**CHAPTER**

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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From monomers to polymer**400**

**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 it is 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.

**Darwin’s FIGURE 15.1.3**

bark spider (Caerostris darwini) is an orb-weaving spider whose web is made of one of the toughest natural polymers ever studied.

AREA OF STUDY 6 | ORGANIC SYNTHESIS

**15.1 Polymers: a diverse class of materials**

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.

+ + + + + + + + ...

... g FIGURE NATURAL Many from Chapters natural are mulberry polymer monomer natural sugar e polymers 15.1.2 molecule polymers molecules 17 silkworm monomers, fibres Monomers and POLYMERS are are 18, used found (Bombyx used join are principally in P to also in in the each nature. mori a polymers textile range other ). glucose For to Cotton r of industry. form example, made applications. polymers. and is o the from Silk fructose. carbohydrates seed amino is For a hair protein o Proteins, example, acid of plants are monomers. produced polymers as silk f of discussed and the s made in Many cotton by 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

**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.

P 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.

401 CHAPTER 15 | FROM MONOMERS TO POLYMERS

r

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o

f

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**402**

AREA OF STUDY 6 | ORGANIC SYNTHESIS

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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.

**straight-chain polymer branched-chain polymer**

**FIGURE 15.1.6**

r

o

o

f

s

g polymer Polymer e chains P Straight-chain polymers have linear molecules. Branched-chain branching off in different directions from the main branching changes the properties of polymer.

the polymers have shorter 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.

polymer chain

P

P

r

o FIGURE weak The is the FIGURE strong also molecules CC heat S bonds S Heat move weak covalent sufficient 15.1.7 15.1.8 required between causes forces o enough A A themselves. bonds thermoplastic thermosetting to CC to between the break the to break between molecules overcome chains.

S the f the molecules. bonds polymer the polymer cross-links C to the s has

within

has chains.

C e

CC CC C C

**FIGURE 15.1.9**

S g

S

S CC CC C S

S

C a

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

403 CHAPTER 15 | FROM MONOMERS TO POLYMERS

**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.

s

• Straight-chain and branched polymers without covalent cross-links are known as thermoplastic polymers. They will soften when heated and can be reshaped.

KEY QUESTIONS

1 Define:

a polymer b monomer c repeating unit. 2 Explain the difference between a thermosetting and

thermoplastic polymer.

P

a

g

e

3 4 • • P Two monomers, of to chains? To in for Polymers between as instead Elastomers links original natural branching. have what your thermosetting polymers that stronger Explain degree answer. either position. rubber chains allow with but r are Which A burn would your polymer covalent and polymers them dispersion are to polymers. be material, o B or answer. hard you to are cross-linked? decompose B bonds, stretch and expect with composed has forces They A rigid a occasional or or and much o the between B, do cross-links, when and Suggest would return polymer not of higher the are melt heated. cross-

polymer you to same known a f degree

chains their and

reason

expect

**404**

AREA OF STUDY 6 | ORGANIC SYNTHESIS

**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.

H

H

H

H

H

H

C C

+ C C

+ C C + ... H

H H

H H

H f

s

**FIGURE 15.2.1**

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.

H H H C C C H H H H C H H C H o

H C

H

or H H

C

C

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

The

o segment H H

*n*

usually represented like this

P A ball-and-stick a

representation g

of a segment e of polyethene

P

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.

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.

**FIGURE 15.2.2**

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P

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 Chloroethene (vinyl chloride) Polychloroethene, It is possible to predict the structure of an addition (PTFE) or polyvinylchloride polymer from the Read through the steps in Worked addition polymer.

**Worked example 15.2.1**

ADDITION POLYMERS: FORMING Draw the addition polymer that has CH

3

Thinking Write the chemical formula for the monomer so that the

POLYMERS Example 15.2.1 o

to predict o

the structure f (PVC)

monomers.

s

of an

double bond is horizontal and the bonds to all other groups are perpendicular to

−CH=CH−CH r 3

as its monomer.

the carbon centres.

Repeat this several times so that the C=C double bonds of neighbouring monomers

**Working**

H

CH P 3

CH

3

H

are adjacent to one another.

C C

Remove and centres This connect gives with the you double single all the e

carbon

structure

bonds. bonds

H

CH

3

H

CH

3

H

CH

3

H

CH

3

H

CH

3

CH

3

H

CH

3

H

CH

3

H

CH

3

H

CH

3

H

of the polymer.

C C

C C

C C

C C

C C g

**Worked H**

CH

3

H

CH

3

H

CH

3

H

CH

3

H

CH

3 a

C C

C C

C C

C C

C C

CH

3

H

CH

3

H

CH

3

H

CH

3

H

CH

3

H

**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.

H

CH

3

CH C

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.

CH

3

CH

3

CH

3

CH

3

CH

3

CH

2

CH

3

CH

2

CH

3

CH

2

CH

3

CH

2

CH

3

CH

2

CH

3

C

C

C

C

C

C

C

C

C

C

F

Cl F Cl F Cl F Cl F Cl

**Thinking Working**

Identify the repeating unit of the polymer. It will contain just two adjacent carbon atoms from the polymer backbone.

CH

3

CH

2

CH

3

C C

F Cl

Remove every second single bond along the length of the chain and form the

CH

3

double bond between the two carbon atoms of the monomer. This gives you

F

CH

2

the structure of the monomer.

CC

CH

3 Worked example: P ADDITION POLYMERS: Draw the structure H CH

3

H

C

C C

**of Try the DETERMINING yourself monomer 15.2.2**

that THE produces MONOMER e

Cl

the following UNIT

polymer.

H

H

POLYETHENE

CH

3

H

C C

H

g CH C 3

H

C

H

CH

3

C

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.

CH

3

H

C C

H

CH

3

H

C C

H

CH

3

H

C C

H

r

o

P

a

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CH

3

H

C C

H

o

f

s

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AREA OF STUDY 6 | ORGANIC SYNTHESIS

P

H H H

H H

H

H

H

H

H H

CC

CC

CC

CC

H H H H

H

H H H

H H

H

H

H

H

H H

CC

CC

CC

CC

H H H H

H

a

H H H

H

H

H

H

H

H H

C

CC

CC

CC

H H H

H

H H H H

H

C

CC C

H H

H

dispersion forces

H H

H H H H

H

FIGURE 15.2.3 Dispersion forces between polyethene molecules polyethene a solid at room temperature. Polyethene can exist in two different structural is manufactured. The manufacturing process affects the polyethene chain and hence the strength of neighbouring chains. This makes the polymer suitable the are forms for the dispersion strong o different degree H C

depending enough of uses.

forces to branching make

on between how on it

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.

CH

2

H

H

H H

C

CC

CC

CC

H H H

H

e

P CH

3

r

o

CH

2

H H CC f H

H

s H H C

g

CH

2

CH

2

CH

3

**... ... FIGURE 15.2.4**

CH CH

2

CH CH

2

CH

2

CH

CH CH

2

CH

3

CH

3

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.

**a b**

**Properties**

• low density

• relatively soft

• low melting point

• non-crystalline

• non-conductor of electricity

**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.

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 accidently 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.

P a

g b

e

P

r

o

o

f

s

chains can pack more tightly than in LDPE

polyethene

**Properties chains**

• High density

• Hard

• Relatively high melting point

• Crystalline sections

• Non-conductor of electricity

**FIGURE 15.2.6**

a

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

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**410**

**Scanning FIGURE 15.2.8**

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.

AREA OF STUDY 6 | ORGANIC SYNTHESIS

POLYTETRAFLUOROETHENE (PTFE) Many applications require polymers with more specialised properties than polyethene. Polytetrafluorethene (PTFE) has the formed from the monomer tetrafluoroethene structure [−CF

2

−CF

2

−]

*n*

and is

commonly known by the brand name Teflon. F

C F outer fabric

in Table 15.2.2 and plumber’s tape, non-stick parts that require lubrication corrosive liquids.

F F F C

+

C C

F

F F

tetrafluoroethene monomers

FIGURE 15.2.7 Tetrafluoroethene also known as Teflon.

TABLE 15.2.2 The properties Property Non-stick Heat resistance Chemical resistance P a Teflon inner lining film g Gore-Tex Gore-Tex camping Good Low Flame Another friction e mechanical resistance clothing raincoat, is coefficient innovative a have + ... of P Polytetrafluoroethene cookware, led monomers and to its pipes C F

F

polytetrafluoroethene use react Applications Teflon hydrophobic aqueous The operating Because artificial r (PTFE) in or melting C F

F together repels a containers segment (PTFE), of solutions). wide temperature hips o CF Its the C F

F point all (oil, to 2 many =CF also strength range and form other fat) of C F

F known 2 designed vocal polytetrafluoroethene Teflon and properties (Figure substances, of is o of 260°C. hydrophilic as applications, or the cords, is Teflon 335°C usually C−F to 15.2.7). are hold both and bonds, C F

F and like (water f represented summarised

machinery reactive this its It (PTFE), including

Teflon C F

F is upper and s more

is extremely resistant to all known chemicals. It is not attacked by strong acids and alkalis and is inert to all organic solvents.

properties Teflon is strong and durable.

Teflon is slippery to the touch. The friction coefficient between two pieces of Teflon is very low.

Teflon is non-flammable.

application of Teflon is in Gore-Tex® (Figure 15.2.8). fabric that ‘breathes’. Liquid water from rain cannot penetrate but water vapour from sweat can escape through it. High-quality

is often made from Gore-Tex.

or

*n*

a

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 (CHCl=CH

2

) as shown in Figure 15.2.9.

H

H

H H H H

weak dispersion force

C C

+

H

H H HH H

chloroethene poly(chloroethene) (polyvinyl chloride) C C

...

...

o ...

...

**FIGURE 15.2.9**

C C C C

ethene poly(ethene)

H

+

H

+

... H + –

o Cl

H H H H

+ ...

Cl H Cl H

stronger r

dipole–dipole bond

C C C C

– Polyvinyl chloride is formed from polymerisation and has dipole–dipole attractions between chains.

dipole and is section OTHER There polymers property in The more drain attractions are 15.4, carbon–chlorine P or that rigid ADDITION many properties pipes. allows may than examples to Incorporating even be form polyethene a

that familiar more POLYMERS bonds between make of commercial widespread and to in g

them additives polymer you. a Teflon. PVC of Each commercial use addition molecule chains. One such e of of of as – Because of the plasticisers, are polar main polar chloroethene of applications this, P and as PVC allow discussed monomers,

is of dipole– harder PVC in PVC.

polymers. Table 15.2.3 shows these polymers offers a unique

interest.

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f

s

**412**

Commercial addition polymers

**Monomer Polymer Properties Examples Application**

Propene Polypropene

(polypropylene)

Durable, cheap

Artificial grass, dishwasher- safe plastic, ice-cream containers, rope

C C

Dichloroethene Polyvinylidene chloride

(PVDC)

Propenenitrile Polypropenenitrile

(acrylic)

Phenylethene (styrene)

H

Methylcyanoacrylate Polymethylcyanoacrylate Polymerises

on contact with water

Super glue methyl cyanoacrylate polymethyl

cyanoacrylate (superglue) H

OCH

3

Methyl-2- methylpropenoate

O

H

Polymethyl methacrylate

Transparent,

Perspex (Perspex)

strong

(a glass substitute)

methyl-2-methyl propenoate

AREA OF STUDY 6 | ORGANIC SYNTHESIS

P

Polyphenylethene (polystyrene)

a

g

**TABLE 15.2.3**

Sticks to self, transparent, stretchy

Strong, able to form fibres

e Hard, brittle, low melting point

Food wrap

C C

Acrylic fibres, fabrics

C C

Toys, packaging, expanded foams

P

propene polypropene

CH

3

H

dichloroethene polyvinylidene

chloride (PVDC)

H Cl

Cl

H

propenenitrile polypropenenitrile

(acrylic)

CN H

H

H

H

O

H

OCH

3

phenylethene (styrene)

C C

C C

C C

r

CH

3

C

CN

C

H

H

H

H

o

polyphenylethene (polystyrene)

polymethyl methacrylate (Perspex)

o

f

s

**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 (−CH

2

−CH

2

−), formed from the addition polymerisation of ethene monomers (CH

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?

H H F

H H P

=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 of branching forces between dense than • Polytetrafluoroethene Teflon and the formula polymerisation s (CF

2

=CF

2

polyethene and polymer HDPE used in (−CF 2 of P 4 Identify monomers a

r

o hence −CF tetrafluoroethene and Gore-Tex, 2 (PTFE), −), more (LDPE) has chains. formed o weaker flexible. is also a has This polymer by known monomers a dispersion the makes high f addition

as with

degree

it less

and draw the structural formulas of the

used to form the following polymers. H

C

Cl

H

Cl

Cl

H

H

Cl

Cl

F F g H

H

e F H

H

C

C

C C C

Cl

**b**

C 3 ...

Draw the repeating a Bromoethene following a H CC section units.

monomers. a of (CH

F the CC

2

CC H addition polymers For each, draw F CC

F

F

formed from at least two

... H

CH

3

H

Cl

H

CH

3

H

Cl

H

CH

3

H

C

C

C C C

Cl

**c**

F

C

H

H

H

F

H

H

H

H

F

H

C

C

C C C =CHBr) b Propene (CH

2

=CHCH

3

) c Acrylonitrile (CH

2

=CHCN)

H 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?

413 CHAPTER 15 | FROM MONOMERS TO POLYMERS

**414**

C C

O

O

HO

HO OH O

C

O

AREA OF STUDY 6 | ORGANIC SYNTHESIS

P

OH

C

O

O

C O

C

a

O

**15.3 Condensation polymerisation**

Addition an condensation monomers functional monomers. Figure produced in each detail, even Another 15.3.1.

broader polyamides polymerisation during must groups The feature polymerisation. reaction have the range react reaction. of and two of condensation links chemically is polyesters, functional polymers, limited In the the monomers For to groups, two a with chemists the molecule reactions condensation condensation use the one into of functional use of on unsaturated is long water each a that polymerisation second polymer end polymers (H small groups 2 of monomers. technique, the molecules chains, on monomer. we neighbouring to will as occur, To known shown examine are obtain These s also the as

in

O

monomer 1

reaction between the two functional different functional groups

O

monomer FIGURE 15.3.1 monomer P C

unit O

O

r 2

groups.

o

o O) is produced f

during

polymer chain

O

C

O

end an ester in TABLE Table additional The of and 15.3.1

the e water differences 15.3.1. molecule. product Comparision Condensation is produced.

These is formed. between of functional reactions addition In this addition groups and case, require condensation the react and that alcohol together the condensation monomers and polymers

to carboxylic form have the polymers acid polymer functional groups chain. are groups react summarised

As to at a form result, each

an

**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. g

Small molecules, often water, are produced during the reaction.

The polymer backbone is a long C−C

The polymer backbone contains functional chain.

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.

O

HO

O

C C HO+ OH polyester +

water OH dicarboxylic acid monomer diol monomer FIGURE 15.3.2

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

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 teraphthalate (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.

**a**

HH

HH

**b c**

P

r

FIGURE 15.3.3 Polyethylene terephthalate (PET) has showing knitted polyester (c) Bottles made of PET O P O fibres used have the recycling a O in clothing. g O code 01.

(b) many PET e

is uses. commonly (a) A scanning used to make electron plastic micrograph bottles.

HO

+

1,4-benzenedicarboxylic acid ethane-1,2-diol

O

O

O

O

O

O

C

C

C HH

C

O

HH

**FIGURE 15.3.4**

C C

C C

monomer unit ester groups 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.

C

C

O

O

C

O

OH

HH

HO C C

OH

HH

O

O

C

C O

O

415 CHAPTER 15 | FROM MONOMERS TO POLYMERS

HH

C C

HH

o

C

o

HH

C C

HH

f

water +

s

**416**

CHEMFILE

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

H

3

C CH

3

HO OH

**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 polycarbonate phosgene plastic. (COCl 2

) In to this

produce

condensation reaction, HCl is released rather is used than to produce H

2

O. Polycarbonate water bottles, plastic

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 oestrogen. regulatory various US European concluded consumers many now mimic Food advertised products ways. and the Food bodies that Governments of P action Drug In any BPA in Safety as recent have the age. ‘BPA Administration of poses food the Authority Regardless, responded years, free’. and a hormone no industry health risk both have to and in

the

are

g

AREA OF STUDY 6 | ORGANIC SYNTHESIS

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.

+

diamine monomer O

O

C

C

HO

OH dicarboxylic acid

f

s

monomer

O

O

H

N

H

o N

H

H

N

H

FIGURE reaction Nylon Nylon a high Polyamides with also C e 15.3.6 is to tensile a produce produced a common diamine Dicarboxylic strength. a are amide polyamide C during monomer example typically N H acid These group P the and and formed of in condensation diamine water. fibres a a r monomers N

H

O

C o C undergo a condensation O

N

H

+

water

N

H

polymerisation

by combining a dicarboxylic condensation polymerisation reaction. polyamide. It can be are often used to acid monomer reaction. Water is

easily drawn into fibres with 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.

H O

HHH

O

H

H

CC

C C

C

C

+

N

C

HO

HH

H

OH

H

H 1,6-hexanedioic acid

1,6-diaminohexane

HHH

H

H

H

H

HH

H

HHH

HHH

H

H

H

H

HH

H

HHH

**FIGURE 15.3.7**

O

C O C C C

C

C

C

C C

C

C

C

C C C

N

N

N

H

H

H

monomeric unit

nylon-6,6

N

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 known as Kevlar (Figure 15.3.8). very lightweight. This makes where extreme strength is required, r

o H

o

O

O

C

HO

Kevlar in nylon Kevlar such particularly with is as an bulletproof O

OH benzene extremely useful rings vests strong in a produces and range material P

anchor of the polymer that is also applications cables. H

N

H

O

C

e +

H

N

H

C C

O N

H a 1,4-benzenedicarboxylic O g C acid 1,4-diaminobenzene

O

C

N

H

Kevlar

O

O

C C

**+ water FIGURE 15.3.8**

N

H

N

H

N

H

N P

monomeric unit

H

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.

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H

C

H

HHH

C C C

HHH

H

C

H

H

C

H

O

C C

H

C

H

HH

C C

HH

H

C

H

H

C

H

f H

C

H

N

H

H s +

water

**418**

**Worked example 15.3.1**

**CONDENSATION POLYMERISATION: FORMING POLYMERS**

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

O CH

3

O

CH

3

HO

C CH

2

CH

CH

2

C OH HO

CH

2

C CH

2 OH CH

3

Thinking 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

f

s

amine and carboxylic acid condense to form an amide.

To form the ester group in the polymer, remove the hydroxyl groups from the

**Working**

The a polyester.

O monomers are a diol and a dicarboxylic acid. Therefore, o

they will react to form

dicarboxylic acid and the hydrogen atoms from the hydroxyl groups of the C diol.

CH

3

CH

2

O C r

o C

CH

3

C CH

2

CH

CH

2

C CH

2 O CH

3

Construct the repeating unit by joining O the two halves. C

CH

3

CH P 2

O C O

CH

3

CH

2

CH

O

CH

2

C CH

2 O CH

3

Write the repeating unit inside square brackets with a subscript n to indicate it is a polymer.

O C e CH

3

CH

2

O C CH 3 g

Worked CONDENSATION Draw Include the at example: CH condensation least 2 CH

O

**Try yourself 15.3.1**

POLYMERISATION: FORMING polymer produced two repeating units. CH

2

C CH

2

O

n CH

3 P

a

**POLYMERS**

from the following monomers.

O O

HO C CH

2

CH

2

CH

2

C OH HO

OH CH

3

AREA OF STUDY 6 | ORGANIC SYNTHESIS

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**

Draw the structure of the monomer(s) used to produce the following polymer.

O

O H

H O

C C

N N

CH

3

s

**Thinking Working**

Determine whether the

O H

H O

CH

3

O H

f H polymer is a polyamide or a polyester and circle the amide or ester linkages.

O C C C

N N

The polymer is a polyamide, due to the presence of the amide O H

C

N CH 3

C C o

o N CH 3

N

Identify the repeating unit. Note that this may

(−CONH−) groups.

H O O N C C

H

N CH 3 r H N

O C O H H O

be composed of 1 or 2 separate monomers. C Within the repeating unit, O split the amide group at the C−N bond.

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).

g C O e C

O C

H

CH

3

P H C

N N

CH

3

N N

H H N N

CH

**3 Worked CONDENSATION a OH**

O C O

H H C

HO H

N N H Draw H the P

example: structure POLYMERISATION: of Try the yourself monomer(s) H

**15.3.2**

DETERMINING THE MONOMER used to produce the following O

O H

CH

3

**UNITS**

polymer.

H

O

N

N C

CH

2

C

N

CH

2

N O CH

2

CH

2

CH

2

CH

2

C

CH

2

CH

2

C

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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.

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 2 3 C D When polyester also Classify polyamides.

**a**

A A produced. diamine diol O a C condensation the and molecule, following and a diamine

a dicarboxylic name C polymers reaction the other is as acid

used polyesters substance to create e or

that a

is

H

• • • • • P Polyethylene a Polyamide condensation monomers Nylon, polyamides. Polyamides amide polyamides The predicted monomers condensation polyester. structure groups Kevlar from r polymers and tougher can have terephthalate on and of polymerisation polymer. their be diamine condensation hydrogen neighbouring proteins derived o polymers monomers. are monomers. formed bonding from are (PET) than of chains, polymers examples o dicarboxylic the by Likewise, is similar between an the structure making example can polyesters. of

the

the f acid

be of of a

O b P

a O

C

N

g N

H

*n*

O

H

H O

O

H

H O

O

C CH

2

N

CH

2

N

C CH

2

C

N

CH

2

N

C CH

2

C

**c**

O

O C

CH

2

CH

2

CH

2

C C

CH

2

CH

2

CH

2 O

O d

CH

2

*n*

O

O

C C

O CH

2

O

*n*

**420**

AREA OF STUDY 6 | ORGANIC SYNTHESIS

s

4 Draw the monomers that make up the following

polymers. a

O

O

C CH

2

C O

O CH

3

O

O

CH

3

CH

2

C

CH

2

CH

2 C O O CH

3

CH

3

**b**

CH

2 O

O C

CH

2

CH

2

CH

2

C CH

2

CH

2

CH

2

N

H

5 Draw the polymer that would be formed from the

following two reactants. a

O

CH

3

O

CH

3

HO C

C

OH HO CH

2 OH CH

3

**b**

H

H

HOOC H

H

H

H 6 H 2

N C

C

C

NH

2

In number refers chain. P the to name Given of the carbons of number this, a

nylon-6,6, deduce in of the carbons the the g

diamine. structure first in 6 the The refers e dicarboxylic of second nylon-4,6. to the

6

CH COOH

P CH

2

421 CHAPTER 15 | FROM MONOMERS TO POLYMERS

r

CH

2

o

CH

2

o CH

2

N

H

f n

s

**422**

AREA OF STUDY 6 | ORGANIC SYNTHESIS

P

a

g

**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 (CF (ETFE). 2

=CF

The 2

) made with a copolymer of ethene monomers. The copolymer is known (CH

2

=CH

as ethene 2

) and tetrafluoroethene tetrafluoroethene stadium has over 100 000 m2 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.

**The FIGURE 15.4.1**

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

e

P

r

o

o

f

s

Another copolymer called styrene–butadiene rubber (SBR) (Figure 15.4.2) is formed from styrene Pure polybutadiene is an (CH

elastomer 2

=CH(C

used 6

H

in 5

)) the and production butadiene of (CH

synthetic 2

=CHCH=CH

rubbers for

2

).

applications such as tyres and golf balls.

H H

H C

6

H

H

H H H H H

C C + CH

2

CH CH

CH

2

C

C C C C C

C

6

styrene butadiene

**FIGURE 15.4.2**

H

5

H

5

H H

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 polymer acrylonitrile–butadiene–styrene (ABS), (CH

which 2

=CHC≡N), is produces used to make the 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.

P

**FIGURE 15.4.3**

P This 3D printer a

uses an ABS g

copolymer filament e

to make an object.

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r

s o CHEMFILE Conducting Polymers insulating Nobel to Zealand), Alan electrically groundbreaking Alan Heegar Prize MacDiarmid Hideki are o properties. conducting in (USA) usually Chemistry conductive polymers Shirakawa for (born known In the polymers. f 2000, was in discovery (Japan) for polymers New

awarded

the

their

These and of

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 (CH≡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.

C H

H

H

H

C

C

C

C

C

H

H

**FIGURE 15.4.4**

C

C

H

H

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.

**424**

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.

AREA OF STUDY 6 | ORGANIC SYNTHESIS

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

P

a

g materials regions, intermolecular presence in opaque and amorphous are influences of transparent BRANCHING As has the branching when crystalline crystallinity crystallinity ADDITIVES Very or colour), plasticisers.

PLASTICISERS Plasticisers their weakening more a a extend Where Being An In The usually discussed polymer intermolecular a unable material few manufacture. some flexible. e solid, large amorphous (cloudy), percentage as UV polymers of contain the regularly the shown the less regions. is polymer the because because to crystalline prevent resulting of as stabilisers effect makes properties present, chains pack are in properties rigid up low forces forces both so in section to are of upon small as As region forces very they the that The it the materials, arranged the and are 95% the in 65%. used crystalline stronger between regions (to between polymer discussed crystalline transmission ordered of light weaker P lined have closely. a polymer polymer the of molecules whereas prevent 15.1, less that the in is the does density their no where the up strengthens brings polymer. and dense the and exist the section The chains the polymer. orderly in in entire that regions not deterioration regions pure molecules LDPE less closely are chains a r section of degree the polymer that between regular the and of pass is light of often flexible. form. These solid are crystalline, arrangement. the polymer scatter the the Increasing is polymer more can directly and and packed through 15.2, unable o more is of transparent polymer arrangement, Most polymer material are chains additives polymer amorphous. amorphous in This be making branching flexible light. HDPE sunlight), forced amorphous through chains include rather chains added the chains to also shown the in overall. material pack material, include o chains. the Figure material (see-through). percentage makes can than slightly are additives they are Amorphous it. to closer in flame in regions. material together Crystalline have with randomly being polymers a Figure stronger pigments 15.4.5. create When and making the polymer with retardants further together. a a f that material amorphous, strength crystallinity

percentage percentage softer 15.4.6 crystalline as extensive far polymers it improve and (to regions tangled

closely

during appear

apart, s

chain

fewer The

and add and less the

are

of

**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 (CH

2

**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.

H

o

f

s

), as shown in Figure 15.4.7.

propene

C

=CHCH

3

H CH

3

H CH

3

H

H H

**FIGURE 15.4.7**

*n*

C Propene

C

C

undergoes addition polymerisation to

*n*

form polypropene.

The way the methyl side groups (−CH

3

o

H

r ) 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.

H

H

C every benzene P In H H polystyrene, second C C side C C

C carbon chain C C benzene makes H atom H

**FIGURE 15.4.9**

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

rings are covalently bonded to

in the polymer chain. The bulky 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.

CH

3

H

HH

CH

3 P H HH CH 3D 3

representations H HH CH a 3 H HH CH 3 H HH g CH

3

H

e

*isotactic polypropene*

2D representations

H H H

H

H H

H H

H H

CC

CC

CC

CC

C

C

H CH

3

H CH

3

H CH

3

H

CH

3

H

CH

3

CH

3

H

CH

3

H H CH

3

CH

3

H H

CH

3

H H H

H

H CH

3

H H

H CH

3

*atactic polypropene*

CC

CC

CC

CC

C

C

HH

HH HH HH HH

H CH

3

H CH

3

H H

H

CH

3

H

H

*H H H H syndiotactic polypropene*

CH

3

**FIGURE 15.4.8**

CH

3

CH

3

H H

H CH

3

CH

3

H H CH

3

CH

3

H

H

H

H H

CC

CC

CC

CC

C

C

HH

HH HH HH HH

H H H CH

3

H

H

H

CH

3 Sections of three different structural forms of polypropene

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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.

**A FIGURE 15.4.12**

scanning electron micrograph from It water. can the hold polymerisation many of P

a polymer times its of hydrogel own acrylic a weight acid.

formed

in

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g

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.

plasticiser molecule

O

**FIGURE 15.4.10**

O

O

H

19

C

9

PVC polymer chains

O

unplasticised PVC plasticised PVC diisononyl phthalate

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**

e

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

P

r

o

o

f

s C

9

H

19

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).

1 2 3 4 PET

Polyethene

High-density terephthalate

polyethene drink bottles,

garbage shampoo

bins, fuel bottles,

tanks, hard etc.

hats, banners, take-away

water pipes, food

food storage containers

containers

cordial electrical covers, plastic floor Polyvinyl chloride

pipes,

bottles,

tiles wrap,

water wire

plastic e plastic Low-density polyethene

shopping squeeze bottles,

bags

tubing, wrap,

P 5 r

6 o reprocessed new products.

by shredding This plastic and is blow-moulding

being

7

**FIGURE 15.4.14**

P

Polypropene

rope, clothing, ice-cream containers, flip-top bottle lids

Polystyrene

polymers are shows Depolymerisation making The then the this other either depolymerisation are recycling International broken method used requires a

to method down produce of number plastic a of into large less polystyrene codes g

new economically monomers, recycling amount are polymers used back of to involves identify energy usually viable or into as recyclable individual fuel and depolymerisation, than by sources. heat. the reprocessing.

plastics.

yield styrene These Figure is usually monomers. monomers fridge in containers, drink insulating

15.4.15 packaging yoghurt

beads,

which

shelves,

low,

cups,

... CH

2

CH CH

2

CH

... high temperature

catalyst

**FIGURE 15.4.15**

CH

CH

2

HC CH

2

polystyrene styrene (monomer)

o

f

s

**HDPE PVC LDPE PP PS OTHER**

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

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**FIGURE 15.4.13**

Includes polycarbonates, ABS, Teflon, various copolymers, nylon & other condensation polymers

**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 macrolecules such as carbohydrates and proteins, which is why they can be broken down.

Polylactic 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.

finding break have digesting terephthalate fungus of jungle Scientists processes microorganisms. Another polyurethane. identified down by Petalotiopsis and oils a P are and approach research investigating common and or now enzymes several polyurethane. The common focusing microspore to team fungus plastics. a

microorganisms biodegradable involved microorganisms from plastics on was In For isolating can Yale found recent within g example, survive such University polymers in capable the years, these as that the on specific

polyethylene the

Amazon very scientists a can e in involves of

diet

2011.

useful

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**b**

**FIGURE 15.4.16**

(a) Polylactic 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.

**a**

**(a)**

H

C

CH

3

P

O

r

O

C

o

o

f

s

**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)

KEY QUESTIONS

1 Identify the strongest type of intermolecular force

present between polymer molecules produced from the following monomers. a Ethene (CH

2

- 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.

P

o

f

s

P 3 r

o

=CH

2

) b Vinyl chloride (CH

2

=CHCl) c Styrene d Propene e Acrylonitrile 2 The following an addition corresponding e

The following side groups are found in different polymers. Sort the groups from smallest to bulkiest. −F (in Teflon), −NC

12

H

8

(in polyvinyl carbazole), −H (in polyethene), −C

6

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 H 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 (CH

(CH

polymerisation H H polymer a 2

monomers (CH 2 =CHC

=CHCH

F

2

=CHCN)

6

H

is 3

F 5

F ) ) a g used copolymer reaction. H formed from

Name the to form the chain.

H

H

F F

...

CC

CC

CC

CC ... H F H F

F

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**Chapter review**

KEY TERMS

addition polymer addition polymerisation amorphous region biodegradable condensation polymer condensation polymerisation copolymer cross-link

polyester polymer polymerisation side group thermoplastic thermosetting

**Polymers: a diverse class of materials 1 Define:**

a monomer b thermoplastic c thermosetting d cross-link e plasticiser. 2 Are the following statements about polymers true or

false? a Each chain in a polymer is the same length. b The chains in thermosetting polymers are held

together by dipole–dipole bonds. c HDPE has no branches d The properties of a polymer are different from the

properties of the monomer. 3 The polymer chains of a certain material can be cross-

linked to varying extents. a Sketch the polymer chains when there is:

i no cross-linking ii a little cross-linking iii a large degree of cross-linking. b Use diagrams to show the effect of stretching each

of these materials. 4 Use a diagram to explain how an elastomer is able to

stretch and return to its original shape. 5 How does the strength of the inter-chain bonding differ

between thermosetting and thermoplastic polymers? 6 Why do thermosetting polymers decompose rather

than melt when heated strongly? 7 Would a thermoplastic or thermosetting polymer be

the most suitable material for the following purposes? a Handle of a kettle b ‘Squeeze’ container for shampoo c Knob of a saucepan lid d Shopping bag e Rope

crystalline region elastomer high-density polyethene low-density polyethene monomer plastic plasticiser polyamide

8 Addition 9 Elastic made a b P Which in A B C D addition Which greatest Describe part Propene Propane

polymerisation from of bands, a to the of degree polymerisation? r polymers support the these following golf properties objects balls of o your cross-linking? with molecules and answer. requires some of saucepan the o cross-linking. material can a material act handles as you monomers f with chose are the s

in

g

e

Chloroethene CH

2

=CHF 10 Ethene (C

2

H

4

) is the smallest alkene. a Why is it described as unsaturated? b Draw the structural formula of ethene. c Could ethane (C

2

) act as a monomer? Explain. 11 Using polyethene as an example, explain the following

terms. a Addition polymerisation b Unsaturated and saturated c Empirical formula 12 Draw a section of the polymer made from each

of these monomers in an addition polymerisation process.

C

H

6

P

a

a CH

3

H

**b**

Cl

H

C C

C

H

H

H

Cl

**c**

CH

3

H

C

C

H

OCOCH

3

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13 PVA (or white) adhesive contains polyvinyl acetate in

water. A section of the polymer is shown below.

H

H

H

H

H

H

C

C

C

C

C

C

H

OCOCH

3

H

OCOCH

3

H

OCOCH

3

Give the structural formula for its monomer, vinyl acetate. 14 A segment of a PVC polymer is shown here.

CH

2

CH

CH

2

CH

CH

2

CH

2

CH

Cl

Cl

Cl

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 Polytetrafluorethene 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.

O

C

CH

Cl

CH

CH

2

Cl

19 Identify each a

o

o

f

s

b H other r the H

H C

two molecules below that could react with to form a condensation polymer.

O P c

H

CH

3

CH

3

HO

CH

CH CH 3

C

O

O

C

C

18 Draw the structure following two O

C

H

H

N

N of the monomers O C O C

react. polymer g formed H CH e 3

H

N

when the

CH

3

CH

2

CH

3

OH

HO C OH

N P

a CH

3

H

H

**d**

O CH

3

O

C

CH

2

C C CH 3 H

OH OH + HO

N

N H

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CH

Cl

CH

2

CHAPTER REVIEW CONTINUED

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

structure of the two monomers.

O

CH

3

O

CH

3

C

CH

2

C CH

2

C

O CH

2

CH CH

2

O

*n*

CH

3 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.

H H

C

6 P

P

r

H

H H

H H CC

H

H

H H e H

C C

6

H H

H H

CC

C

H

25 Explain techniques a b Production molecules Incorporation how C

will the conditions affect following of side the groups that properties polymer C

favour g with CC

production of benzene longer a polymer.

polymer

rings

H

CC

CC

H

H

5

CN

H

5

HH

(−C

6 26 H

5

) Is a plastic thermoplastic that or can thermosetting? a be recycled more likely to be

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?

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o

o

f

s