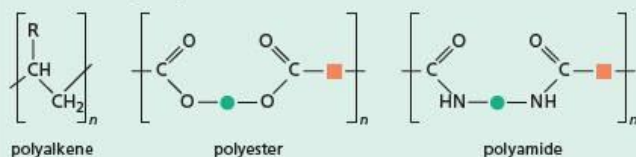


# 28 Addition and condensation polymers

## Functional groups:



*This topic takes a more detailed look at the addition polymerisation of alkenes, first met in Topic 14, and at condensation polymerisation to form polyesters and polyamides, met in Topics 26 and 27 respectively.*

## Learning outcomes

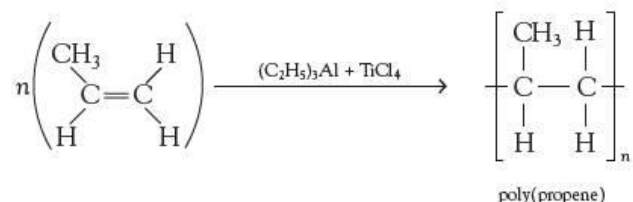
By the end of this topic you should be able to:

- 21.1a)** describe the formation of polyesters and polyamides
- 21.1b)** describe the characteristics of condensation polymerisation in polyesters as exemplified by Terylene, in polyamides as exemplified by polypeptides, proteins, nylon 6, nylon 6,6 and Kevlar
- 21.1c)** deduce the repeat unit of a condensation polymer obtained from a given monomer or pair of monomers
- 21.1d)** identify the monomer(s) present in a given section of a condensation polymer molecule
- 21.2a)** predict the type of polymerisation reaction for a given monomer or pair of monomers
- 21.2b)** deduce the type of polymerisation reaction which produces a given section of a polymer molecule
- 21.3a)** discuss the properties and structure of polymers based on their methods of formation (addition or condensation, see also Topic 14)
- 21.3b)** discuss how the presence of side-chains and intermolecular forces affect the properties of polymeric materials (e.g. polyalkenes, PTFE (Teflon), Kevlar)
- 21.3c)** explain the significance of hydrogen-bonding in the pairing of bases in DNA in relation to the replication of genetic information
- 21.3d)** distinguish between the primary, secondary ( $\alpha$ -helix and  $\beta$ -sheet) and tertiary structures of proteins and explain the stabilisation of secondary structure (through hydrogen bonding between C=O and N—H bonds of peptide groups) and tertiary structure (through interactions between R-groups)
- 21.3e)** describe how polymers have been designed to act as non-solvent based adhesives, e.g. epoxy resins and superglues, and as conducting polymers, e.g. polyacetylene
- 21.4a)** recognise that polyalkenes are chemically inert and can therefore be difficult to biodegrade
- 21.4b)** recognise that a number of polymers can be degraded by the action of light
- 21.4c)** recognise that polyesters and polyamides are biodegradable by hydrolysis
- 21.4d)** describe the hydrolysis of proteins.

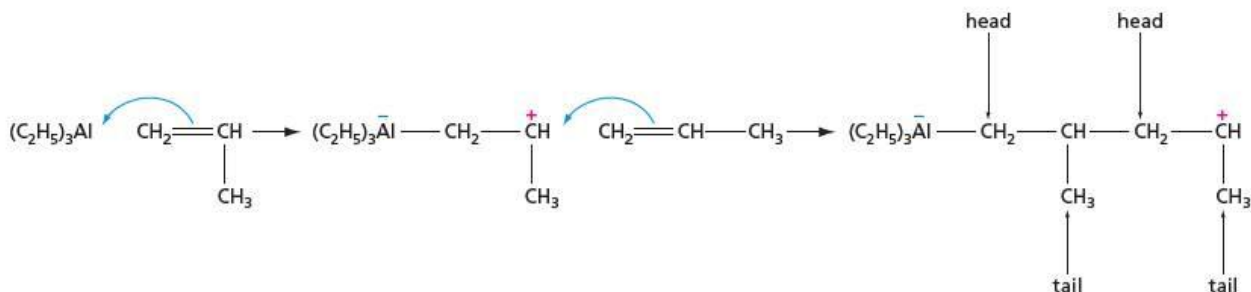
## 28.1 Addition polymers

We saw in Topic 14 how ethene could be polymerised in different ways to produce low-density poly(ethene), LDPE, and high-density poly(ethene), HDPE. Addition polymers with a variety of properties can be made by polymerising other compounds containing double bonds.

**Propene** (obtained by catalytic cracking) can be polymerised in a similar way to ethene, using the Ziegler–Natta catalyst (see section 14.4):

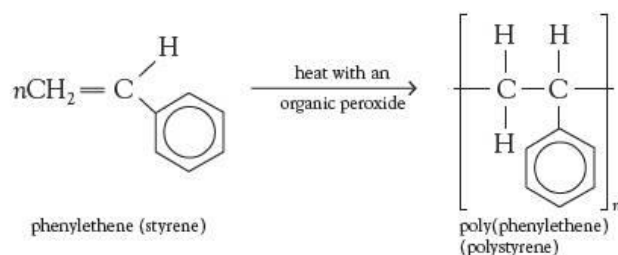


During polymerisation, the propene subunits line up in a regular head-to-tail arrangement, because as each propene molecule is added to the growing chain, the more stable secondary carbocation (see page 248) is formed as an intermediate (see Figure 28.1). Note that only two of the three carbon atoms in propene become part of the chain: the third one remains as a methyl side group at the 'tail'. The triethyl aluminium is an electrophile, acting as a homogeneous catalyst.



**Figure 28.1** The propene units line up head to tail.

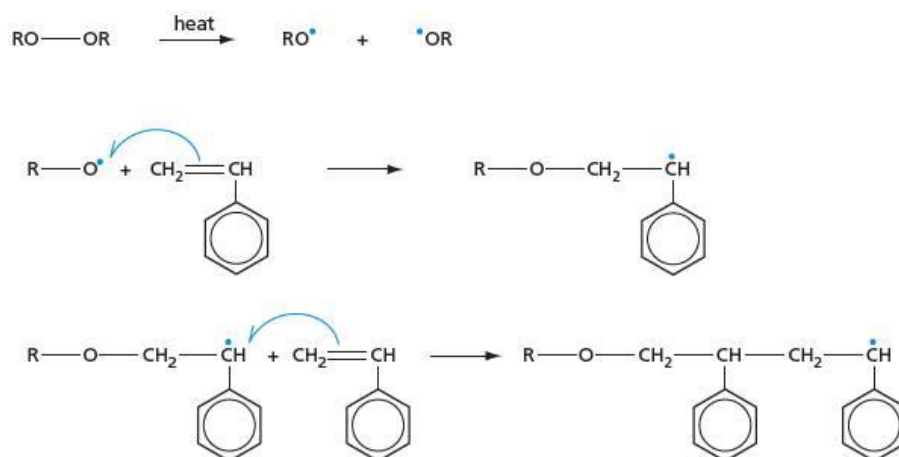
**Phenylethene** can be polymerised to form poly(phenylethene), otherwise known as polystyrene:



Phenylethene is obtained commercially by reacting together ethene and benzene followed by dehydrogenation. It is an important component of the co-polymers SBR and ABS (see the panel on pages 471–472).

The mechanism of this polymerisation is similar to that of the polymerisation of propene, but it involves radicals as intermediates, rather than cations. The more stable secondary radical is formed at each stage and the polymer forms in a regular head-to-tail chain (see Figure 28.2). The initial alkoxy radical is formed when the weak O—O bond in the peroxide is broken by heat.

**Figure 28.2** In phenylethene, the monomer units line up head to tail.

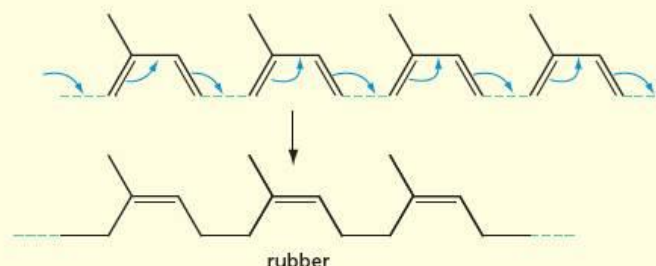
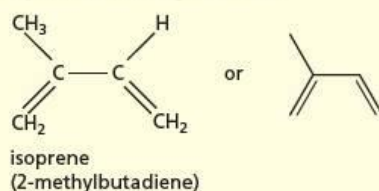


Poly(phenylethene) is used for packaging (for example, egg boxes), and model kits (because when it is moulded it can depict fine details exactly). When an inert gas is bubbled through the phenylethene as it is being polymerised, the familiar white, very light, solid known as **expanded polystyrene** is formed. This is used as a protective packaging, and for sound and heat insulation.

### Rubber – natural and synthetic co-polymers

The rubber tree is indigenous to South America, but large plantations have been established in India and Malaysia. When its bark is stripped, it oozes a white sticky liquid called latex, which is an emulsion of rubber in water. Purification of this produces rubber. In its natural state, rubber is not particularly useful. It has a low melting point, is sticky and has a low tensile strength. In 1839, Charles Goodyear discovered the process of **vulcanisation**, which involves heating natural rubber with sulfur. This produces a substance with a higher melting point and of greater strength. Rubber is an addition polymer of 2-methylbutadiene (isoprene) (see Figure 28.3).

**Figure 28.3** Isoprene undergoes addition polymerisation to form rubber.



Note that when a diene undergoes addition polymerisation, a double bond is still present in the product. This double bond may be *cis* or *trans*. In natural rubber, the long chain is *cis* across all the double bonds. From different trees, a naturally occurring substance called gutta percha can be obtained; this is an isomer of rubber in which all double bonds are *trans*. Gutta percha is harder than rubber, and in the 19th century was used as a coating for golf balls.



**Figure 28.4** A rubber tree being tapped. The white latex is converted to rubber suitable for tyres by the process of vulcanisation.



The presence of the double bond in rubber allows further addition reactions to take place. If liquid rubber is heated with sulfur, sulfur atoms add across some of the double bonds in different chains, cross-linking the rubber molecules (see Figure 28.5). This is what happens during the vulcanisation process. It stops the chains from moving past each other, and gives the material more rigidity.

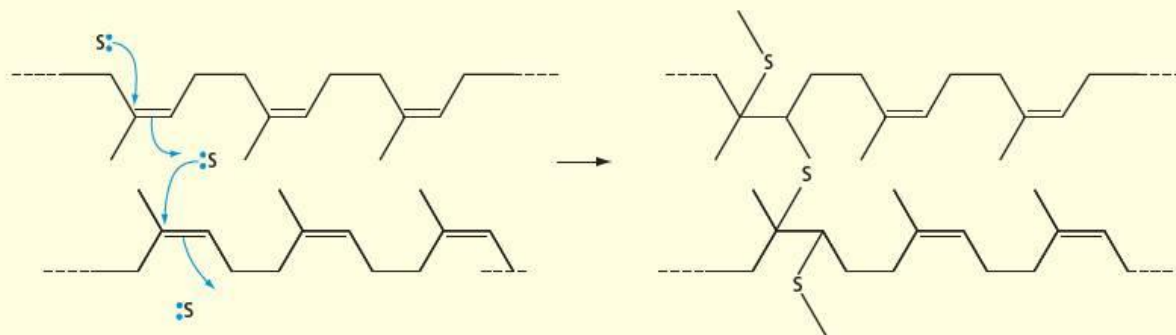
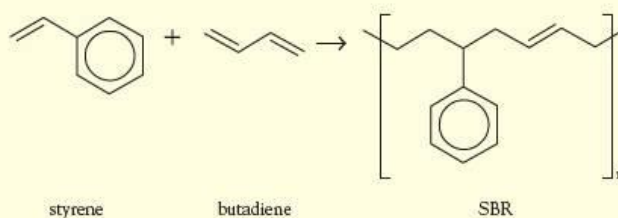


Figure 28.5 Vulcanisation of rubber

Not all double bonds have sulfur added to them. That would make the substance too hard. About 5% sulfur by mass is adequate to give the desired properties. Many millions of tonnes of vulcanised rubber are made each year for the manufacture of car tyres.

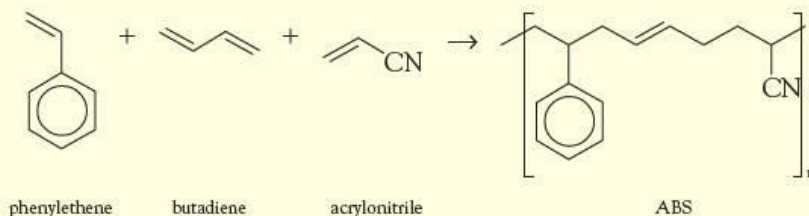
Synthetic rubber-like polymers were developed when rubber was in short supply during the Second World War. The one most commonly used today is a co-polymer of phenylethene and butadiene, called **SBR** (styrene–butadiene rubber).

A **co-polymer** is formed when two or more different alkenes are polymerised together. Even if the ratio of monomers is 50:50, there is no guarantee that the monomer fragments will alternate along the chain. The order is fairly random (in contrast to condensation co-polymerisation – see sections 28.2 and 28.3).



The product SBR still contains a double bond, and so can be vulcanised just like natural rubber.

Another co-polymer involving phenylethene and butadiene as reagents, along with acrylonitrile, is the tough, rigid plastic **ABS**, or acrylonitrile–butadiene–styrene:



Once again, the monomers join together in a fairly random manner, so the drawing of a particular 'repeat unit' does not imply a regular order. ABS is used for suitcases, telephones and other objects that need to be strong and hard, but not too brittle.

**Figure 28.6** Products made from rubber, SBR and ABS

## Addition polymerisation of other ethene derivatives

Most compounds containing the  $>C=C<$  group will undergo polymerisation. Several important polymers are made from monomers in which some or all of the hydrogen atoms in ethene have been replaced by other atoms or groups. Some of them, with their uses, are listed in Table 28.1.

**Table 28.1** Structures and uses of some addition polymers

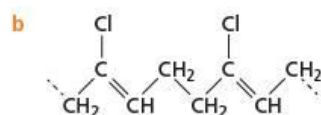
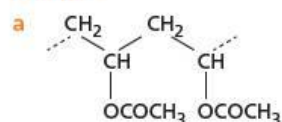
Monomer	Polymer	Uses
chloroethene $CH_2=CHCl$	poly(chloroethene) (polyvinylchloride, PVC)	guttering, water pipes, windows, floor coverings
tetrafluoroethene $CF_2=CF_2$	poly(tetrafluoroethene) (Teflon, PTFE)	non-stick cookware, bridge bearings
methyl 2-methylpropenoate $CH_2=C(CH_3)CO_2CH_3$	poly(methyl 2-methylpropenoate) (Perspex)	protective 'glass', car rear lights, shop signs
methyl 2-cyanopropenoate $CH_2=C(CN)CO_2CH_3$	poly(methyl 2-cyanopropenoate) (cyanoacrylate)	instant 'superglue'
cyanoethene $CH_2=CH-CN$	poly(cyanoethene) (acrylic)	co-polymerised with components of 'acrylic' fibres, ABS

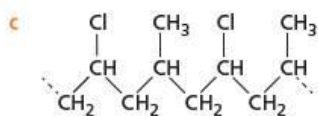
### Worked example 1

Draw **two** repeat units of the polymer formed from each of the following monomers or pair of monomers.

- a  $CH_2=CH-OCOCH_3$   
 b  $CH_2=CCl-CH=CH_2$   
 c  $CH_2=CHCl$  and  $CH_2=CH-CH_3$

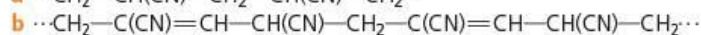
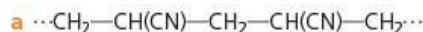
**Answer**



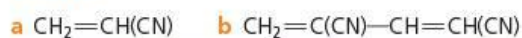


### Worked example 2

The following are sections of addition polymers. Draw the monomer(s) from which they are formed.

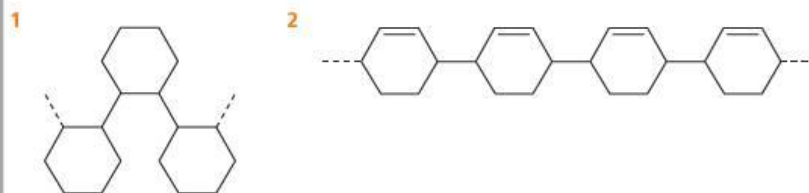


### Answer



Now try this

Suggest the monomer(s) from which the following polymers have been made.

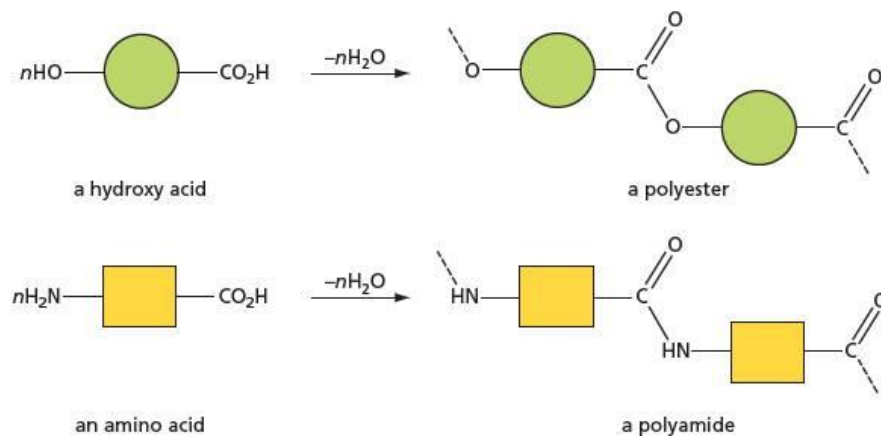


## 28.2 Condensation polymers

There are two strategies for making condensation polymers. Each strategy results in a different type of polymer.

The first strategy, producing **type I** polymers, starts with a monomer containing two different functional groups that can condense together to form either ester or amide groups (see Figure 28.7).

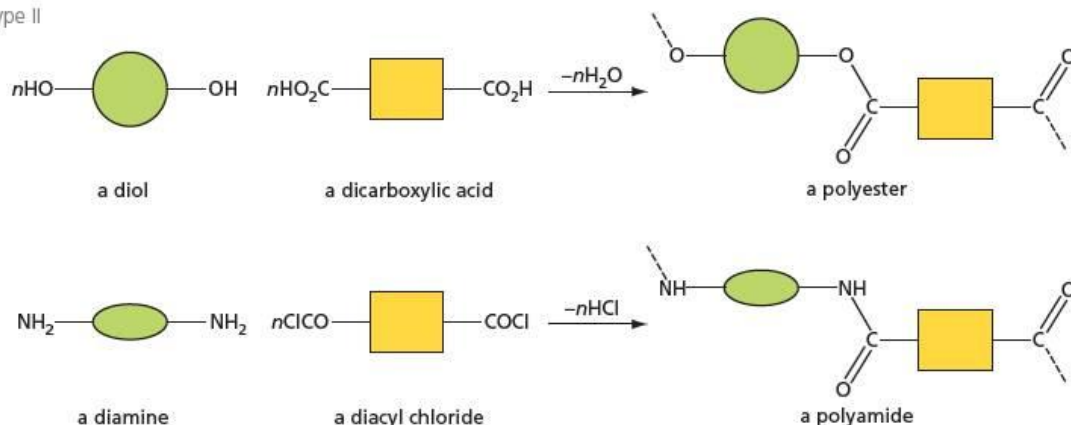
**Figure 28.7** Formation of type I condensation polymers





The second strategy, forming **type II** polymers, starts with two different monomers, one containing two carboxylic acid groups or two acyl chloride groups, and the other containing two alcohol groups or two amine groups (see Figure 28.8).

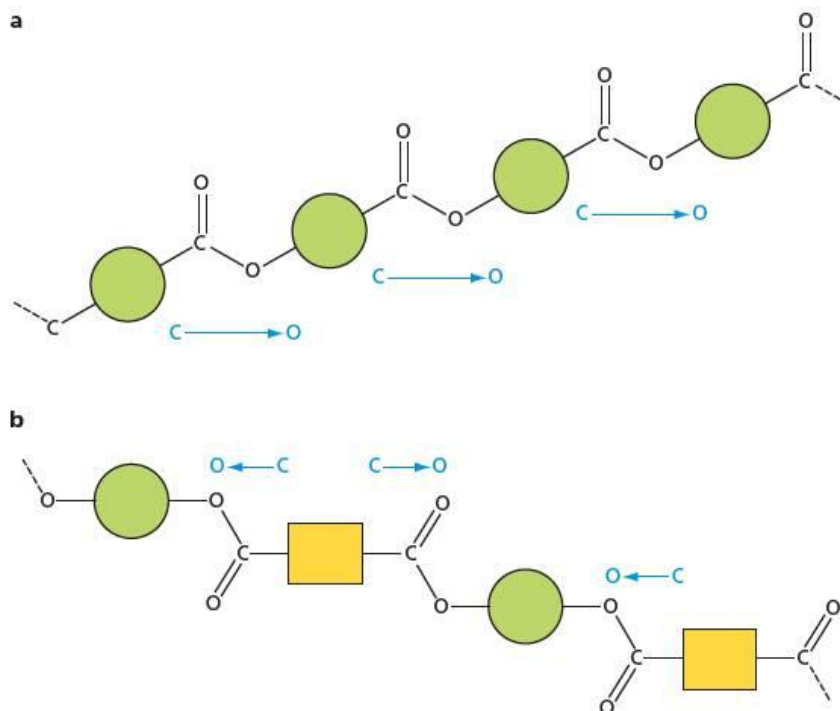
**Figure 28.8** Formation of type II condensation polymers



The two types of polymer differ in the direction of successive functional groups along the chain. In type I polymers, the direction of each ester or amide linkage is the same (see Figure 28.9a), whereas in type II polymers, the direction of the ester or amide linkages alternates (see Figure 28.9b).

Table 28.2 lists some common condensation polymers. The different nylons (polyamides) are named according to the number of carbon atoms contained within each monomer: the first number is the number of carbon atoms in the diamine, and the second is the number of carbon atoms in the diacid.

**Figure 28.9** The orientation of adjacent ester linkages in **a** a type I polyester and **b** a type II polyester



**Table 28.2** The monomers of some condensation polymers

Name	Formula(e) of monomer(s)	Type of polymer
<b>Polyesters</b>		
Terylene	HOCH <sub>2</sub> CH <sub>2</sub> OH HO <sub>2</sub> C—C <sub>6</sub> H <sub>4</sub> —CO <sub>2</sub> H	type II
polylactic acid (PLA)	HOCH(CH <sub>3</sub> )CO <sub>2</sub> H	type I
<b>Polyamides</b>		
nylon 6,6	NH <sub>2</sub> —(CH <sub>2</sub> ) <sub>6</sub> —NH <sub>2</sub> HO <sub>2</sub> C—(CH <sub>2</sub> ) <sub>4</sub> —CO <sub>2</sub> H	type II
nylon 6,10	NH <sub>2</sub> —(CH <sub>2</sub> ) <sub>6</sub> —NH <sub>2</sub> HO <sub>2</sub> C—(CH <sub>2</sub> ) <sub>8</sub> —CO <sub>2</sub> H	type II
nylon 6	NH <sub>2</sub> —(CH <sub>2</sub> ) <sub>5</sub> —CO <sub>2</sub> H	type I
polypeptides (proteins)	NH <sub>2</sub> —CHR—CO <sub>2</sub> H (R = various side chains)	type I

**Worked example**

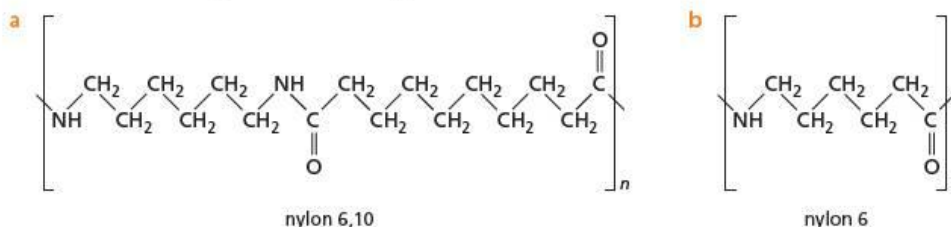
Draw the repeat unit of the chain of:

**a** nylon 6,10

**b** nylon 6.

**Answer**

The repeat unit is the smallest unit from which the polymer chain can be built up by repetition. That of nylon 6,10 will include one molecule of each of the two monomers, while that of nylon 6 will contain just the one monomer unit:

**Now try this**

- 1** Kevlar is a polymer which is five times stronger than steel on an equal-weight basis. It is used in bicycle tyres, racing sails and body armour because of its high tensile strength-to-weight ratio.

Kevlar is made from the following two monomers.



- a** Draw the repeat unit of the polymer Kevlar.  
**b** Decide whether Kevlar is a type I or a type II polymer.
- 2** A biodegradable co-polymer can be made from lactic acid, CH<sub>3</sub>CH(OH)CO<sub>2</sub>H, and 3-hydroxypropanoic acid, HOCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H. Draw the repeat unit of this co-polymer.

Like simple esters and amides, polyesters and polyamides can be hydrolysed by strong acids or alkalis. Many common fibres used for clothing, such as nylon, polyesters, wool and silk (both of which are proteins), can be dissolved accidentally by careless splashes of laboratory acids or alkalis.

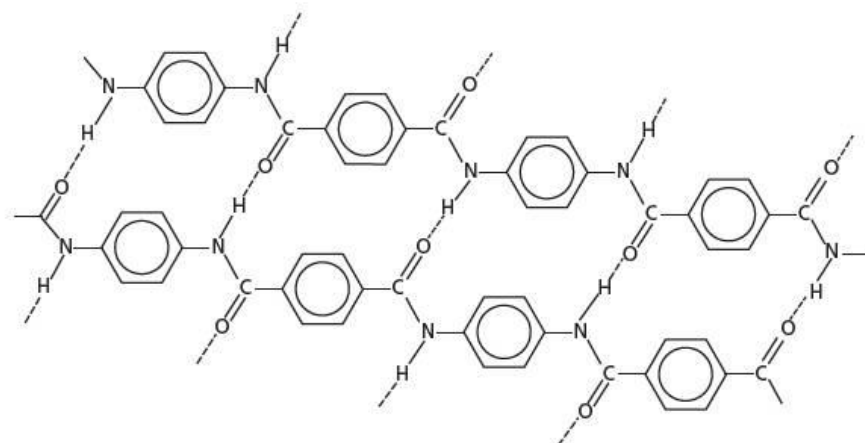


**Figure 28.10** Some uses of nylon

## 28.3 Further polymers and their properties

### Kevlar

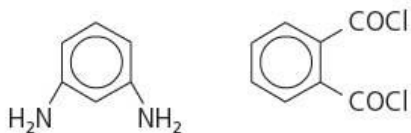
Kevlar owes its strength to the many regular hydrogen bonds between its chains. Because of the 1,4-disubstituted arrangement of the functional groups in the two aryl rings, the long chains of Kevlar are linear in shape. They can readily align side-by-side and form strong interchain hydrogen bonds (see Figure 28.8).

**Figure 28.11** Hydrogen bonding between adjacent chains of Kevlar

The tensile strength of Kevlar is five times that of steel, on a weight-for-weight basis (its density is small: about  $1.5 \text{ g cm}^{-3}$ ), yet it is quite flexible. It finds uses in tyres for cars and bicycles, bullet-proof vests and the 'skins' on modern drumheads.

### Now try this

Nomex is a related polymer, made from 1,3-diaminobenzene and benzene-1,3-dicarbonyl chloride, which is used in fire-proof clothing.



- Draw the structure of part of a chain of Nomex, showing **two** repeat units, and suggest how the strength of the interchain hydrogen bonds might differ from that in Kevlar. Explain your reasoning.
- How might the flexibility of Nomex compare to that of Kevlar?

A dramatic use of Kevlar, together with glass-reinforced polyester, is illustrated by the footbridge at Aberfeldy in Scotland (see Figure 28.12). This was the first bridge to use composite materials and was built in 1992. It was much lighter than the possible alternatives made from steel or concrete, and was built for only a third of their cost.

**Figure 28.12** The Aberfeldy footbridge is made from glass-reinforced polyester. Its cables are made from Kevlar



### Cross-linked polymers

Earlier in this topic we saw how rubber was vulcanised through the cross-linking of the chains of the rubber molecules with sulfur atoms. This made the rubber harder, stronger, less flexible and less 'sticky'. The interchain hydrogen bonding in Kevlar has a similar effect in that Kevlar is more rigid and stronger than polyamides such as nylon 6,6 or nylon 6,10.

The interchain bonding in Kevlar produces two-dimensional sheets, which can bend and slide over each other. More rigidity can be produced if the polymer chains are cross-linked by covalent bonds into a three-dimensional lattice. One of the first polymers to have these properties was **bakelite**, developed in 1907 in New York by the Belgian chemist Leo Baekeland. Bakelite was the world's first synthetic plastic,

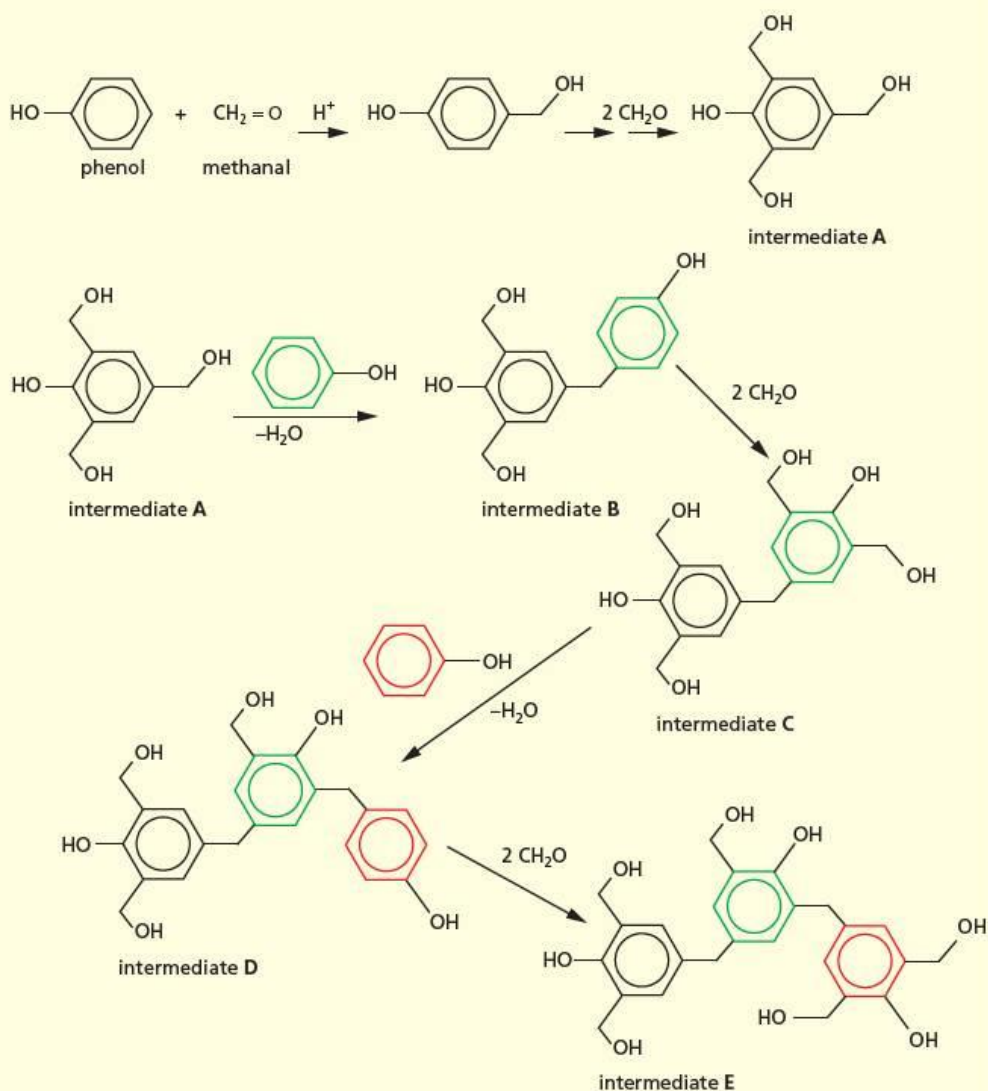


made from phenol and methanol, and its manufacture marked the start of the plastics age. It is a **thermosetting** condensation polymer: as the monomers are heated together, the mixture becomes more and more viscous and eventually sets solid. Further heating does not melt the polymer, but causes it to char. Bakelite is quite brittle, but strong enough to be used in many applications where a hard, electrically insulating, heat-resistant material is required.

The main molecular requirement for cross-linking is for the polymer chain to contain side groups that can link to other chains (see Figures 28.13 and 28.14).

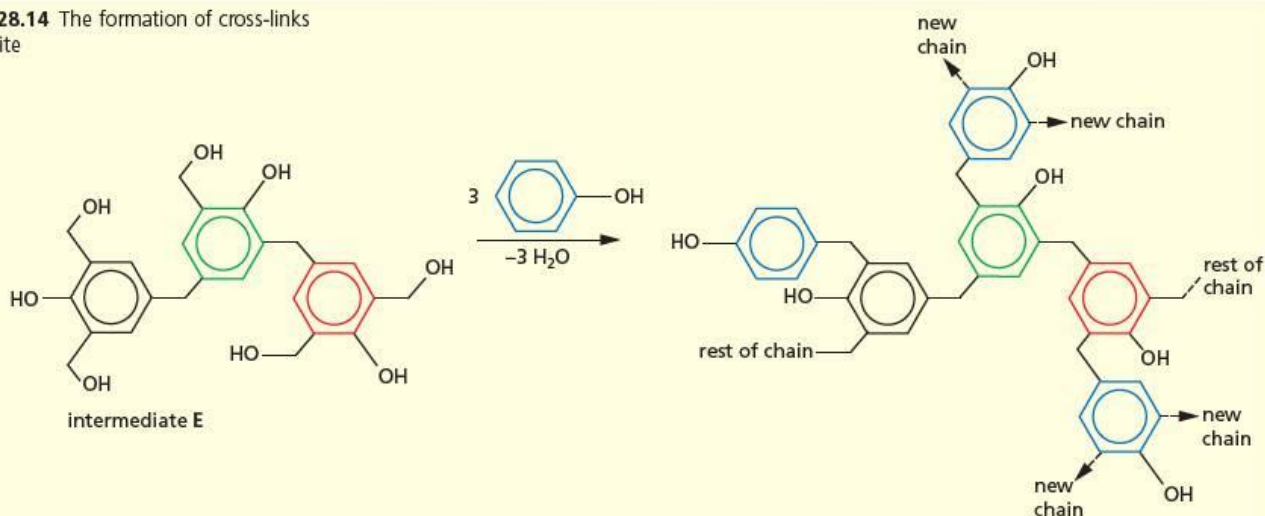
As can be seen in Figure 28.13, the acid-catalysed reaction between phenol and methanal produces intermediate **A**, which has three  $\text{—CH}_2\text{OH}$  groups on the phenolic benzene ring in the 2-, 4- and 6-positions (a similar orientation to that found during the bromination of phenol, see Topic 25). Each of these is able to undergo a condensation reaction with another phenol molecule (for simplicity, only one group is shown in the figure as reacting) to give intermediate **B**. The newly attached phenol ring can then react with more methanal, giving intermediate **C**, which can condense with another phenol, giving intermediate **D**. Reaction of **D** with two more methanal molecules produces intermediate **E**. Compound **E** contains five  $\text{—CH}_2\text{OH}$  groups, two of which are needed to continue the linear chain, leaving three available for condensation with three new phenol molecules (see Figure 28.14).

**Figure 28.13** The building-up of the linear chains in bakelite





**Figure 28.14** The formation of cross-links in bakelite



Each of these new phenolic benzene rings can now start two chains, independently of the original one. You can see how complicated matters can become! Although the structure of bakelite can become very involved, it is relatively easy to work out the ratio of phenol to methanal that is needed to make it.

### Worked example

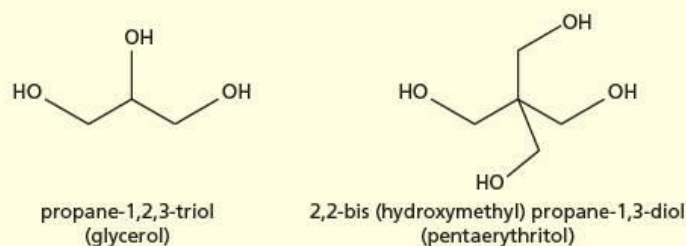
- a** Calculate the phenol:methanal ratio in bakelite.  
**b** State the assumptions you made in your calculation.

#### Answer

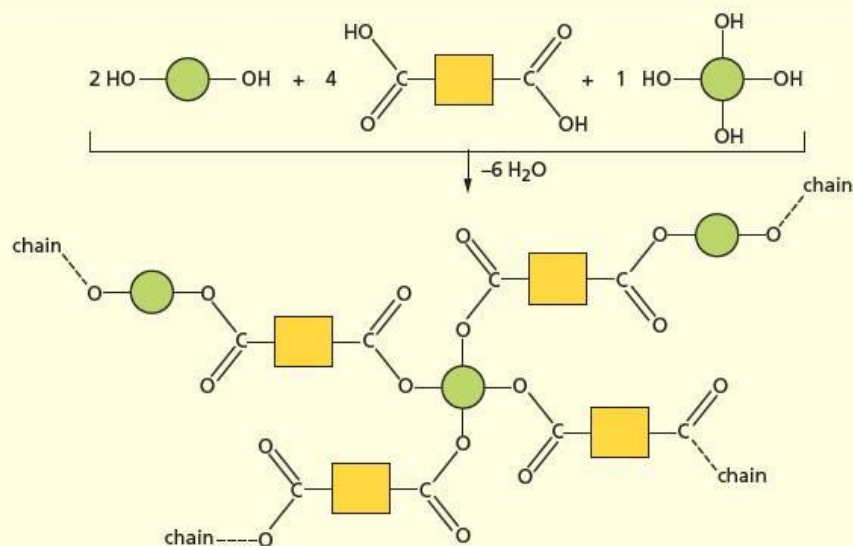
- a** One way would be to write out the formula of a section of the bakelite molecule, and count the number of phenol rings and methanal  $\text{—CH}_2\text{—}$  groups. An easier way is to recognise that each phenol is joined to three  $\text{—CH}_2\text{—}$  groups derived from methanal, and each  $\text{—CH}_2\text{—}$  group is joined to two phenolic rings. So the phenol:methanal ratio is 2:3.  
**b** The main assumption is that each phenol reacts with the maximum number of methanal molecules that it can (three). It is also assumed that the sample of bakelite is so large that the 'boundary effects', of phenolic rings at the edges of the polymer not being joined to other  $\text{—CH}_2\text{—}$  groups, are very small.

Cross-linking of polymers does not have to result in such an inflexible solid as bakelite, but cross-linking is often introduced to provide added strength to a flexible polymer. For example, if a small amount of a tri- or tetra-hydroxy alcohol (see Figure 28.15) is added to the monomer mix for a polyester, a stronger cross-linked polymer can form (see Figure 28.16).

**Figure 28.15** Two polyhydroxy alcohols



**Figure 28.16** Cross-linking in condensation polymers



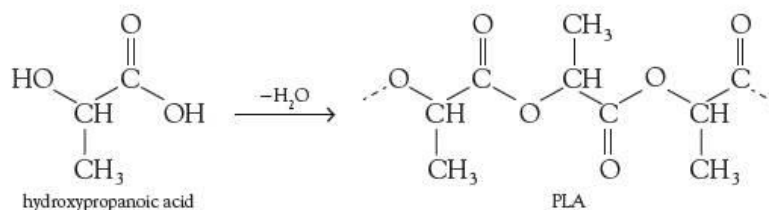
## PTFE

The opposite effect is noticed with polytetrafluoroethene, PTFE (see Topic 14). Here, all of the hydrogen atoms in the polymer have been replaced by fluorine atoms. Fluorine is the most electronegative element in the Periodic Table, and strongly attracts the electrons in covalent bonds attached to it. This means that the electrons are held firmly and are not easily polarised. This results in very weak van der Waals' forces between PTFE molecules and each other and, more importantly, between PTFE molecules and other molecules. It is the intermolecular forces that cause molecules to stick together, and so PTFE is used as a non-stick surface on cookware, and also for the bearings at the ends of bridges that might expand and contract with changes in the environment's temperature.

## 'Ecopolymers'

Until recently, the raw materials for most polymers came from the products of the refining of crude oil, which is a finite, non-renewable and diminishing resource. Also, the disposal of polymeric materials after their useful life has caused problems of pollution, since many are non-biodegradable. Both of these problems have been partially overcome by an increase in the recycling of polymers: thermal cracking of polyethene can convert it into its monomer, ethene, which can then be reused; the polyethylene-terephthalate (PET) from plastic bottles can be converted into a wool-like material for fleeces and other clothing.

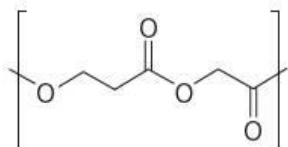
An alternative solution is to use renewable plant material to make polymers that are also biodegradable. The most commonly used is poly(2-hydroxypropanoic acid) (poly(lactic acid), PLA).



Hydroxypropanoic acid is a naturally occurring compound, which is made industrially by the fermentation of corn starch or sugar. PLA is easily hydrolysed, either chemically or by esterase enzymes, to re-form hydroxypropanoic acid, which is readily metabolised by all living matter into  $\text{CO}_2$  and water.

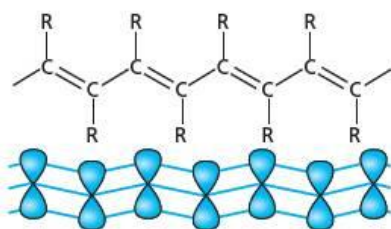
## Now try this

The repeat unit of another biodegradable polymer is as follows:



Draw the structures of the products of the hydrolysis of this monomer.

**Figure 28.17** A biodegradable screw made of PLA



**Figure 28.18** The structure of a 'molecular wire'

## Conducting polymers

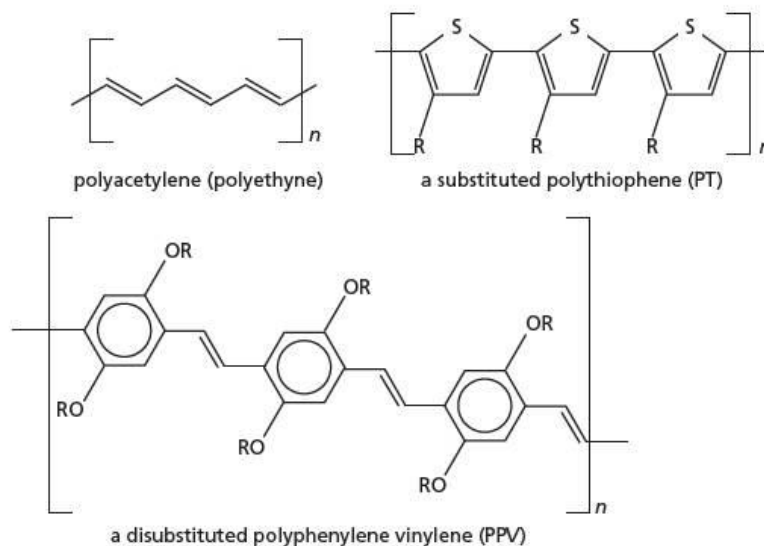
Graphite is a conductor of electricity because within each of its layers of carbon atoms there are delocalised electrons covering every atom within the layer. Thus, when a potential difference is applied at opposite ends of the layer, the delocalised electrons will flow from one end to the other.

Some long-chain polymer molecules act as 'molecular wires'. They contain **conjugated double bonds**, which means that the  $\pi$  bonds on adjacent alkene units overlap, and the  $\pi$  electrons become delocalised throughout the whole length of the polymer chain (see Figure 28.18).

Just as with the three-dimensional delocalised electrons in metals, or the two-dimensional delocalised electrons in the sheets of graphite or graphene, these one-dimensional delocalised electrons can conduct a current when a potential difference is applied to the ends of the polymer. An eventual aim is to construct micro-miniature circuits that can lead electrical signals to 'molecular microchips' in the heart of computing devices that will be thousands of times smaller than today's silicon-based units.

Three main classes of conducting polymers are the polyacetylenes, the polyphenylene vinylenes and the polythiophenes (see Figure 28.19).

**Figure 28.19** Three types of conducting polymer





These polymers are not used as ordinary conductors – their conductivity is less than that of copper, for example – but as semiconductors, for use in organic polymer light-emitting diodes (OP-LEDs) and photovoltaic (solar) panels, for converting electrical energy into light, or light into electrical energy. For their use in OP-LEDs, by altering the nature of the side groups R and OR, the molecules can be made to electroluminesce (that is, emit light when an electrode potential is applied) in any part of the spectrum, from red, through yellow and green, to blue. An everyday use of OP-LEDs is for traffic lights (see Figure 28.20).

**Figure 28.20** Red, yellow and green OP-LED used in traffic lights



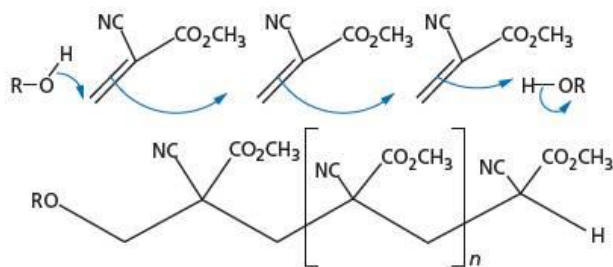
## Polymer glues

Most glues achieve their stickiness through the van der Waals' forces that exist between their molecules and the molecules of the two surfaces they stick together. To be an effective and strong glue, the other property they need is for their own molecules to stick to each other strongly. If they are polymeric, consisting of long molecules, this last quality is fairly well assured. There are two important types of polymer glue; one is an addition polymer and the other is a condensation polymer. In each case, the setting of the glue is a result of its continued polymerisation 'in situ', in other words whilst it is in contact with the surfaces being stuck.

### Addition polymer adhesives

A common addition polymer adhesive has already been mentioned in Table 28.1, poly(cyanoacrylate), or 'superglue'. Because of its two electron-withdrawing groups at one end of the ethene  $C=C$ , it has the unusual property of its polymerisation being catalysed by nucleophiles, such as water (this is why it is so dangerous if it is in contact with the skin or the eyes). The glue is applied as the low- $M_r$  low-viscosity monomer, which spreads well into uneven surfaces. Once the two surfaces are brought together, the polymerisation of the monomer is catalysed either by nucleophilic groups on the surfaces (for example,  $-OH$  groups) or by moisture in the air (see Figure 28.21).

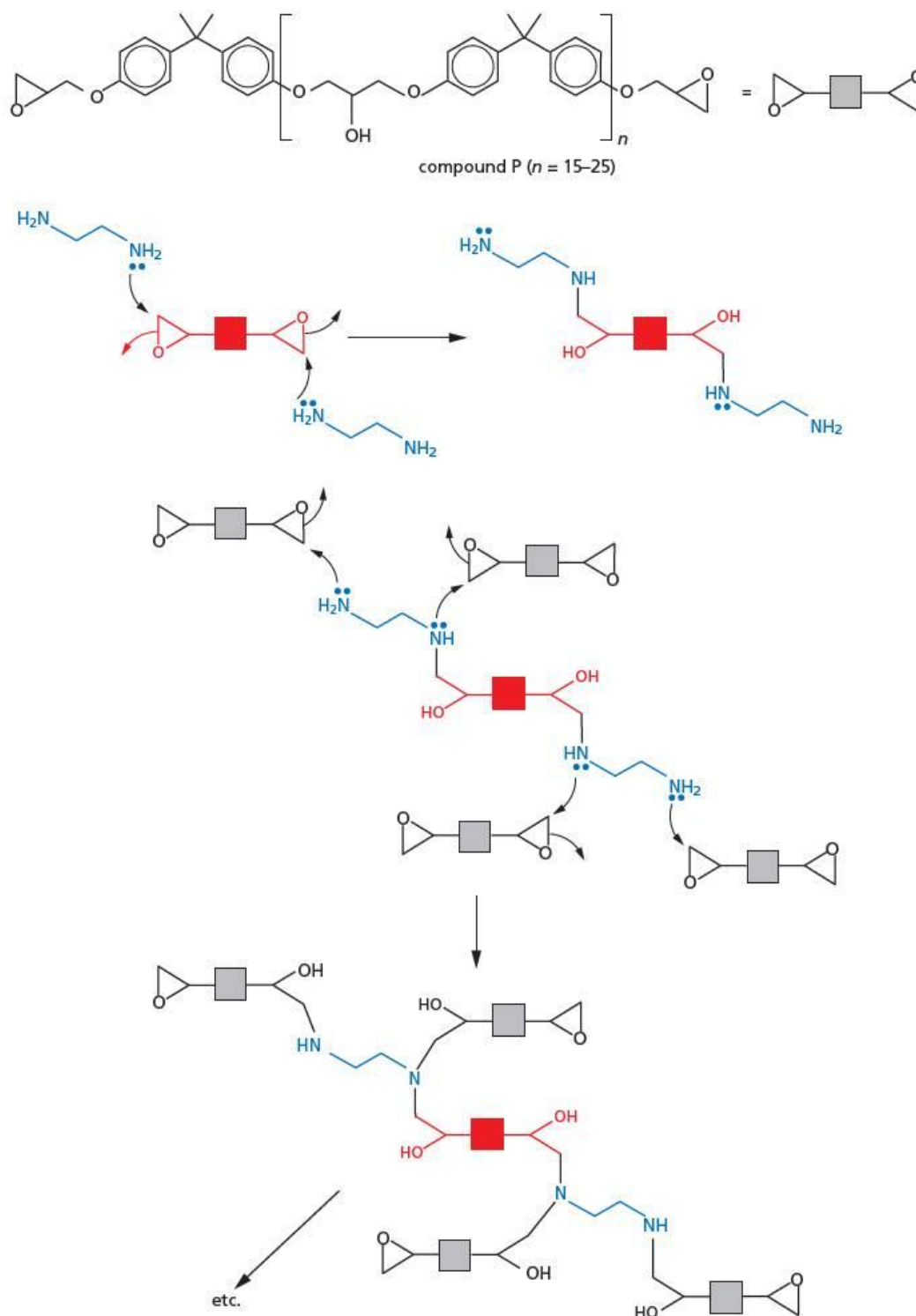
**Figure 28.21** The polymerisation of methyl cyanoacrylate to form 'superglue'



### Condensation polymer adhesives

A common group of condensation polymer adhesives are the epoxy resins. These are supplied as separate tubes of the two components, which are thoroughly mixed immediately prior to use. One component consists of a mixture of a medium-length polymer containing epoxy groups (compound **P** in Figure 28.22), and the other component (called the 'hardener') contains a diamine which opens up the epoxy rings by nucleophilic attack, and allows cross-linking to take place. The result is an inert thermosetting adhesive of tremendous strength. Figure 28.22 shows a simplified outline of this process.

**Figure 28.22** An outline of the cross-linking of epoxy compounds by amines to form a hard epoxy-resin adhesive



## 28.4 Proteins

There are three main classes of polymers that occur in nature: the proteins, the nucleic acids, and the polysaccharides such as starch and cellulose. In this section and the following section we shall look at some of the properties of the first two of these.

**Figure 28.23** Some important protein-containing foods



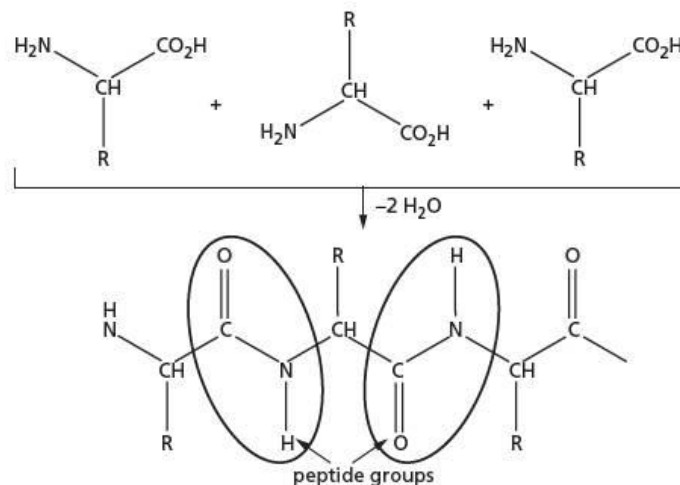
Proteins make up about 16% of the human body. They not only occur as components of blood, skin, bone, nails, hair, nerves, muscles and tendons, but also are responsible for the smooth workings of the body in their roles as enzymes, receptors and hormones. Protein-containing foods, such as meat, beans, cheese, eggs and milk, are therefore important constituents in our diet (see Figure 28.23). Their importance to us is emphasised by their name, which is derived from the Greek *proteios*, meaning foremost or primary.

### The structure of proteins

The backbone of a protein is one or more chains made up of polymers of amino acids. Some proteins also have non-amino-acid groups called **prosthetic groups** (for example, the haem group in haemoglobin). The shape and physical and biochemical properties of a protein are the direct result of the number, type and sequence of the amino acids that make it up. This amino acid sequence is determined by the **gene**, the sequence of organic bases in the length of DNA that codes for the protein. Amino acids do not join together to form proteins randomly, but join in a well-ordered and predetermined sequence.

The amino acids are joined by amide bonds between the amino group of one acid and the carboxyl group of another (see Figure 28.24). Proteins are therefore composed of polyamides, and are condensation polymers. As we saw in section 27.6, when an amide bond is formed between two amino acids, it is called a **peptide bond**, and simple proteins (those that contain just one chain, and no prosthetic groups) are also known as **polypeptides**.

**Figure 28.24** Structure of a polypeptide

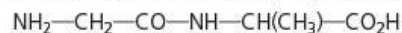




The formulae of peptides are often described by the following shorthand. The customary three-letter abbreviations for all the amino acids in the chain are written down, starting with the **N terminal** (the end of the chain that has a free  $\text{—NH}_2$  group) on the left, and finishing with the **C terminal** (the end that has a free  $\text{—CO}_2\text{H}$  group) on the right.

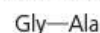
### Worked example

Convert the following structural formula into the correct shorthand:

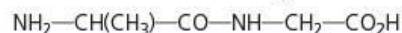


### Answer

This structure contains one peptide bond in the middle, so it is a **dipeptide**, containing two amino acid residues. The residue to the left of the peptide bond is glycine (Gly) and that to the right is alanine (Ala) (see Figure 27.18). The shorthand formula is therefore:

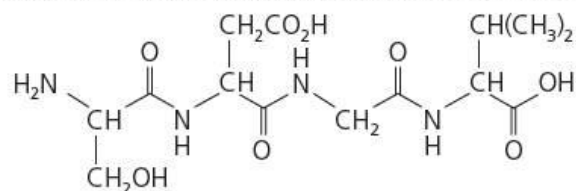


Note that this is a different compound from Ala—Gly, because of the left-to-right direction of the peptide bond. The structural formula of Ala—Gly is:



### Now try this

- 1 Draw the structural formulae of the following two tripeptides (use Figure 27.18 to help you):
  - a Val—Ser—Tyr
  - b Tyr—Ala—Gly
- 2 Use the customary three-letter abbreviations to describe the following tetrapeptide:



The amide (peptide) bonds in proteins can be hydrolysed by the same reagents as hydrolyse simple amides: hot aqueous acid or hot aqueous alkali. They can also be hydrolysed by a variety of proteolytic enzymes. Many of these (for example, trypsin and pepsin) are found in the digestive system, where they help to break down the proteins in our food into smaller peptides and amino acids, which can then readily be absorbed through the intestinal wall.

Biochemists recognise various levels of protein structure.

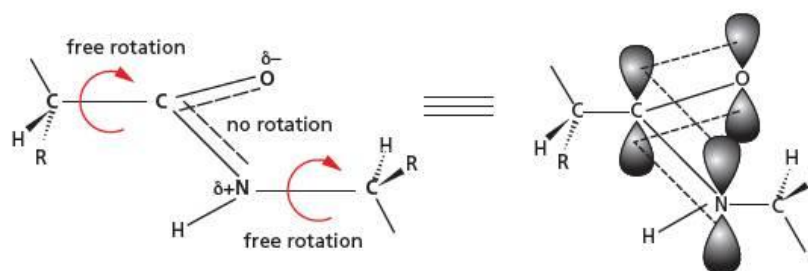
### Primary structure

The primary structure of proteins is the sequence of amino acids, covalently joined by peptide bonds, making up the polypeptide chain, as described above. This sequence is determined by the arrangement of organic bases in the section of DNA that codes for the protein.

### Secondary structure

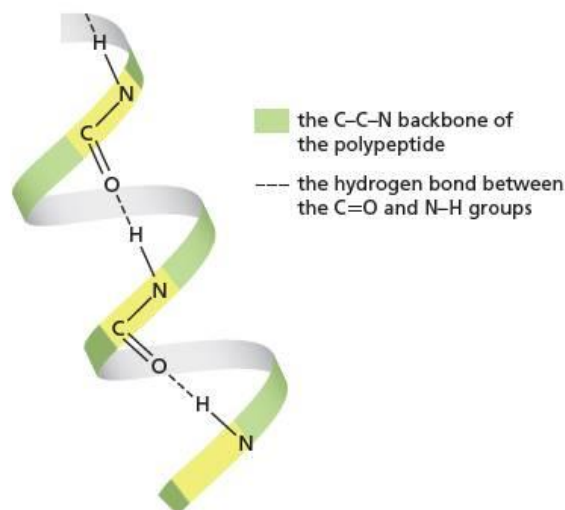
The amino acid chain that constitutes a polypeptide is quite flexible, with two-thirds of the bonds within the chain being single bonds, around which free rotation is allowed. The other third of the bonds in the chain are the C—N bonds within peptide groups. Because of the overlap between the lone pair of electrons on the nitrogen atom (in a p orbital) and the  $\pi$  bond of the carbonyl group next to it, the peptide group is rigid and planar. It exists in the *trans* arrangement (see Figure 28.25).

**Figure 28.25** Overlap of p orbitals makes the peptide group planar



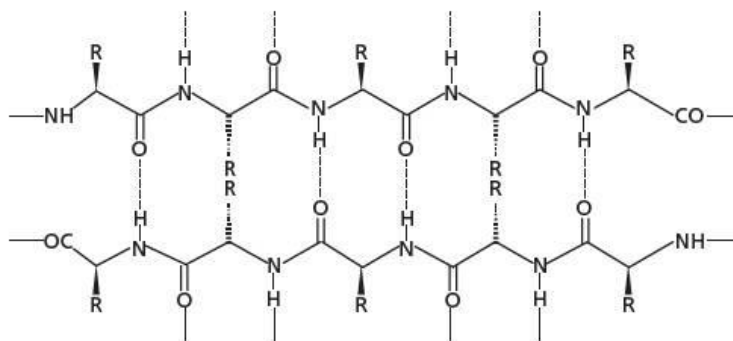
This inflexibility of the peptide group allows parts of the polypeptide chain to take up an  **$\alpha$ -helical arrangement** (see Figure 28.26). This lends strength and rigidity to some protein structures. Strong hydrogen bonds can form between the N—H of one peptide group and the C=O of another one three/four amino acids along the chain.

**Figure 28.26** The  $\alpha$  helix in proteins



The  $\alpha$ -helix confers **one-dimensional** rigidity to the polypeptide chain. Another type of secondary structure is the  **$\beta$ -pleated sheet**. This is formed by the C=O group of one chain hydrogen bonding to the N—H group in the same chain, or another chain, but separated by many amino acid residues. The resulting sheet of anti-parallel hydrogen-bonded chains confers a degree of **two-dimensional** rigidity to the polypeptide chain. The chains are described as *anti*-parallel because adjacent chains run in opposite directions, as shown in Figure 28.27.

**Figure 28.27** The  $\beta$ -pleated sheet in proteins (The tetrahedral arrangement of bonds around the  $sp^3$  carbon in the chain means that the R groups stick out above or below the planar sheet.)

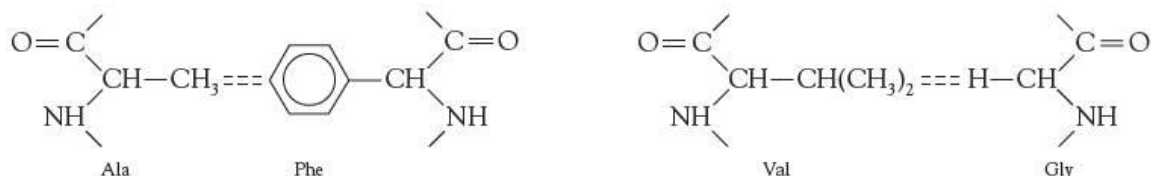


### Tertiary structure

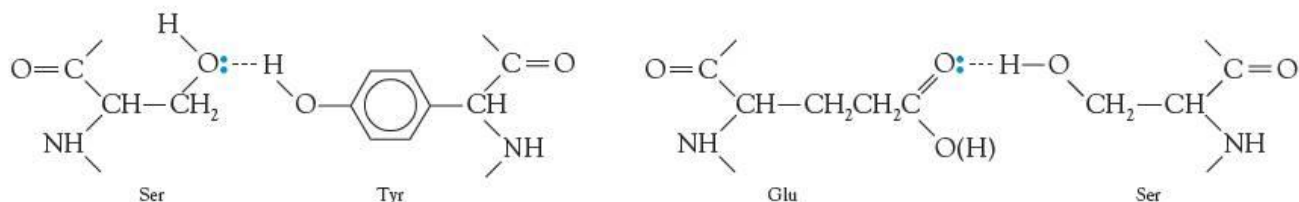
Even if a particular polypeptide chain contains regions of  $\alpha$ -helices or  $\beta$ -pleated sheets, there will be many amino acids not involved in these regions. Other interactions can occur between the side groups of these amino acids, which cause the chain to twist and fold.

We can recognise four different interactions between side chains, which are associated with their different structures.

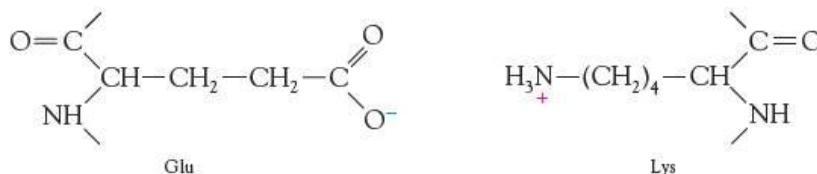
- Van der Waals' attractions occur between nonpolar side chains, for example, glycine, alanine, valine and phenylalanine.



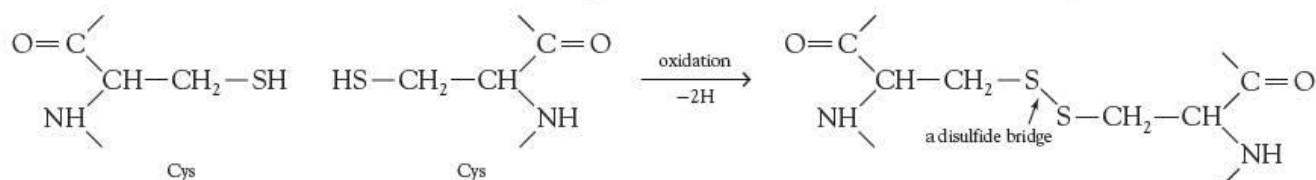
- Hydrogen bonding occurs between side chains that contain  $\text{—OH}$  (for example, serine and tyrosine),  $\text{—NH}_2/\text{—NH}_3^+$  (for example, lysine) and  $\text{—CO}_2\text{H}/\text{—CO}_2^-$  (for example, aspartic acid and glutamic acid).



- Ionic attractions occur between side chains containing functional groups that exist in their anionic form at pH7 (for example, aspartic acid and glutamic acid) and those that exist in their cationic form (for example, lysine and arginine).



- Disulfide bridges can form between the side chains of two cysteine residues.



The **tertiary structure** confers some **three-dimensional** rigidity to the polypeptide, and is important in determining both the overall shape and the function of the protein. For example, many enzymes are globular (fairly spherical) proteins that are soluble in water. In these, the non-polar side chains are often pointing towards the central hydrophobic part of the molecule, whereas the hydrogen-bonding and ionic groups are on the outside, where they can be solvated by water molecules.

The strongest of the tertiary interactions is the disulfide bridge. Once these are formed, by an oxidation reaction, the various parts of the chain are drawn together, and this allows the other interactions to play their part in creating the overall three-dimensional structure.

## 28.5 DNA

The genes of all organisms are composed of chains of deoxyribonucleic acid, DNA. It stores the information needed to make specific proteins in the cell.

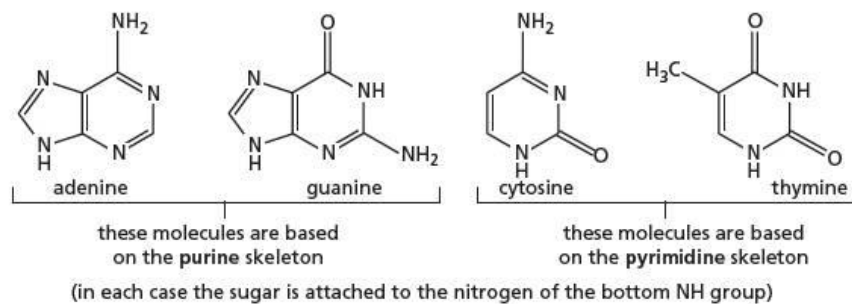
Like proteins, DNA consists of a **primary structure**, which comprises the covalent bonds joining the monomers together, and a **secondary structure**, which is formed by hydrogen bonding between the chains.

The monomer units of DNA are called nucleoside phosphates. These consist of the sugar molecule deoxyribose, which has a cyclic organic base bonded to carbon atom 1, and a phosphate group bonded to carbon atom 5. All DNA molecules contain just four different bases. In a particular DNA molecule, these are arranged in a specific order along the chains.

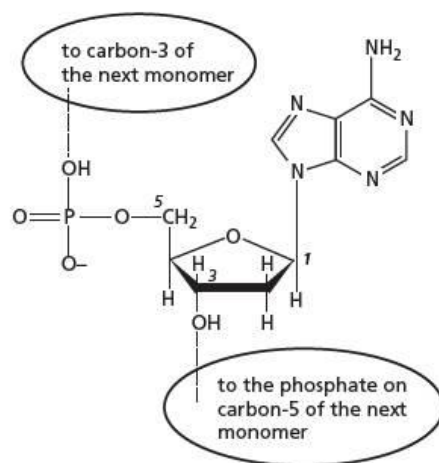


Figure 28.28 shows the structures of the four bases and Figure 28.29 shows how adenine forms the monomer unit adenosine phosphate.

**Figure 28.28** The four bases of DNA

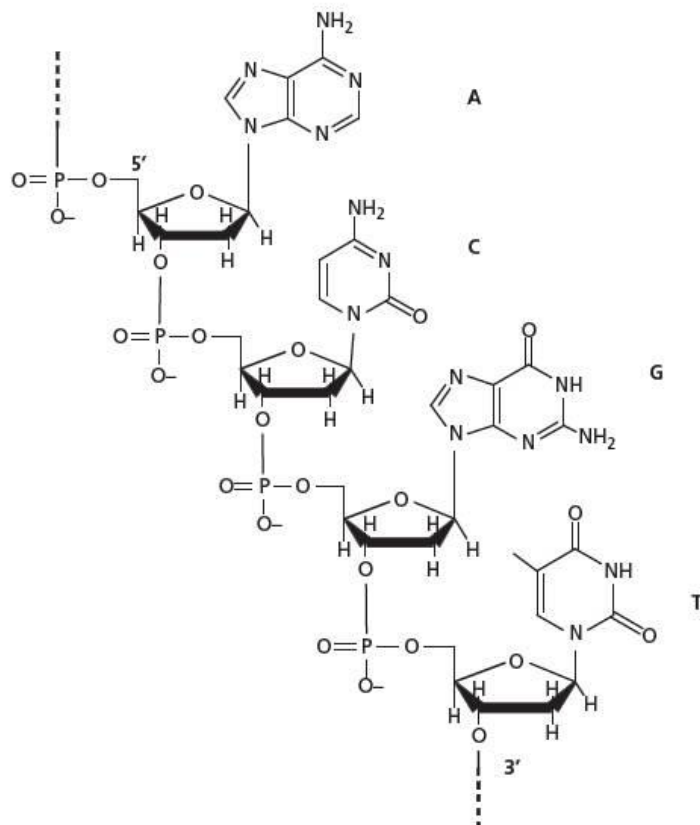


**Figure 28.29** The monomer unit adenosine phosphate



Many thousands of monomer units join up in a specific sequence of bases to form a linear condensation polymer.

**Figure 28.30** Part of a single strand of DNA showing the four bases A, C, G and T



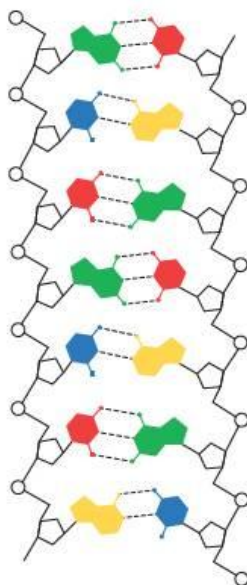
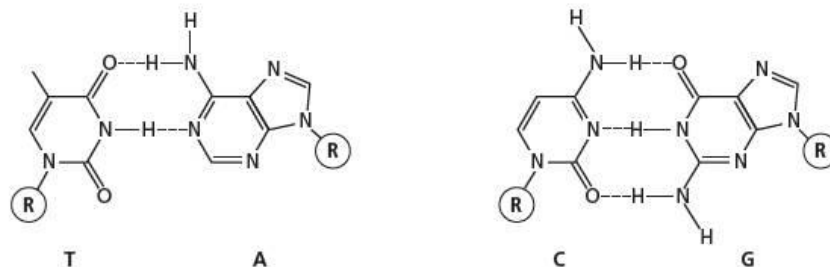
Just as with proteins, DNA has a hydrogen-bonded secondary structure. A DNA molecule consists of a double helix of two sugar-phosphate strands coiled around each other, with the purine and pyrimidine bases (both of which are planar molecules) arranged in hydrogen-bonded pairs, one from each chain, stacked above each other on the inside of the double helix.

The pairing of the bases is unique: adenine (A) always pairs with thymine (T), and guanine (G) always pairs with cytosine (C).

As can be seen from their molecular structures, a purine molecule, with its two rings of atoms, is larger than a single-ring pyrimidine molecule. To allow the distance between the sugar-phosphate chains to be constant, the base pairs must consist of one purine and one pyrimidine (see Figure 28.28): there is not enough space between the chains to accommodate two purines, and two pyrimidines would not be close enough to hydrogen-bond with each other.

But why should adenine pair with thymine and not with cytosine, or guanine pair with cytosine and not with thymine? The answer lies in the number of hydrogen bonds that can form between the bases, and the directional sense of those hydrogen bonds. Figure 28.31 shows the hydrogen bonding that occurs.

**Figure 28.31** The hydrogen bonded base pairs T—A and C—G (R represents the deoxyribose ring to which the base is joined.)



**Figure 28.32** A section of the double-stranded DNA molecule

The overall structure is shown in Figure 28.32.

## 28.6 Distinguishing between addition and condensation polymers

We can recognise which type of polymer will be formed from given monomers by looking at their structures.

- If each of the monomers contains a  $C=C$  group, they are likely to produce an addition polymer (even if they also contain acid, ester or amide groups).
- If the monomers contain two different functional groups (carboxylic acid or acyl chloride, amine or alcohol) at the end of a chain of carbon atoms, they are likely to produce a condensation polymer.

We can recognise what type of polymerisation has produced a polymer by looking at a section of the backbone chain.

- If the *chain* contains only carbon atoms, the polymer is an addition polymer (even if any side chains contain ester or amide groups).
- If the chain contains hetero atoms (that is atoms that are not carbon – usually oxygen or nitrogen), the polymer is a condensation polymer.

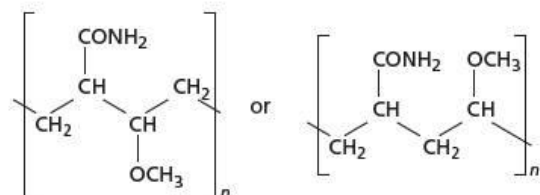
### Worked example 1

Predict the type of polymerisation that each of the following pairs of molecules will undergo, and draw the structure of the repeat unit.

- $CH_2=CH-CONH_2$  and  $CH_3OCH=CH_2$
- $NH_2CH_2CH_2NH_2$  and  $ClCOCH_2CH(CH_3)COCl$

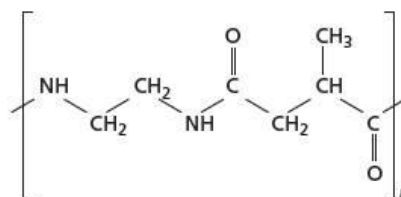
**Answer**

- a** These two monomers will form an addition polymer, because each monomer contains a  $C=C$  group. The repeat unit is either



Which one is formed depends on the orientation of the monomers.

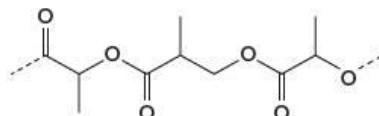
- b** These two monomers will form a condensation polymer, because each monomer contains two functional groups. The repeat unit is:



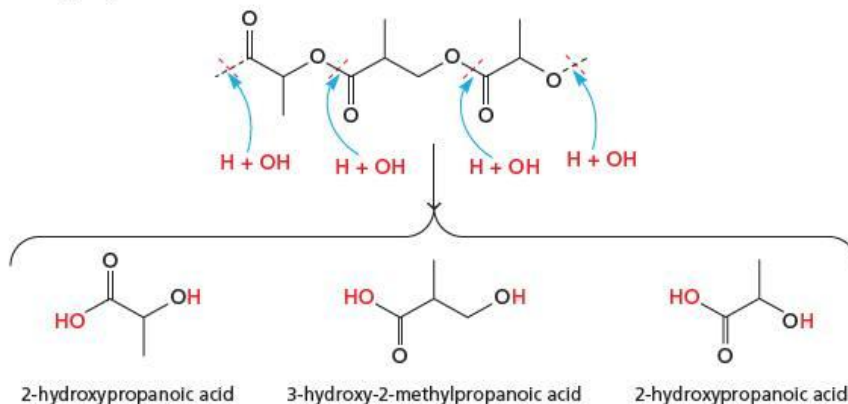
Identifying the monomers that have produced a condensation polymer is relatively straightforward: the chain is broken at the ester or amide bonds, an H atom is added to the  $\text{---O}$  or  $\text{---NH}$  groups so formed, and an  $\text{---OH}$  is added to the  $\text{---CO}$  groups.

**Worked example 2**

Draw the structures of the monomers used to make the following section of a co-polymer:

**Answer**

Splitting the co-polymer section at the ester groups produces three hydroxyacid molecules, of which two are identical, so the monomers are 2-hydroxypropanoic acid and 3-hydroxy-2-methylpropanoic acid:

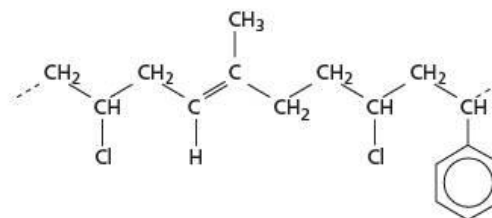


Identifying the monomers that have produced an addition polymer can be a little more difficult. If there are no  $C=C$  bonds in the chain, the carbon chain is split into two-carbon sections. Each of these will have been formed from a substituted ethene as monomer. If, however, the carbon chain contains  $C=C$  bonds, these are likely to have come from butadiene-like monomers, so the chain is split into a four-carbon unit at this point, with the  $C=C$  bond in the middle of the four-carbon unit.



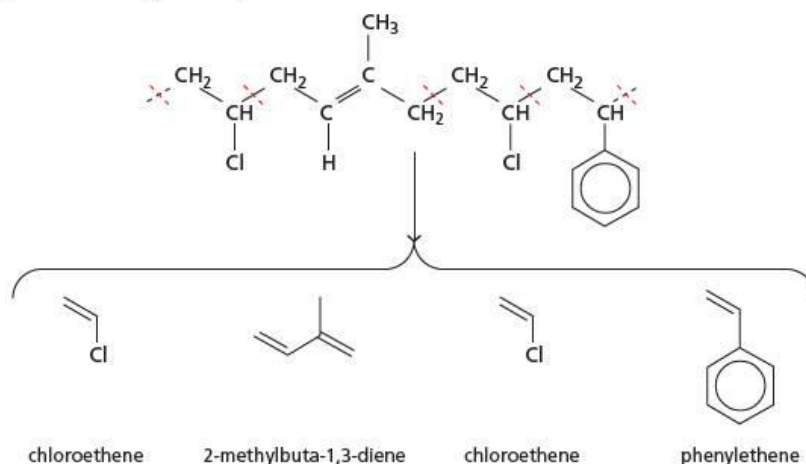
## Worked example 3

Draw the structures of the monomers used to make the following section of a co-polymer:



## Answer

The polymer contains a double bond, so it is split into a four-carbon unit at this point. All single-bonded lengths are split into two-carbon units:

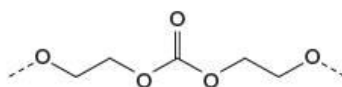


Thus the monomers are chloroethene, phenylethene and 2-methylbuta-1,3-diene.

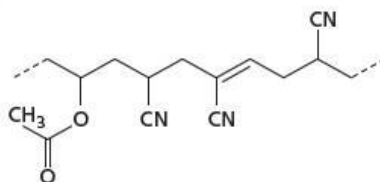
## Now try this

Identify the monomers used to make the following sections of polymer molecules.

1

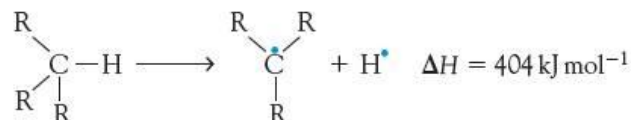


2

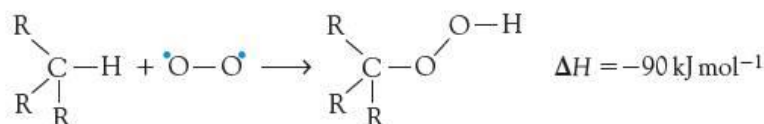


## 28.7 The disposal of polymers

We saw in section 14.4 how polyalkenes can be disposed of, by incineration, recycling, depolymerisation or bacterial fermentation. Some polymers can also be broken down by ultraviolet rays or strong sunlight. Because of the radical-stabilising effect of alkyl groups, the bond between a hydrogen atom and a tertiary carbon atom is weaker than the usual C—H bond (bond energy  $420 \text{ kJ mol}^{-1}$ ).

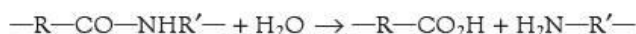
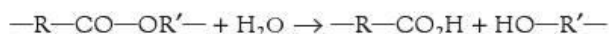


Oxygen molecules (which are di-radicals) can readily react with tertiary C—H groups.



The hydroperoxides formed by this reaction can undergo further bond breaking and molecular rearrangements, resulting in smaller molecules that can be more easily metabolised by bacteria in the environment.

The main way that condensation polymers are broken down in the environment is by the hydrolysis of their ester or amide bonds.



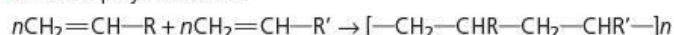
Esterase and peptidase enzymes in soil bacteria can carry out these transformations.

## Summary

- Many different **addition polymers** can be made by polymerising ethene molecules in which one or more hydrogen atoms have been replaced by other atoms or groups.
- Co-polymers** are polymers made from more than one type of monomer.
- Condensation polymers** are usually either polyesters or polyamides.
- Condensation polymers can be divided into two categories – **type I** and **type II** – depending on the relative orientation of adjacent functional groups within the chain.
- The properties and uses of various polymers depend on their chemical structures, and the bonding between the chains.
- Proteins and nucleic acids are two important natural examples of condensation polymers.
- Addition and condensation polymers can be distinguished, and the structures of their monomers determined, by studying the make-up of the backbone chain.

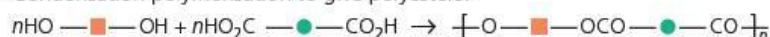
### Key reactions you should know

- Addition polymerisation:

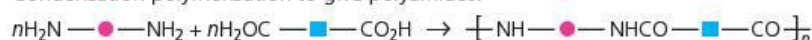


(The proportions of  $\text{CH}_2=\text{CHR}$  and  $\text{CH}_2=\text{CHR}'$  can be varied.)

- Condensation polymerisation to give polyesters:



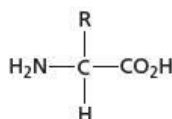
- Condensation polymerisation to give polyamides:



## Examination practice questions

Please see the data section of the CD for any  $A_r$  values you may need.

- 1 Proteins exist in an enormous variety of sizes and structures in living organisms. They have a wide range of functions which are dependent upon their structures. The structure and properties of an individual protein are a result of the primary structure – the sequence of amino acids that form the protein.
- a Proteins are described as condensation polymers.
- Write a balanced equation for the condensation reaction between two glycine molecules,  $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ .
  - Draw the skeletal formula for the organic product. [2]
- b X-ray analysis has shown that in many proteins there are regions with a regular arrangement within the polypeptide chain. This is called the secondary structure and exists in two main forms.
- State the two forms of secondary structure found in proteins.
  - Draw a diagram to illustrate **one** form of secondary structure. [4]
- c There are around 20 different common amino acids found in humans most of which have the same general structure.



The nature of the group R affects which bonds are formed as the secondary structure of the protein is further folded to give the tertiary structure.

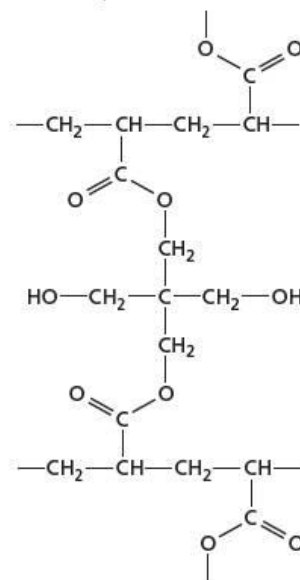
Copy and complete the table indicating the type of **tertiary** bonding that each pair of the amino acid residues is likely to produce.

residue 1	residue 2	type of tertiary bonding
$-\text{HNCH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)\text{CO}-$	$-\text{HNCH}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{CO}-$	
$-\text{HNCH}(\text{CH}_3)\text{CO}-$	$-\text{HNCH}(\text{CH}_3)\text{CO}-$	
$-\text{HNCH}(\text{CH}_2\text{SH})\text{CO}-$	$-\text{HNCH}(\text{CH}_2\text{SH})\text{CO}-$	
$-\text{HNCH}(\text{CH}_2\text{OH})\text{CO}-$	$-\text{HNCH}(\text{CH}_2\text{CO}_2\text{H})\text{CO}-$	

[4]

[Cambridge International AS & A Level Chemistry 9701, Paper 41 Q6 November 2011]

- 2 In recent years there has been considerable interest in a range of polymers known as 'hydrogels'. These polymers are hydrophilic and can absorb large quantities of water.
- a The diagram shows part of the structure of a hydrogel.



The hydrogel is formed from chains of one polymer which are cross-linked using another molecule.

- Draw the structure of the monomer used in the polymer chains.
  - State the type of polymerisation used to form these chains.
  - Draw the structure of the molecule used to cross-link the polymer chains.
  - During the cross-linking, a small molecule is formed as a by-product. Identify this molecule. [5]
- b Once a hydrogel has absorbed water, it can be dried and re-used many times. Explain why this is possible, referring to the structure above. [2]
- c Not every available side chain in the polymer is cross-linked, and the amount of cross-linking affects the properties of the hydrogel.
- The amount of cross-linking has little effect on the ability of the gel to absorb water. Suggest why this is the case.
  - Suggest **one** property of the hydrogel that will change if more cross-linking takes place. Explain how the increased cross-linking brings about this change. [3]

[Cambridge International AS & A Level Chemistry 9701, Paper 42 Q8 June 2013]