the polar carbon–chlorine bond in polyvinyl chloride (PVC), the polymer chains are held together strongly by dipole–dipole attractions. Pure PVC is quite rigid at room temperature. When a plasticiser is introduced between the chains, the chains can slide past each other, making the polymer softer and more flexible. By varying the amount of plasticiser used, PVC can be produced with a wide range of flexibilities. You can see the difference between the packing of PVC without and with plasticiser in Figure 15.4.10. Diisononyl phthalate is a plasticiser that is used to make PVC into vinyl floor coverings.

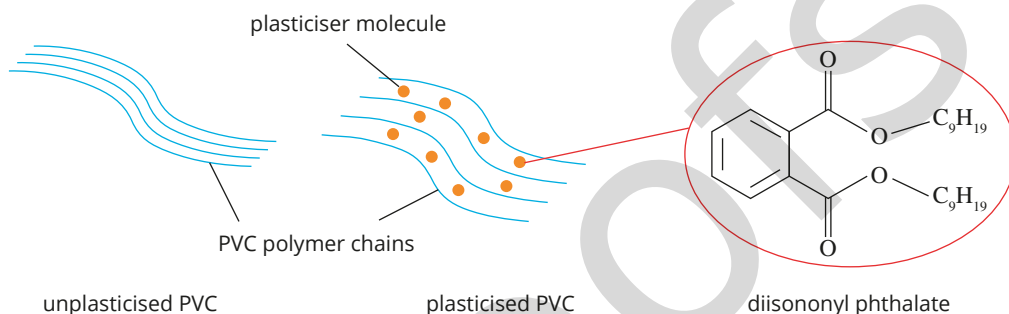


FIGURE 15.4.10 The presence of a plasticiser between the polymer chains weakens the attractive forces.

FOAMED POLYMERS

Foamed polymers are formed by blowing a gas through melted polymer materials. Foaming can drastically change the physical properties of a polymer material, as shown by the two examples of polystyrene in Figure 15.4.11. Polystyrene foam is produced by introducing pentane into melted polystyrene beads. The beads swell up to produce the lightweight, insulating, shock-absorbing foam that is commonly used for take-away hot drink containers, bean bag beans and packaging materials.



FIGURE 15.4.11 A model plane made of rigid polystyrene sitting on a block of foamed polystyrene.

RECYCLING PLASTICS

Australians consume more than 1.5 million tonnes (1.5 billion kilograms) of polymer materials every year, which includes many different plastics. Many polymers are derived from petroleum, a non-renewable resource, which increases the environmental impact associated with their production. Therefore, the disposal of the waste polymer material is a serious issue.

Plastics are durable, chemically resistant and lightweight. These properties make plastics very useful, but they also mean that plastics biodegrade very slowly. Once discarded, plastics persist for a very long time, possibly hundreds of years. Because synthetic polymers have low density, waste plastic takes up more volume than other kinds of waste. Waste plastics occupy the limited space available in landfills and litter the environment. Burning plastics raises concerns about pollution from harmful combustion by-products. For example, hydrogen chloride is formed by the combustion of waste containing PVC.

The problems related to disposal have resulted in more waste plastic being collected from users to be recycled. There are two ways of recycling plastics. Reprocessing involves shredding, melting and reshaping used plastic into new, clean products as shown in Figure 15.4.13. This method can be used only with thermoplastic polymers. For example, reprocessed polyethene can be used for manufacturing carry bags, rubbish bins and liners and bottle crates. One of the issues with recycling polymers in this way is that the different types of plastic need to be completely separated before they are melted. If not, the different polymers do not usually mix and instead form different layers, reducing the usefulness of the recycled polymer. A numbering scale is used to identify plastics for recycling (Figure 15.4.14).



FIGURE 15.4.13 This plastic is being reprocessed by shredding and blow-moulding new products.

1	2	3	4	5	6	7
PET	HDPE	PVC	LDPE	PP	PS	OTHER
Polyethene terephthalate	High-density polyethene	Polyvinyl chloride	Low-density polyethene	Polypropene	Polystyrene	Includes polycarbonates, ABS, Teflon, various copolymers, nylon & other condensation polymers
drink bottles, shampoo bottles, etc. take-away food containers	garbage bins, fuel tanks, hard hats, banners, water pipes, food storage containers	plastic wrap, cordial bottles, electrical wire covers, water pipes, floor tiles	plastic wrap, squeeze bottles, plastic tubing, shopping bags	rope, clothing, ice-cream containers, flip-top bottle lids	yoghurt containers, fridge shelves, drink cups, insulating beads, packaging	

FIGURE 15.4.14 International number codes are used to identify recyclable plastics.

The other method of plastic recycling involves depolymerisation, in which polymers are broken down into monomers, usually by heat. These monomers are then either used to produce new polymers or as fuel sources. Figure 15.4.15 shows the depolymerisation of polystyrene back into individual styrene monomers. Depolymerisation requires a large amount of energy and the yield is usually low, making this recycling method less economically viable than reprocessing.

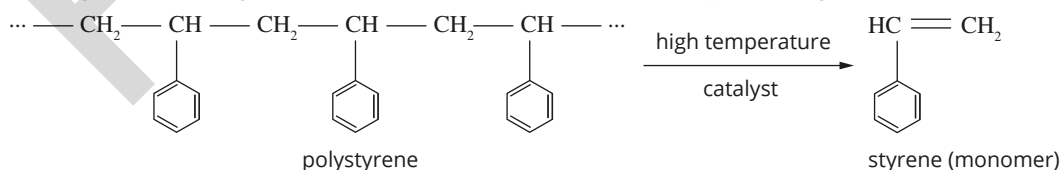


FIGURE 15.4.15 Depolymerisation of polystyrene at high temperature with a catalyst re-forms styrene monomers.

EXTENSION

Biodegradable polymers

Biodegradable materials break down naturally by the action of microorganisms. Most polymers and plastics are non-biodegradable, which is a major environmental problem. However, biodegradable polymers are being developed and used more widely. Most biodegradable polymers are condensation polymers that are made from renewable plant materials such as corn and starch. Their structure is often similar to those of biological macromolecules such as carbohydrates and proteins, which is why they can be broken down.

Poly(lactic acid) is one such material (Figure 15.4.16). It is a polyester that is commonly used as a packaging material or in bags and cups, as well as in medical applications. It is broken down by microorganisms into its lactic acid monomers, which occur naturally and pose no environmental or biological risk.

A second approach to form biodegradable polymers involves including additives such as transition metals in the polymers used to make food wrappings and shopping bags. These additives promote degradation of polymer chains to smaller, biodegradable compounds over time.

Another approach to biodegradable polymers involves finding and investigating microorganisms that can break down common plastics. In recent years, scientists have identified several microorganisms capable of digesting oils and common plastics such as polyethylene terephthalate or polyurethane. For example, the fungus *Petalotiopsis microspore* can survive on a diet of polyurethane. The fungus was found in the Amazon jungle by a research team from Yale University in 2011. Scientists are now focusing on isolating the specific processes and enzymes involved within these very useful microorganisms.

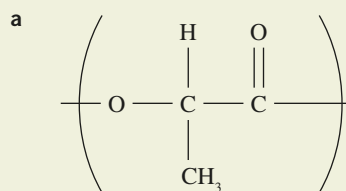


FIGURE 15.4.16 (a) Poly(lactic acid) is a biodegradable polymer produced from corn starch. (b) One of its applications is as a barrier to protect young plants from the ravages of frost. By the time the plastic degrades, the plants are big enough to survive on their own.

15.4 Review

SUMMARY

- Materials composed of polymers offer an almost limitless variety of properties, enabling them to be used for many different purposes.
- The percentage crystallinity of a polymer is a measure of the relative amounts of crystalline (ordered) regions and amorphous (disordered) regions in the material.
- No polymer is entirely crystalline. Some are entirely amorphous; most consist of both structures.
- Polymers can be designed for a particular purpose by selecting suitable monomers, reaction conditions or additives.
- Factors that affect the physical properties of polymers include the:
 - polarity of side groups in the polymer
 - use of more than one monomer (copolymers)
 - polymer chain length
 - extent of branching of polymer chains, e.g. LDPE and HDPE
 - inclusion of additives such as plasticisers with the polymer.
- A copolymer is a polymer that is made from more than one monomer.
- Plasticisers are organic molecules that soften a plastic because they weaken intermolecular attractions between polymer chains.
- Because most polymers are made from non-renewable resources and are not biodegradable they pose an environmental risk.

KEY QUESTIONS

- 1 Identify the strongest type of intermolecular force present between polymer molecules produced from the following monomers.
 - a Ethene ($\text{CH}_2=\text{CH}_2$)
 - b Vinyl chloride ($\text{CH}_2=\text{CHCl}$)
 - c Styrene ($\text{CH}_2=\text{CHC}_6\text{H}_5$)
 - d Propene ($\text{CH}_2=\text{CHCH}_3$)
 - e Acrylonitrile ($\text{CH}_2=\text{CHCN}$)
- 2 The following polymer is a copolymer formed from an addition polymerisation reaction. Name the corresponding monomers used to form the chain.
$$\begin{array}{cccccccc} \text{H} & \text{H} & \text{F} & \text{F} & \text{H} & \text{H} & \text{F} & \text{F} \\ | & | & | & | & | & | & | & | \\ \dots - \text{C} - & \text{C} - & \text{C} - & \text{C} - & \text{C} - & \text{C} - & \text{C} - & \text{C} - \dots \\ | & | & | & | & | & | & | & | \\ \text{H} & \text{H} & \text{F} & \text{F} & \text{H} & \text{H} & \text{F} & \text{F} \end{array}$$
- 3 The following side groups are found in different polymers. Sort the groups from smallest to bulkiest.
-F (in Teflon), $-\text{NC}_{12}\text{H}_8$ (in polyvinyl carbazole), -H (in polyethene), $-\text{C}_6\text{H}_5$ (in polystyrene), -Cl (in polyvinyl chloride)
- 4 Identify whether the following features of a polymer chain will increase or decrease the crystallinity of the polymer material.
 - a Regular (non-random) arrangement of side groups
 - b Less branching
 - c Larger side groups
- 5 Identify the desired outcome of the following modification techniques used by polymer chemists.
 - a Inclusion of a plasticiser
 - b Foaming
 - c Using a catalyst to prevent branching of polymer chains

Chapter review

KEY TERMS

addition polymer	crystalline region	polyester
addition polymerisation	elastomer	polymer
amorphous region	high-density polyethene	polymerisation
biodegradable	low-density polyethene	side group
condensation polymer	monomer	thermoplastic
condensation polymerisation	plastic	thermosetting
copolymer	plasticiser	
cross-link	polyamide	

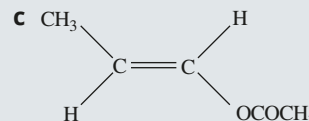
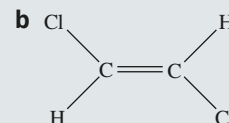
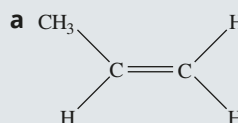
Polymers: a diverse class of materials

- Define:
 - monomer
 - thermoplastic
 - thermosetting
 - cross-link
 - plasticiser.
- Are the following statements about polymers true or false?
 - Each chain in a polymer is the same length.
 - The chains in thermosetting polymers are held together by dipole-dipole bonds.
 - HDPE has no branches
 - The properties of a polymer are different from the properties of the monomer.
- The polymer chains of a certain material can be cross-linked to varying extents.
 - Sketch the polymer chains when there is:
 - no cross-linking
 - a little cross-linking
 - a large degree of cross-linking.
 - Use diagrams to show the effect of stretching each of these materials.
- Use a diagram to explain how an elastomer is able to stretch and return to its original shape.
- How does the strength of the inter-chain bonding differ between thermosetting and thermoplastic polymers?
- Why do thermosetting polymers decompose rather than melt when heated strongly?
- Would a thermoplastic or thermosetting polymer be the most suitable material for the following purposes?
 - Handle of a kettle
 - 'Squeeze' container for shampoo
 - Knob of a saucepan lid
 - Shopping bag
 - Rope

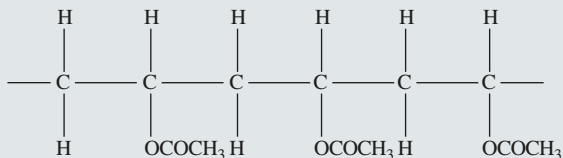
- Elastic bands, golf balls and saucepan handles are made from polymers with some cross-linking.
 - Which of these objects requires a material with the greatest degree of cross-linking?
 - Describe the properties of the material you chose in part **a** to support your answer.

Addition polymerisation

- Which of the following molecules can act as monomers in addition polymerisation?
 - Propene
 - Propane
 - Chloroethene
 - $\text{CH}_2=\text{CHF}$
- Ethene (C_2H_4) is the smallest alkene.
 - Why is it described as unsaturated?
 - Draw the structural formula of ethene.
 - Could ethane (C_2H_6) act as a monomer? Explain.
- Using polyethene as an example, explain the following terms.
 - Addition polymerisation
 - Unsaturated and saturated
 - Empirical formula
- Draw a section of the polymer made from each of these monomers in an addition polymerisation process.

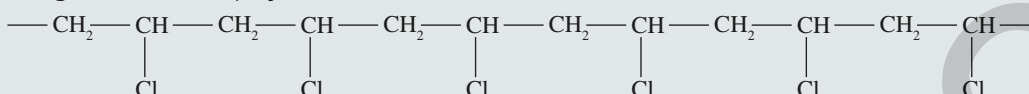


- 13** PVA (or white) adhesive contains polyvinyl acetate in water. A section of the polymer is shown below.



Give the structural formula for its monomer, vinyl acetate.

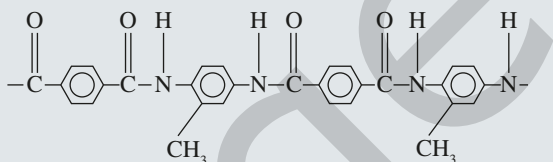
- 14** A segment of a PVC polymer is shown here.



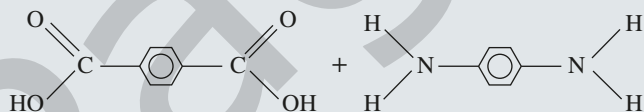
- a** Draw the structure of the monomer used to make PVC.
b How many repeating monomer units are shown in the section of polymer?
c What is the strongest type of bonding between PVC polymer chains?
- 15 a** What properties make plasticised PVC a suitable material for the covering of electrical cables?
b Explain how the structure of PVC chains give rise to these properties.
- 16** Polytetrafluoroethene has a higher melting point than polyethene. Explain why.

Condensation polymerisation

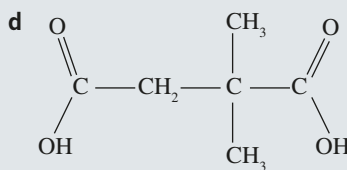
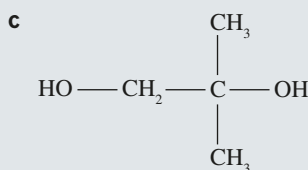
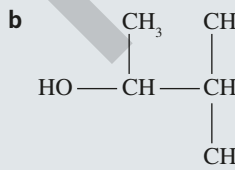
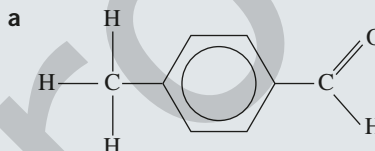
- 17** The structure of a polyamide is shown below. Draw the structure of the two monomers.



- 18** Draw the structure of the polymer formed when the following two monomers react.

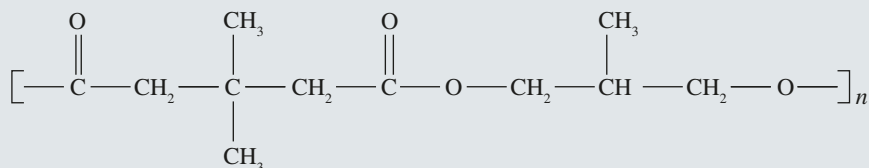


- 19** Identify the two molecules below that could react with each other to form a condensation polymer.



CHAPTER REVIEW CONTINUED

- 20 The structure of a polyester is shown below. Draw the structure of the two monomers.

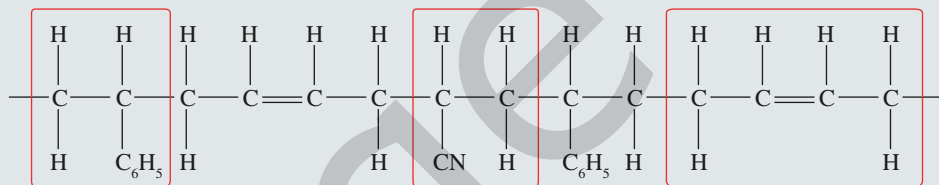


- 21 In this chapter, you learnt about two different types of condensation polymers. In the case of polyesters, the polymer is generally formed by the reaction between two monomers, dicarboxylic acids and diols. However, condensation polymerisation does not always have to occur between two different monomers. It is possible to have a condensation polymerisation reaction with just one molecule.

Use what you know about polyesters to construct the structural formula of a single monomer that can undergo condensation polymerisation.

Designing polymers for a purpose

- 22 Plasticisers can be added to polymers to change their properties. What effect does the addition of a plasticiser have on the hardness and softening temperature of a polymer?
- 23 What properties are most likely to cause a polymer to contain crystalline regions?
- 24 Part of the copolymer acrylonitrile–butadiene–styrene (ABS) that Lego® is made from is shown here. Identify the chemical formula of the monomers responsible for the sections in each box.



- 25 Explain how the following polymer production techniques will affect the properties of a polymer.
- Production conditions that favour longer polymer molecules
 - Incorporation of side groups with benzene rings ($-\text{C}_6\text{H}_5$)
- 26 Is a plastic that can be recycled more likely to be thermoplastic or thermosetting?

Connecting the main ideas

- 27 Describe two differences between addition and condensation polymerisation.
- 28 A polymer chemist is investigating the properties of polymers by increasing the length of chains in a controlled way. The chemist identified the effect on the relative molecular mass, melting point, strength of inter-chain forces and electrical conductivity. What would you expect the results for each property test to have been?