

Chemistry (A-level)

Electrophoresis (Chapter 27):

- **Electrophoresis:** the separation of charged particles by their different rates of movement in an electric field

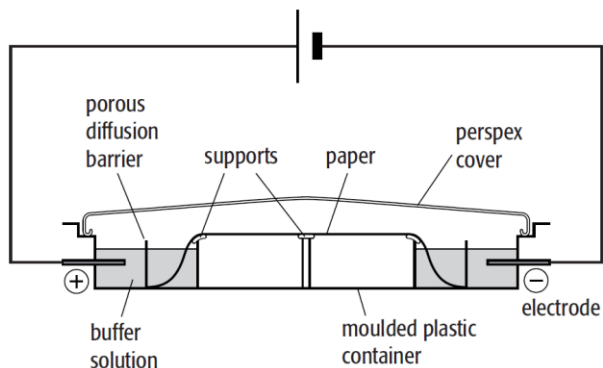


Figure 27.10 This apparatus shows how paper electrophoresis is carried out.

- The sample is placed on absorbent paper or on a gel supported on a solid base
- A buffer solution carries the ions along
- The rate of ion movements towards the oppositely charged electrode depends on:
 - Size – larger ions will move slower
 - Charge – higher charges will move quicker
- Ions therefore will be separated as the electric field is applied, creating a series of lines or bands (**electropherogram**), where UV light may be used
- E.g. Amino acid A has a positively charged side-chain; amino acid B is neutral; amino acid C is negatively charged (figure 27.12) & at the pH of 7 (figure 27.13):

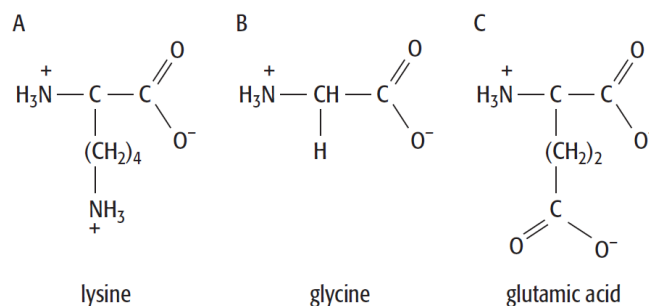
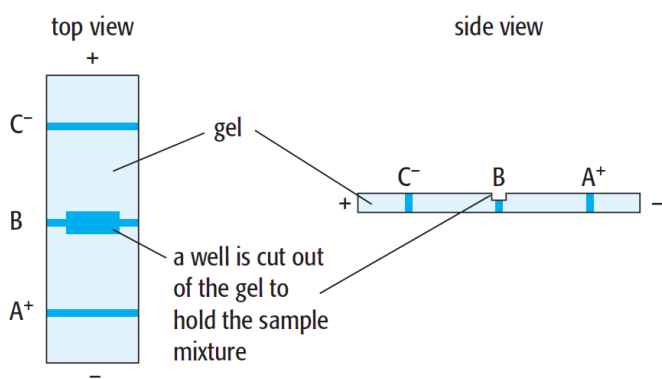


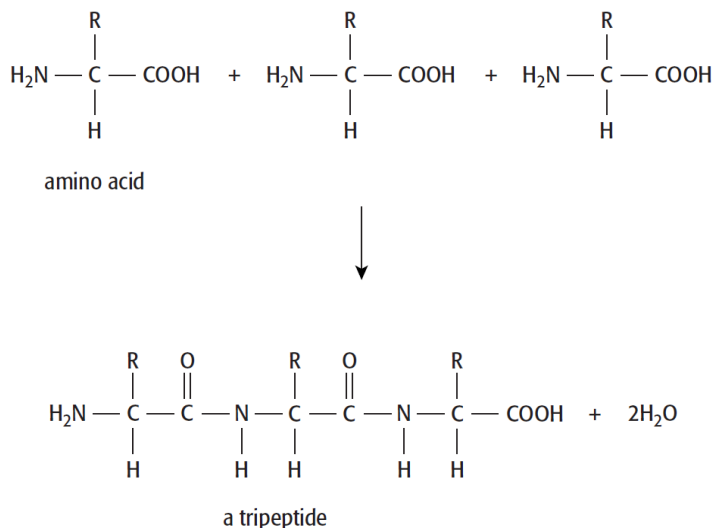
Figure 27.13 The charge on amino acids depends on the pH of the solution.

Figure 27.12 The principle of gel electrophoresis.

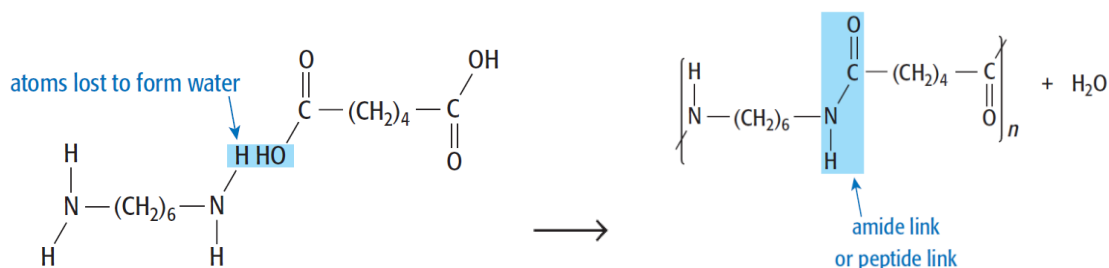
- Buffer used to get figure 27.13 (control the pH) as amino acids react in acidic and alkaline solutions to form ions, so the charge on the ions depends on the pH, therefore pH will affect the movement of ions
- In protein separations, they are usually converted to negatively charges by a chemical and a dye can be added; hence they will all move towards the positive electrode

Polymerisation (Chapter 28):

- Formation of peptides from amino acids is called **condensation** reaction (addition reaction, followed by an elimination reaction) where a peptide link (also called amide links in synthetic polymers such as **nylons**) forms as each amino acid monomer joins the chain; is characterised by monomers that contain two different functional groups capable of reacting with each other:
 - Found within the same molecule, as in amino acids
 - Found in two different molecules, as in nylon 6,6
 - Leads to the formation of small molecules such as H₂O or HCl



- Polypeptides and proteins are types of **polyamide**
- All nylons are made in reactions between -NH₂ & -COOH or -COCl, e.g. 1,6-diaminohexane reacts with hexanedioic acid to make nylon 6,6 (where 6,6 refers to the number of carbon atoms in each monomer unit):



- Hexanedioyl dichloride, ClOC(CH₂)₄COCl, can be used as a more reactive and expensive monomer than hexanedioic acid
- Nylon 6** is not formed from condensation reaction, as it is made from the compound caprolactam (cyclic amide), which when heated with N₂, the ring breaks open at the amide group

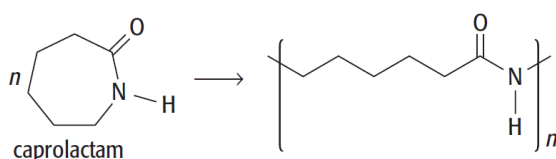


Figure 28.2 Nylon 6 is not formed by condensation polymerisation as no small molecule is given off. The reaction is called 'ring-opening' polymerisation.

- Caprolactam is made from **6-aminohexanoic acid**, with its NH₂ and COOH groups at either end of the molecule, resulting to a condensation reaction, releasing water; hence forming nylon 6
- Nylon has low density, strong and elastic – useful for fibres in the clothing industry
- **Kevlar®** is a polyamide containing benzene rings; is strong, flexible and resistant to fire and abrasions, as it has long, linear polymer chains that line up next to each other in a regular pattern due to extensive hydrogen bonding between the polymer chains; hence used in making bullet-proof vests, ropes, fire-protective clothing and as reinforcement of other materials (rubber in tyres)

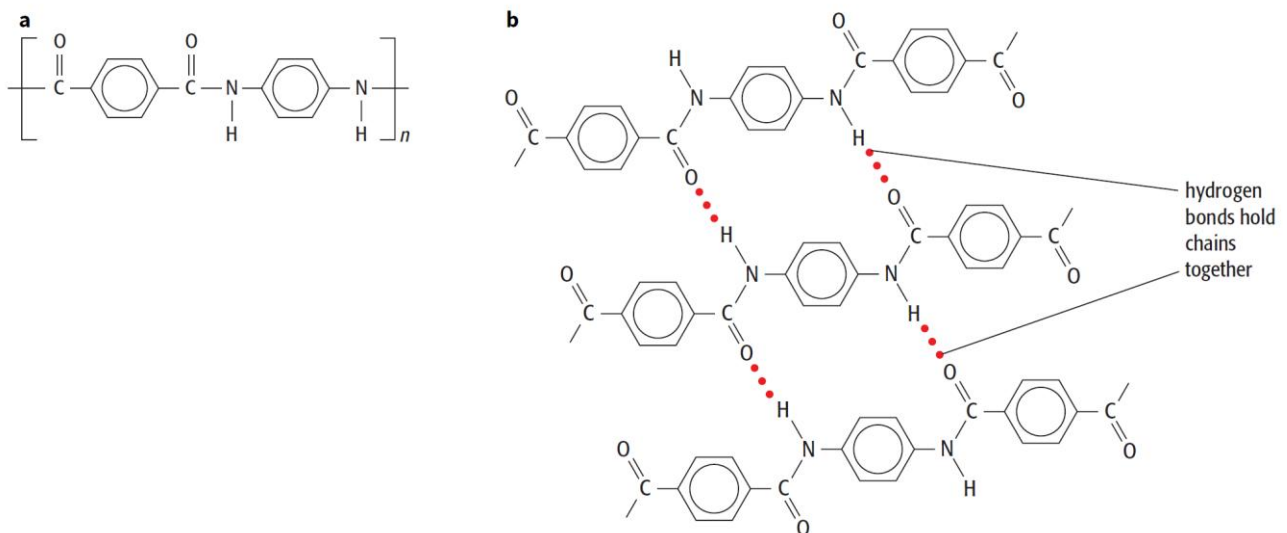


Figure 28.4 a The formula showing the repeat of Kevlar®. b The hydrogen bonding between chains of the polyamide. The latest tennis rackets contain Kevlar®, where its low density and strength are important. The wings of fighter jets can also be made of Kevlar®.

- The amino acids found in proteins are α -amino acids:

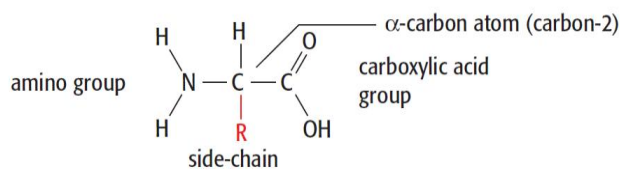


Figure 28.5 The generalised structure of an amino acid, highlighting the key features.

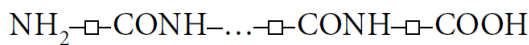
- Their side-chains (R groups) can be classified as non-polar, polar or electrically charged (acidic or basic):

Type of side-chain	Example	Structure
non-polar	alanine (Ala)	$\begin{array}{c} \text{H} \\ \\ \text{NH}_2 - \text{C} - \text{COOH} \\ \\ \text{CH}_3 \end{array}$
	valine (Val)	$\begin{array}{c} \text{H} \\ \\ \text{NH}_2 - \text{C} - \text{COOH} \\ \\ \text{CH} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

polar	serine (Ser)	$\begin{array}{c} \text{H} \\ \\ \text{NH}_2 - \text{C} - \text{COOH} \\ \\ \text{CH}_2\text{OH} \end{array}$
electrically charged (acidic or basic)	aspartic acid (Asp)	$\begin{array}{c} \text{H} \\ \\ \text{NH}_2 - \text{C} - \text{COOH} \\ \\ \text{CH}_2\text{COOH} \end{array}$
	lysine (Lys)	$\begin{array}{c} \text{H} \\ \\ \text{NH}_2 - \text{C} - \text{COOH} \\ \\ (\text{CH}_2)_4\text{NH}_2 \end{array}$

Table 28.1 Examples of the three different classes of side-chains (in red) in the amino acids found in proteins.

- Amino acids are amphoteric, where at pH 7 it exists as zwitterions (refer to organic chemistry amino acids)
- An amino acid unit within a polypeptide chain is called an **amino acid residue**; which sequence starts from the free NH₂ group (the N-terminal end):



- Facts about proteins:
 - Formed from condensation reactions
 - The polypeptide chain is not branched
 - Each protein has a unique sequence of amino acids, which is determined by DNA; has a particular biological function
- Structures of proteins:
 - **Primary structure:** the sequence of amino acids in the polypeptide chain.
 - **Secondary structure:** a regular structural arrangement stabilised by hydrogen bonding between the NH group of one peptide bond and the CO group of another peptide bond.
 - **Tertiary structure:** the further folding of the polypeptide chain into a three-dimensional (3-D) shape. This 3-D shape is stabilised by attractive forces and bonding between the amino acid side-chains (R groups)
- Primary structure:
 - Is written with the amino acids numbered from the N-terminal end
 - Determines the way that the protein can fold to form its secondary and tertiary structure
 - Is held together by covalent bonds

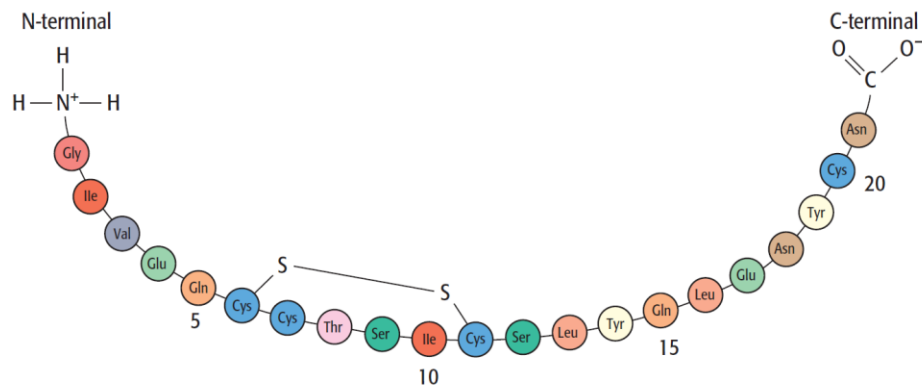


Figure 28.6 The primary structure of the insulin A chain, a short polypeptide of 21 amino acids.

- Secondary structure:
 - Where the side-chains of the amino acids are not involved
 - The side-chains of the residues stick out on the outside of the helix
 - There may be more than one secondary structure in a protein
 - Two types:
 - α -helix:
 - The backbone twists around in a spiral, creating a rod-like structure; all the –NH and –CO groups of each peptide bond are involved in hydrogen bond formation (stabilising the structure), which lie parallel with the long axis of the helix with each –NH forming a weak

intermolecular link to a $-\text{CO}$ group of amino acid residues further along the backbone

▪ β -pleated sheet:

- Hydrogen bonds are formed between $-\text{NH}$ and $-\text{CO}$ groups in different polypeptide chain:

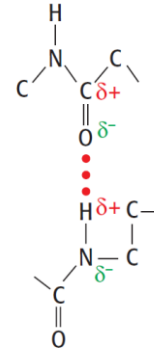
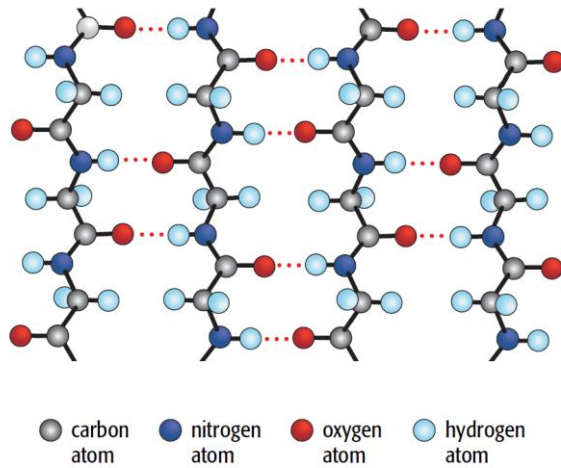
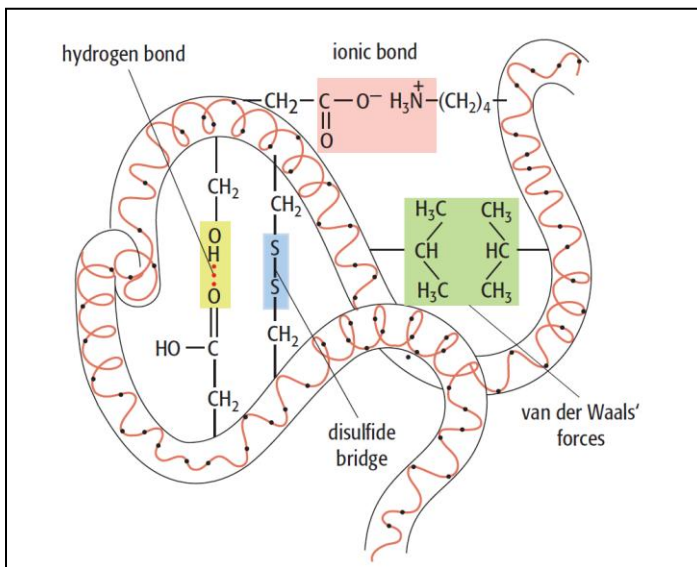


Figure 28.8 a An α -helix. b Detail of one hydrogen bond in the α -helix.

Figure 28.9 A β -pleated sheet in silk. The hydrogen bonds are formed between separate polypeptide chains.

• Tertiary structure:



➤ The complex 3-D shape is stabilised by:

- **Disulfide bridges** – these are covalent (S – S) bonds:

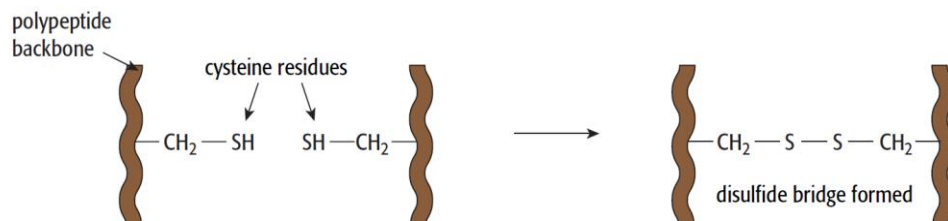


Figure 28.12 The formation of a disulfide bridge from two cysteine residues.

- Weak van der Waals' forces (Dipole-induced dipole forces) – when two non-polar residues are close to one another

- Relatively weak hydrogen bonds – between polar side-chains having hydrogen atoms attached to the highly electronegative atoms of hydrogen or oxygen
- Ionic bonds (salt bridges) – between ionised acidic side-chains and ionised basic side-chains

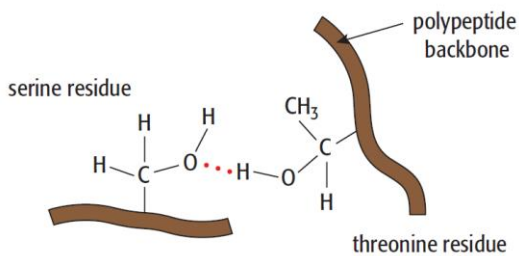


Figure 28.13 A hydrogen bond (shown by three red dots) formed between serine and threonine residues.

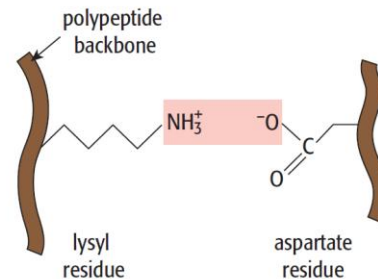


Figure 28.14 An ionic bond formed between an aspartate residue and a lysyl residue (from lysine).

- Two main types of **nucleic acids** (polynucleotides – made by condensation polymerisation of **nucleotides**) are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
- The nucleotides of DNA are made up of three components:
 - A sugar called deoxyribose
 - A phosphate group (attached by a phosphoester link to deoxyribose)
 - A nitrogen-containing base (4-types):
 - Adenine (A) – two rings
 - Guanine (G)
 - Thymine (T) – one ring
 - Cytosine (C)

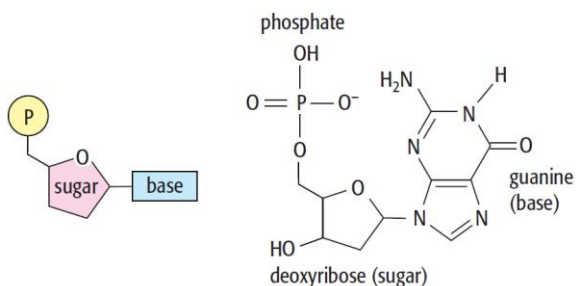


Figure 28.15 The three components that make up a nucleotide. You do not need to recall the detailed structure shown in the displayed formula.

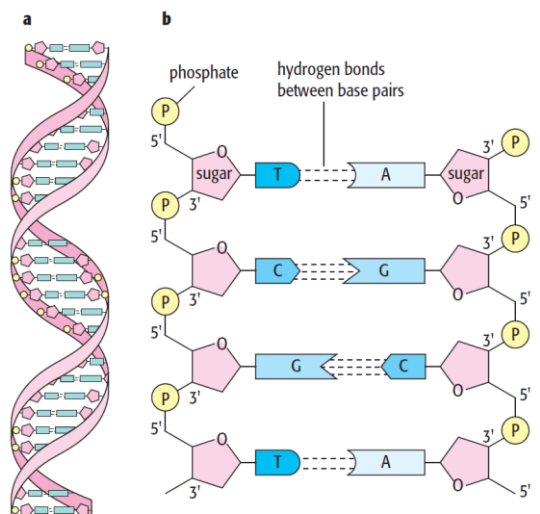


Figure 28.16 **a** Part of the DNA double helix. **b** An outline structure of DNA, showing base pairing. The chain has been 'straightened out' to make the base pairing clearer.

- The structure of DNA is kept stable by:
 - Van der Waals' attractive forces between one base pair and the next
 - Hydrogen bonds between base pairs:

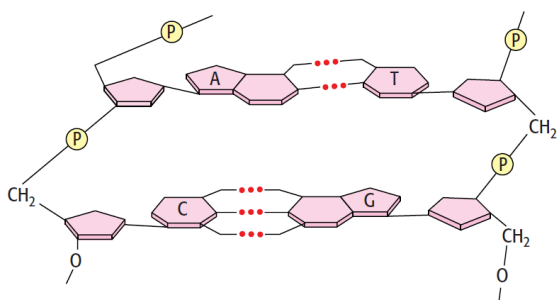


Figure 28.17 The detailed structure of part of a DNA molecule, showing the hydrogen bonding between the base pairs.

- The process of copying DNA during cell division is called **replication**

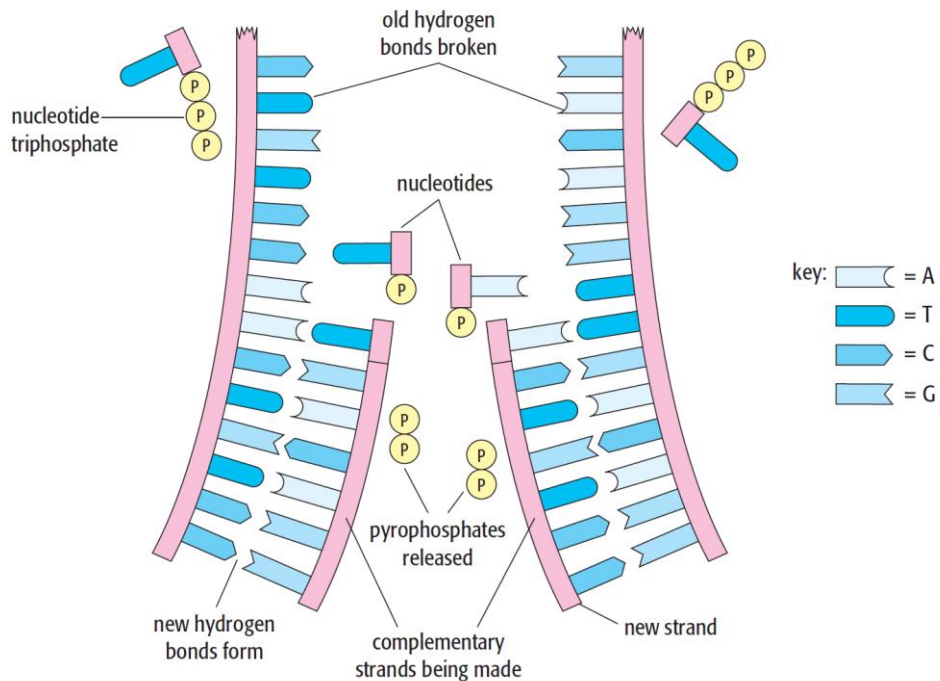
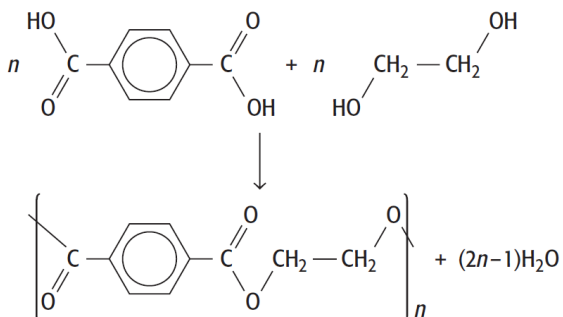
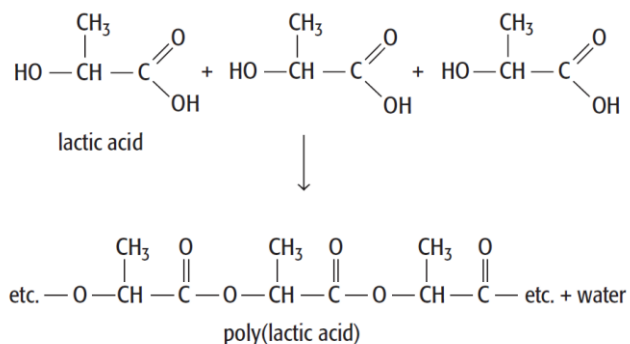


Figure 28.18 A strand of DNA acting as template for replication.

- Polyesters** are another type of condensation polymer, which can be made by reacting dicarboxylic acids with diols, e.g. benzene-1,4-dicarboxylic acid and ethane-1,2-diol to produce the most common polyester fibre – **Terylene®** (antimony(III) oxide catalyst, 280°C):



- Poly(lactic acid), PLA, is another polyester, made from one monomer: lactic acid (2-hydroxypropanoic acid); can be hydrolysed in acidic conditions to break down the polymer chains (biodegradable)



- **Low-density poly(ethene) (LDPE)** has a heavily, randomly branched non-polar polymer chains – which interacts by weak VDW's forces – that causes the low density and low melting point due to the inability to pack neatly together – however is non-biodegradable
- **High-density poly(ethene)** consists of straight chains which could pack closely together, forming high-density and high melting point poly(ethene) – however is non-biodegradable

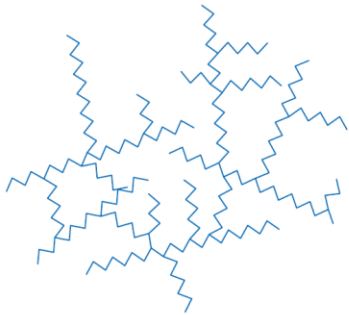


Figure 28.20 The branched chains of LDPE. The van der Waals' forces between the non-polar polymer chains are affected not only by the size of the chains but also their inability to pack closely together, reducing the effectiveness of instantaneous dipoles in one chain to induce dipoles on neighbouring chains.

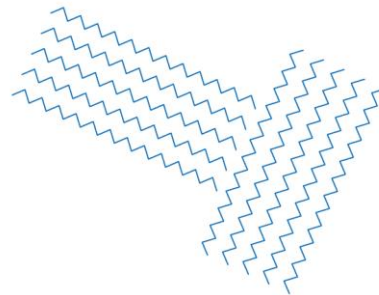
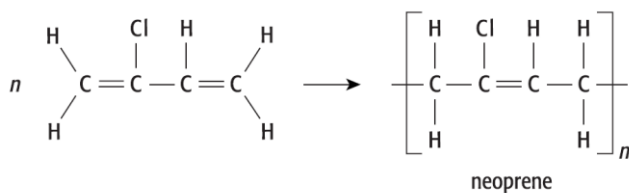


Figure 28.21 The unbranched chains of HDPE can pack closely together in regions of regular patterns, increasing the surface area of contact between neighbouring chains resulting in stronger van der Waals' forces being set up between chains.

- Neoprene, a synthetic rubber, can be made from the polymerisation of 2-chloro-1,3-butadiene in an addition reaction:



- Natural rubbers have undergone vulcanisation to make them more resilient and hardwearing, by linking rubber polymer chains by covalent bonds across 'sulfur bridges':

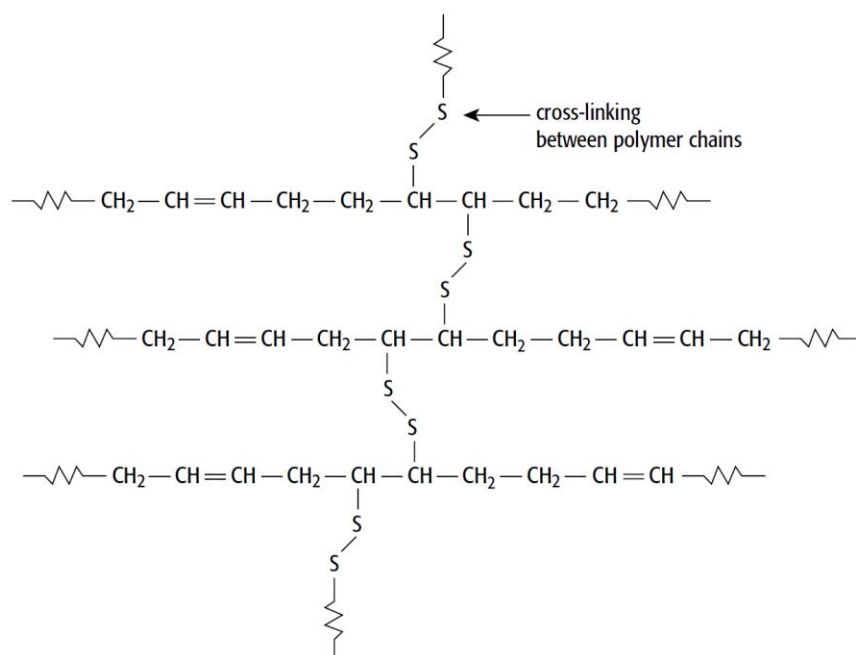


Figure 28.22 The sulfur bridges between polymer chains make rubber more resilient.

- Non-solvent based adhesives is often a polymer containing silicon bonded to oxygen ('silyl modified polymers' (SMPs)), which sets by reacting with the moisture present in the air – water hydrolyses the silicon-oxygen parts of the polymer chain, forming cross-linkages between each other; this effectively bonds the polymer chains to each other with strong covalent bonds
 - The cross-linking siloxane grouping is – Si – O – Si – (an ether group)

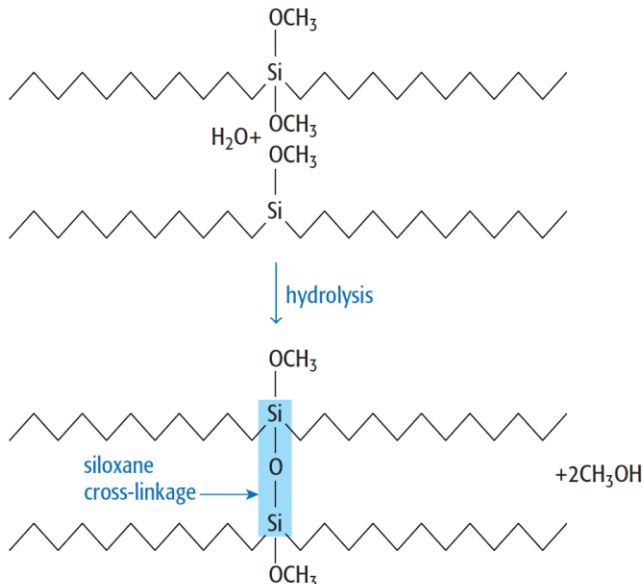
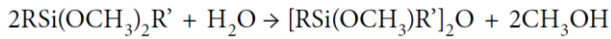


Figure 28.23 This shows how hydrolysis of a Si—O—CH₃ grouping can form a siloxane cross-link between polymer chains. As an adhesive sets (cures) many of these strong covalent links will be formed to produce a giant network.



Figure 28.24 Silyl modified polymers (SMPs) are a safer option than traditional adhesives, which use potentially harmful organic solvents.

- **Epoxy resins** are common examples of polymers that form extensive networks of covalent cross-links (thermosets) formed by condensation polymerisation – very strong and cannot be melted and remoulded
- These thermosetting glues are formed when the two reactants, epoxyethane (a reactive, triangular molecule, CH₂CH₂O) and a diamine, are mixed as pastes

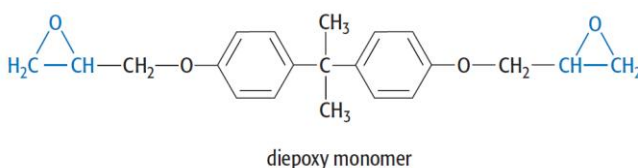


Figure 28.25 A diepoxy monomer.

- This can be reacted with a diamine, H₂N – R – NH₂, to form a hard, strong epoxy resin
- Another fast-acting fixing agent, Super Glue[®], uses addition reaction to stick objects together. The monomer is CH₂=C(CN)COOCH₃, methyl cyanoacrylate, and the addition takes place across the carbon – carbon double bond; is initiated by the presence of moisture

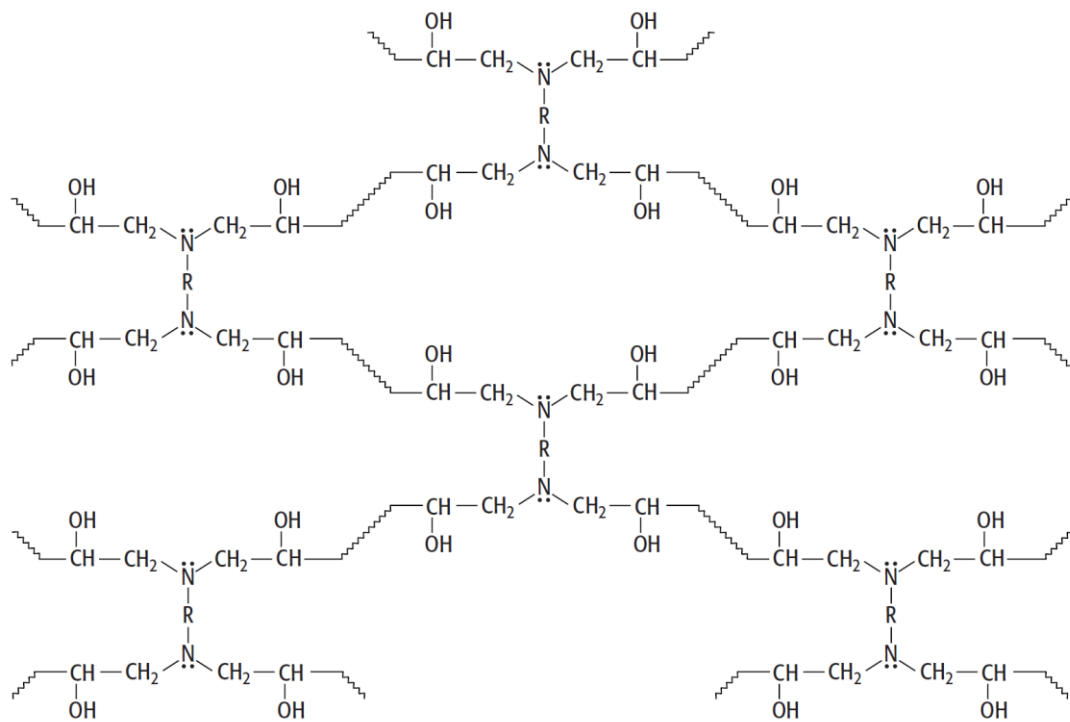


Figure 28.26 The extensive cross-linking in a thermosetting epoxy resin.

- Biodegradable plastics:
 - In polyamides, such as nylons, the amide links, $-\text{CO}-\text{NH}-$, can be broken down by hydrolysis in acidic conditions found in land-fill waste dumps
 - In polyesters, the ester links are similarly broken down by acid hydrolysis
- Photodegradable plastics:
 - Polymer chains with carbonyl groups ($\text{C}=\text{O}$) at intervals down their length; they absorb UV light causing the bonds in the region of the carbonyl group to weaken and break down
- Acetylene (or ethyne) hydrocarbon creates a polymer which can conduct electricity; its molecular formula is C_2H_2 :

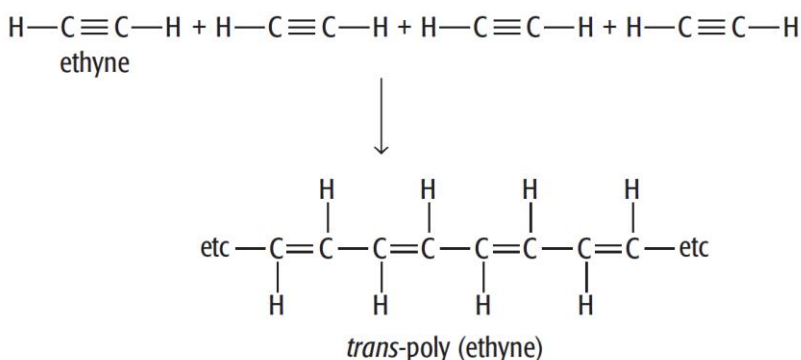


Figure 28.28 The polymerisation of ethyne (acetylene) to form a conducting polymer.

- The ability to conduct electricity is due to the alternating double and single carbon-carbon bonds in the poly(ethyne), which causes its π bonding to spread down the length of the polymer chain; the overlapping p orbitals on neighbouring carbon

atoms result in long bands of delocalised electrons that are free to move along the length of the polymer chains, just like benzene

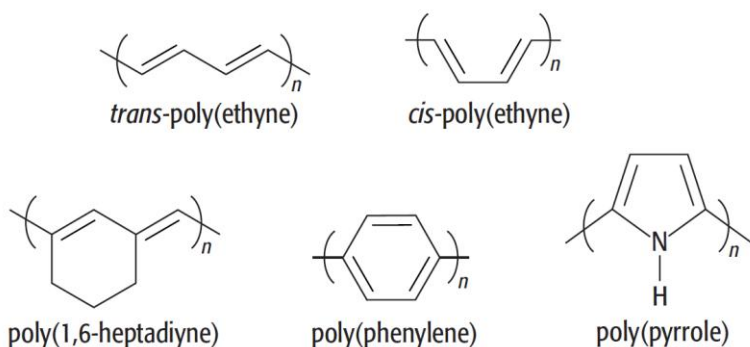
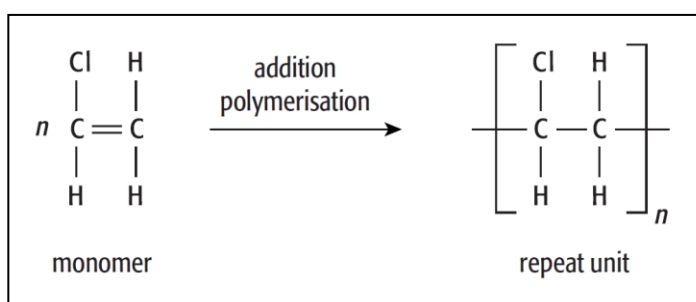
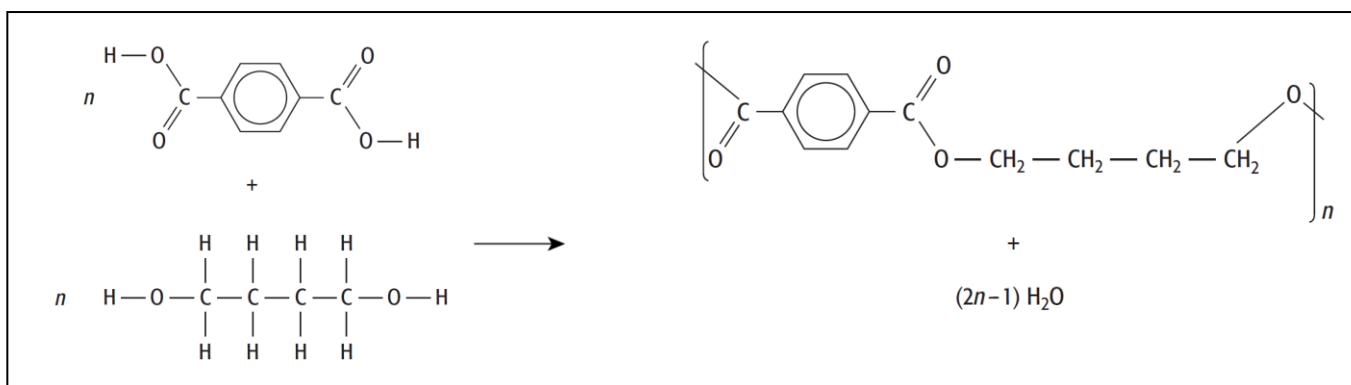


Figure 28.29 Some examples of conducting polymers – note the alternate double and single carbon–carbon bonds.

- Predicting the type of polymerisation reaction for given monomers:
 - Addition polymers:
 - Monomers which contain C=C double bond
 - Condensation polymers:
 - Look out for two functional groups that will react with each other, giving off a small molecule
 - Functional groups:
 - Amines (-NH₂) and carboxylic acids (-COOH) producing a polyamide and H₂O
 - Amines (-NH₂) and acyl chlorides (-COCl) producing a polyamide and HCl
 - Carboxylic acids (-COOH) and alcohols (-OH) producing a polyester and H₂O
 - Acyl chlorides (-COCl) and alcohols (-OH) producing a polyester and HCl
- Deducing the repeat unit of a polymer for given monomer(s):
 - Addition polymers:

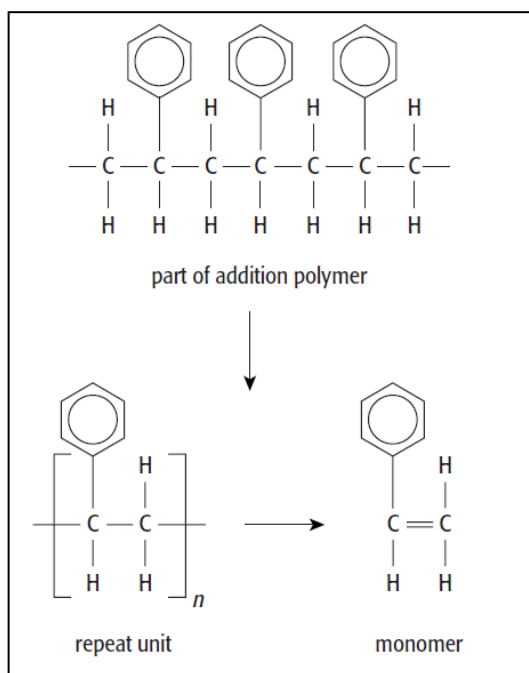


- Condensation polymers:

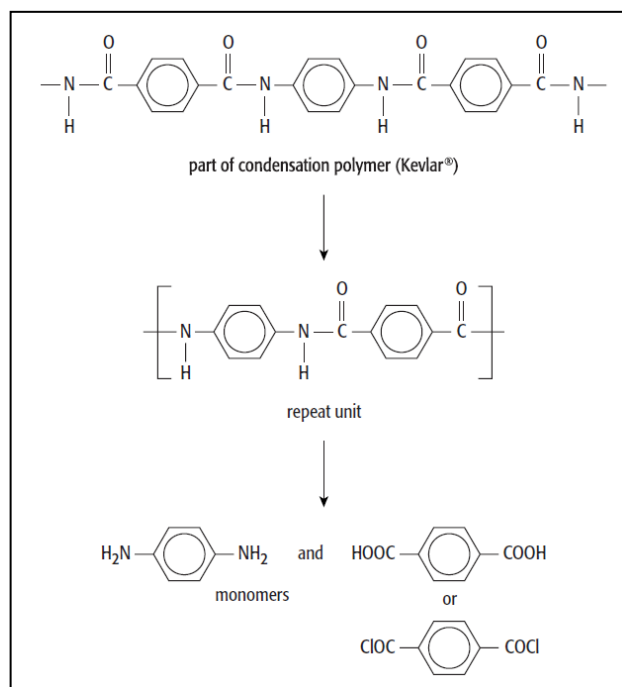


- Identifying the monomer(s) present in a given section of a polymer chain:

➤ Addition polymers:



Condensation polymers:



- PTFE or Teflon®** is like poly(ethene), but all the hydrogen atoms have been replaced by fluorine atoms which has three lone pairs of electrons and this means that rotation about the carbon-carbon single bonds is inhibited, whereas in poly(ethene) there is free rotation about these bonds, forming rod-like molecules that are packed together closely giving strong intermolecular forces and increasing the crystalline properties of the polymer.
- The strong C-F bonds make the polymer chemically inert, but the effect of the fluorine atom lone pair electrons effectively means that for small molecules, with a limited 'point of contact', the van der Waals forces are weak: this causes the 'non-stick' property of PTFE