Book 7

Topic 14
Materials Chemistry

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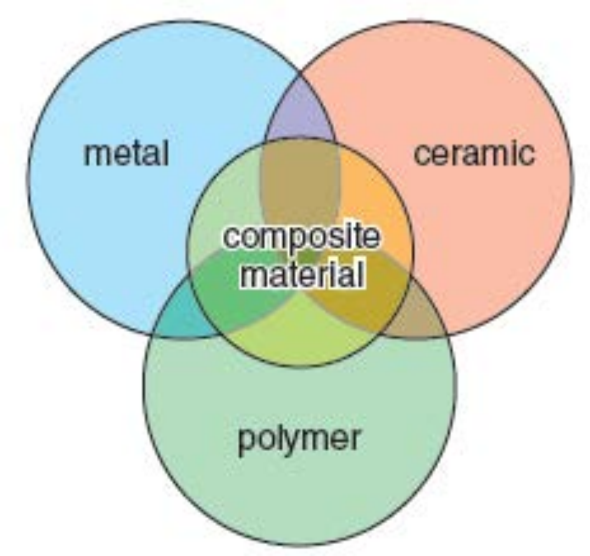
47.1 Types of materials (p.2)

Carbonated drinks are marketed in aluminium (metal) cans, synthetic polymer bottles and glass (ceramic) bottles

- Materials are classified into four main categories:

- Metals,
- Polymers,
- Ceramics
- Composite materials



47.1 Types of materials (p.2)

Classification of materials

Metals

- stiff, hard, strong and shiny (when polished).
- ductile and malleable.
- conduct electricity and heat
- Pure metals can be made stronger by alloying.
- metals and alloys are used for many different purposes because of their properties.

Polymers (聚合物)

- long-chain molecules which are formed when small molecules of monomers join together.
- Examples: polythene, nylon and cellulose.

47.1 Types of materials (p.2)

Ceramics (陶瓷)

- inorganic compounds of metals and non-metals.
- often oxides, nitrides or carbides.
- Glass, porcelain and cement are in this class.

Composite materials (複合材料)

- mixtures that contain two or more different materials.
- In a composite material, the properties of the components combine to give a material which is more useful for a particular purpose than the individual components.
- Adding fibre if a synthetic polymer on its own may not be strong enough to meet the requirements.

47.2 Natural and synthetic polymers (p.4)

- Polymers can be classified as **natural** or **synthetic** polymers.
- **Natural polymers** are those polymers that occur in nature and that which are isolated from plants and animal resources. Cellulose, starch, proteins are a few examples of natural polymers.
- **Synthetic polymers** are synthesised in the laboratory or factory through a series of chemical reactions from compounds of low relative molecular masses. Nylon, polythene and polyester are a few examples of synthetic polymers.

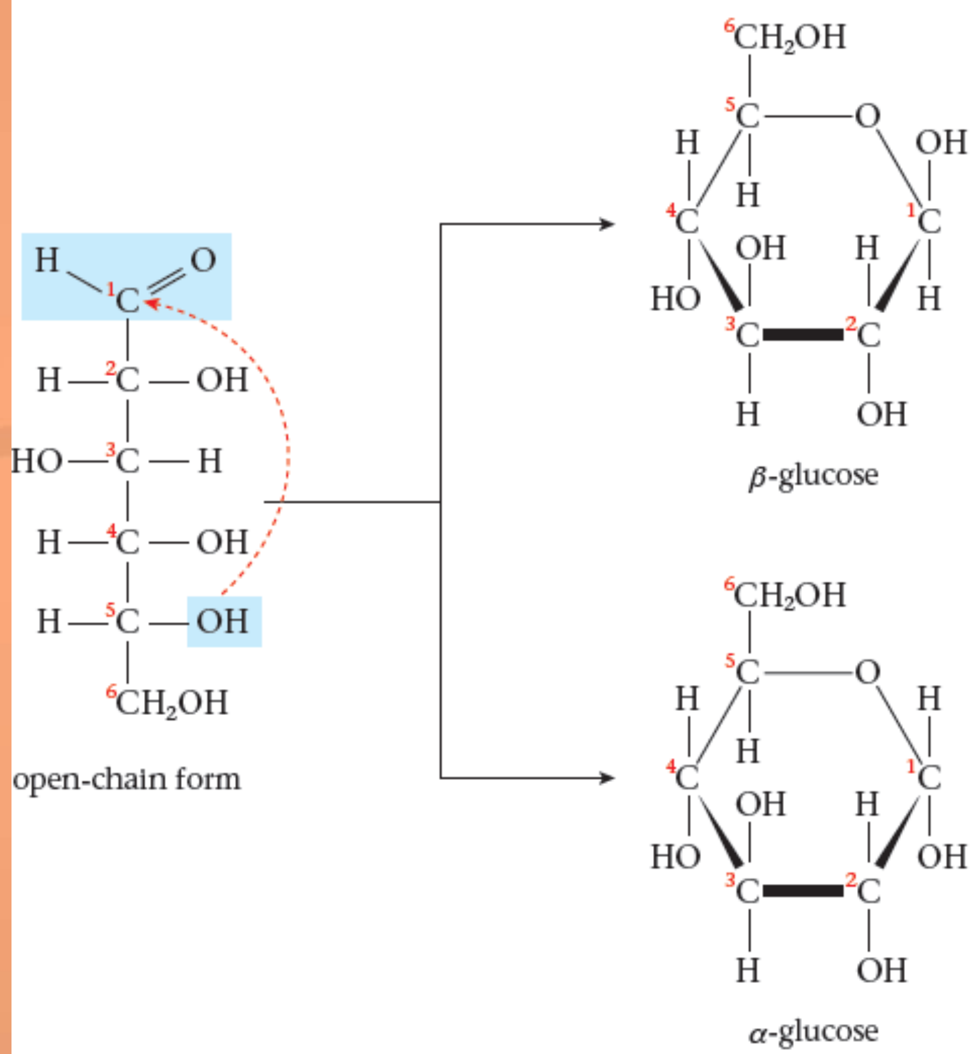
47.3 Cellulose (p.4)

- Cellulose (纖維素) is the most abundant natural polymer on Earth. It is the main component of cell walls of plant cells.
- The largest use of cellulose is in the manufacture of paper and paper products.
- Cellulose is a natural polymer of the β-glucose monomer.

47.3 Cellulose (p.4)

Glucose

- has the molecular formula $C_6H_{12}O_6$. It can exist in either the open-chain form or the ring form.
- In a glucose solution, the open-chain form cyclises into ring structures. This happens when the carbon atom with the double bonded oxygen (C1) joins to the fifth carbon atom (C5) via a bridging oxygen



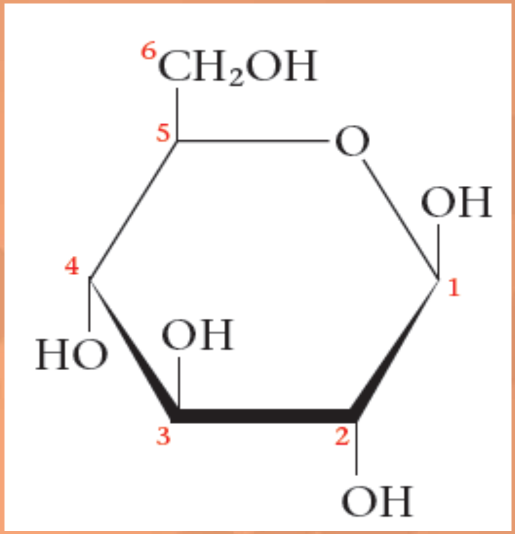
47.3 Cellulose (p.4)

- The cyclisation reaction can happen in two ways. When an –OH group is formed on the first carbon atom, it can either be on the same side of the ring as the CH_2OH group on the fifth carbon atom (β-glucose) or on the opposite side of the ring (α-glucose).
- A dynamic equilibrium exists among the β, α and open-chain forms, and there is a continual interconversion among them.

47.3 Cellulose (p.4)

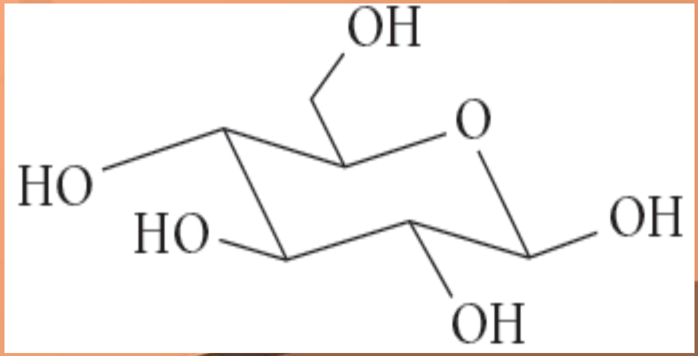
- The edge of the ring nearest the reader is represented by bold lines, and the letter C for the carbon atoms in the ring are usually omitted.

The skeletal formula of β -glucose



- The skeletal formula can, however, be misleading as it suggests that the six-membered ring of glucose is planar, which is not the case. In reality β -glucose exists as puckered rings.

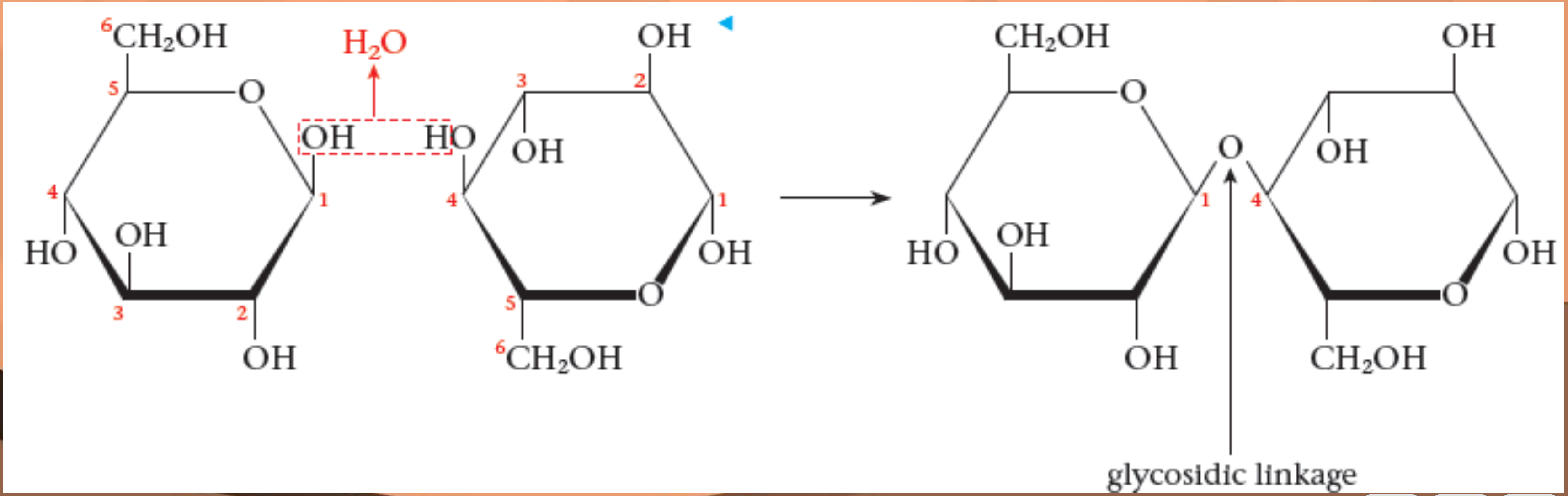
β –glucose as puckered ring



47.3 Cellulose (p.4)

Structure of cellulose

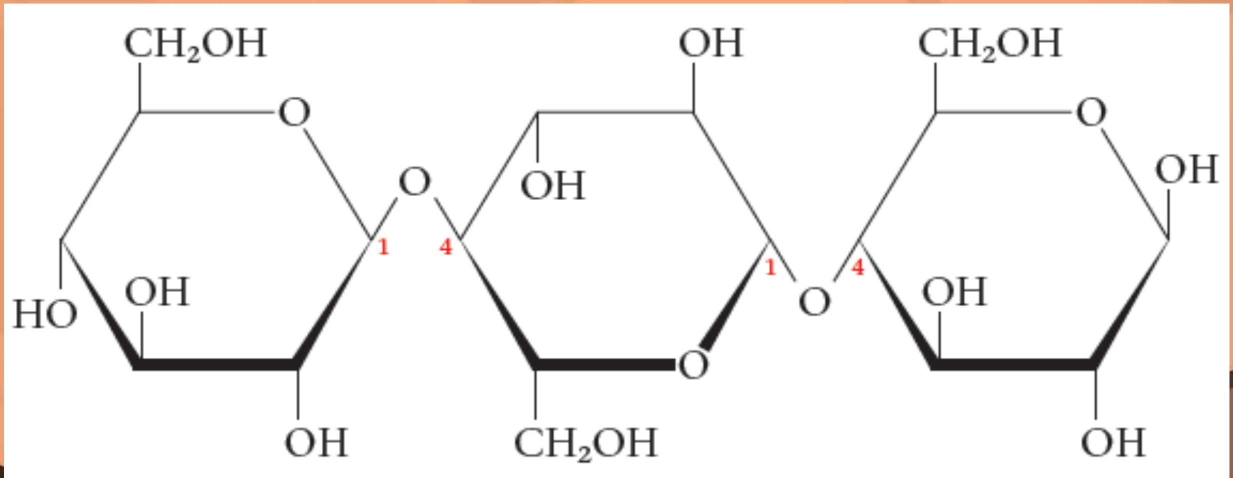
- Two β -glucose molecules can link together via an oxygen atom at the first carbon atom (C1) of one molecule and the fourth carbon atom (C4) of the other molecule, with the elimination of a water molecule
- A condensation reaction occurs. The link between the two glucose units is called a **glycosidic linkage(糖苷鍵合)**.



47.3 Cellulose (p.4)

- The position of the next β - glucose molecule joined to the dimer will need to be the same as the first one. This time the glycosidic linkage is formed below the ring structure.

A dimer is formed by the combination of two smaller identical molecules.

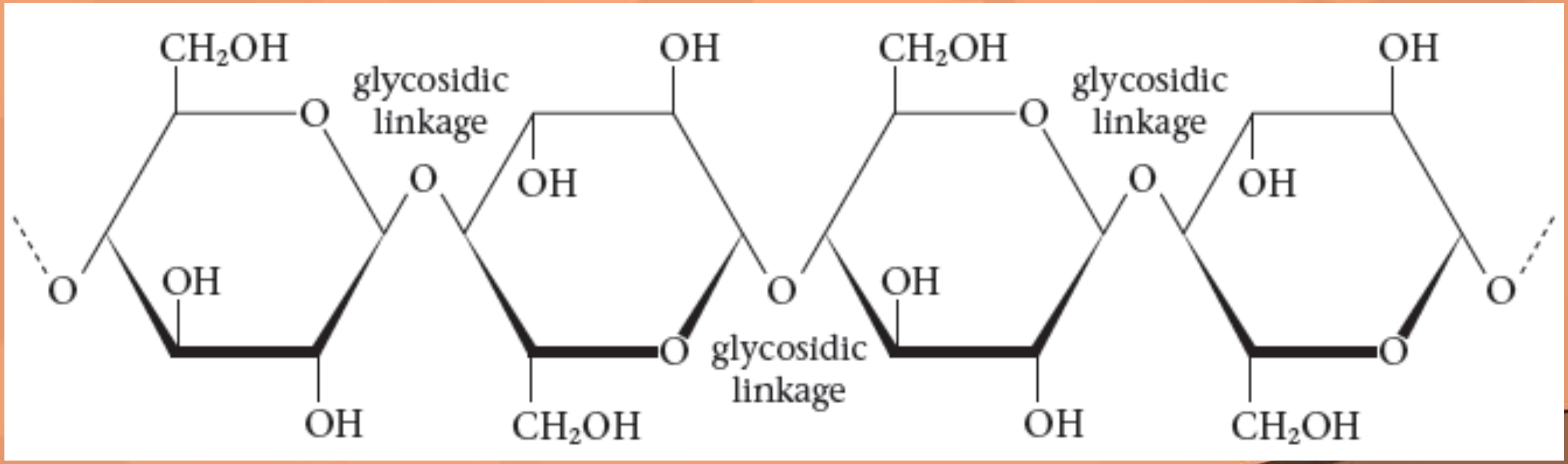


47.3 Cellulose (p.4)

- Cellulose is an unbranched condensation polymer of β - glucose. Up to 15 000 glucose units, joined via glycosidic linkages, are present in each molecule

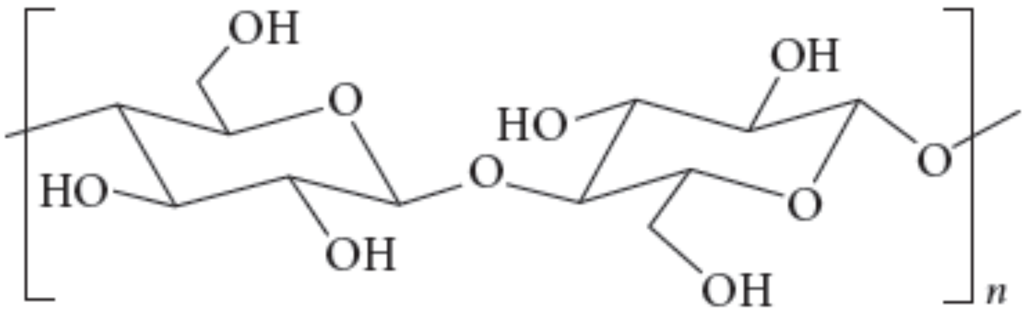
.

A part of the structure of a cellulose molecule



47.3 Cellulose (p.4)

The structure of cellulose can also be represented as:

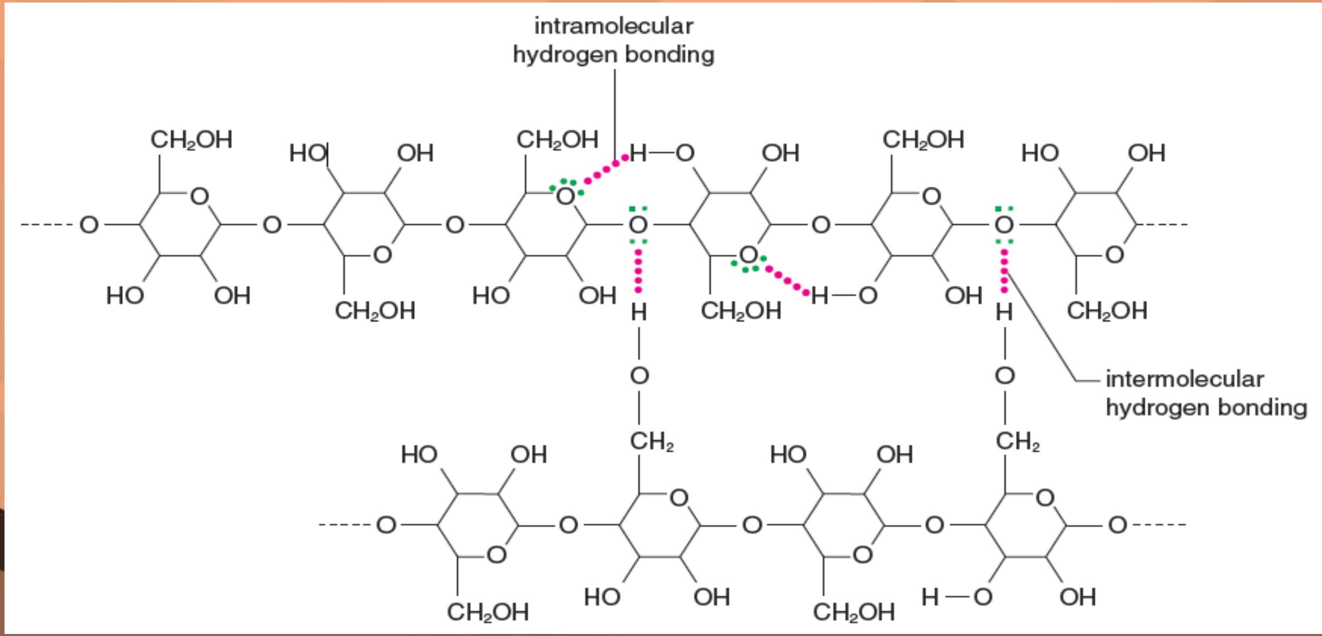


- The molecular formula of cellulose is $(C_6H_{10}O_5)n$.
- Molecules of cellulose contain various numbers of β - glucose units. Hence the relative molecular mass of cellulose falls into a wide range, generally from 2.5×10^5 to 1.0×10^6.

47.3 Cellulose (p.4)

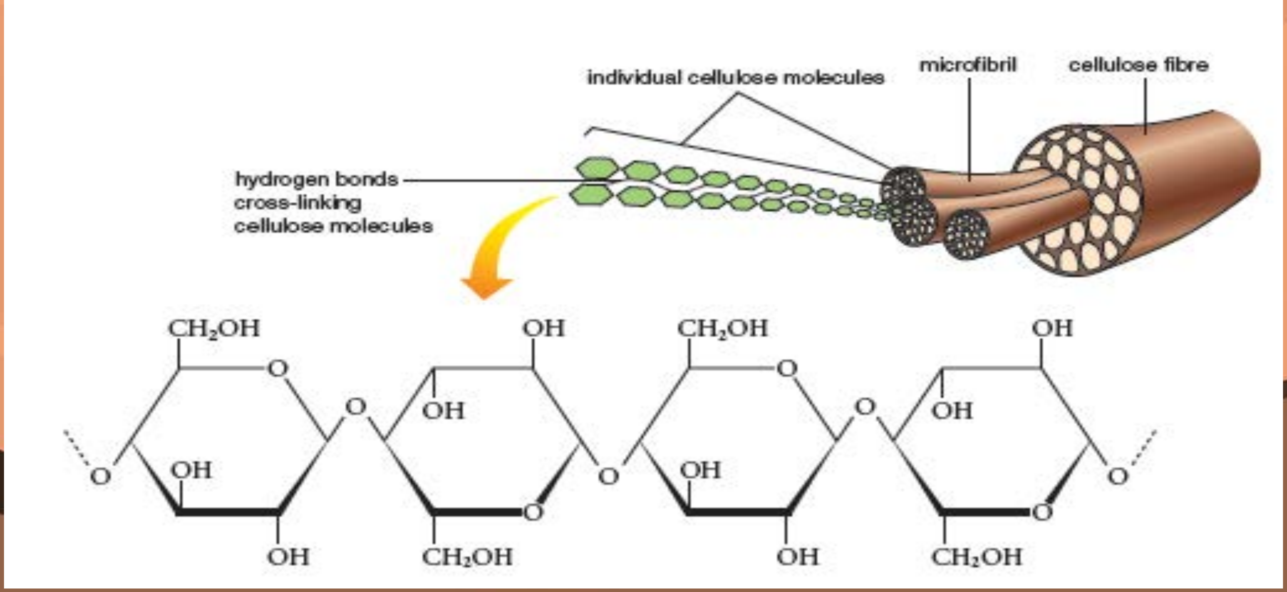
Properties of cellulose

- Cellulose is insoluble in water.
- This is due to the fact that the –OH groups in cellulose molecules can form extensive intramolecular and intermolecular hydrogen bonding.
- The –OH groups are less available to form hydrogen bonds with water molecules.

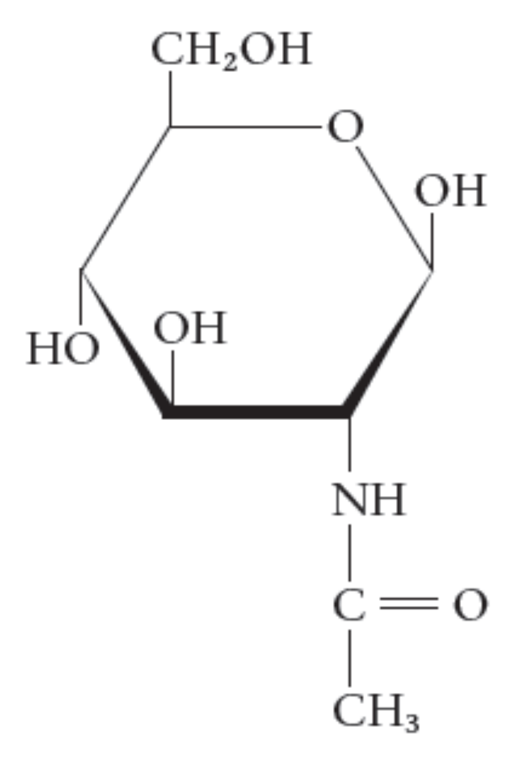


47.3 Cellulose (p.4)

- A cellulose molecule has a linear structure. The molecules can pack closely together.
- The –OH groups of one molecule can form hydrogen bonds with –OH groups of other molecules lying parallel to it.
- Up to 60 or 70 individual cellulose molecules can be held together to form a column known as a microfibril
- Bundles consisting of many microfibrils are assembled together to form the cellulose fibres which give strength to cell walls in plants.

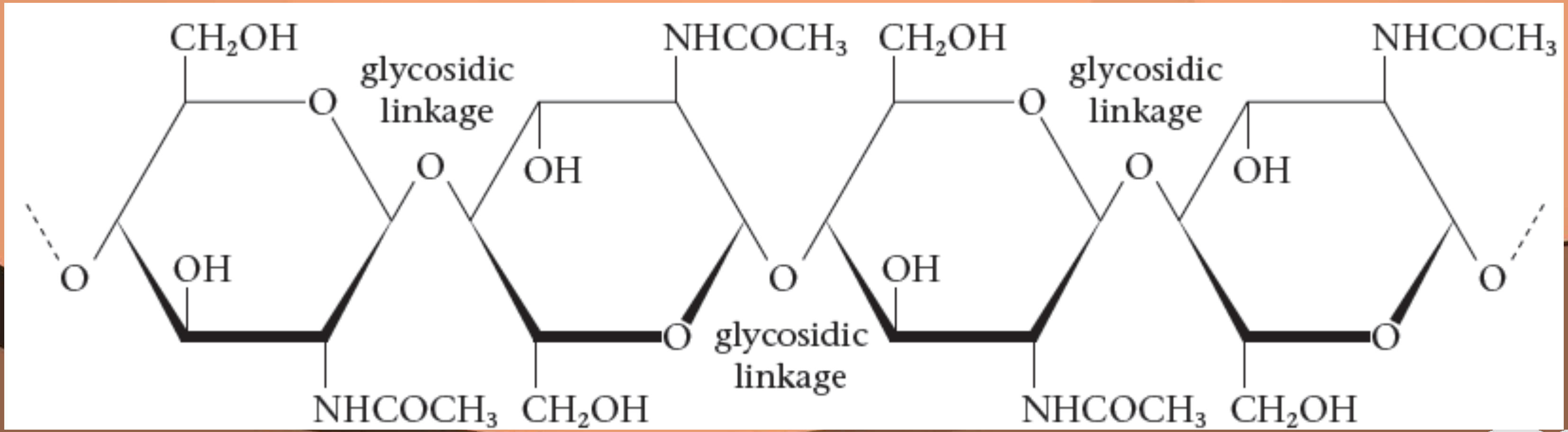


47.4 Chitin (p.9)



Chitin (甲殼素)

- a natural polymer, is an important component of this exoskeleton. It is the second most abundant natural polymer on Earth.
- Chitin is a polymer of the N-acetylglucosamine monomer

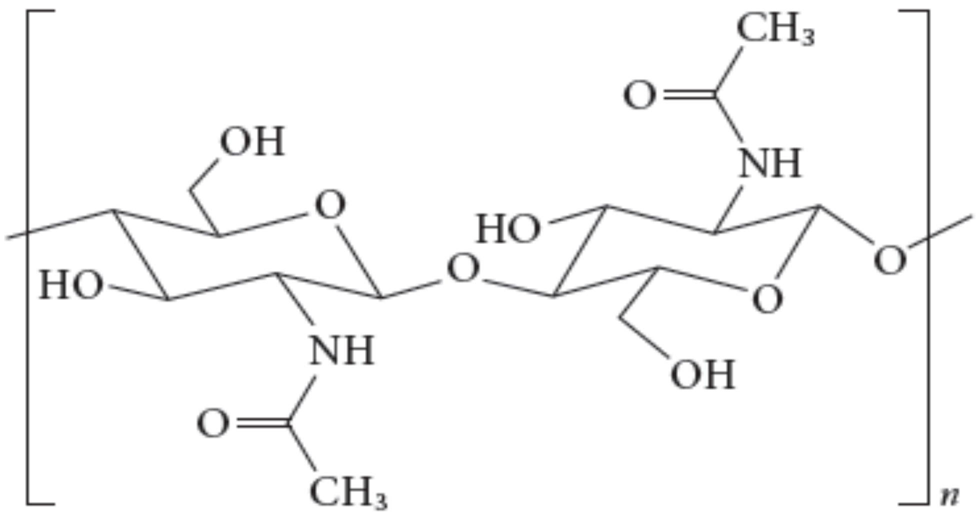


47.4 Chitin (p.9)

- The structure of chitin resembles that of cellulose, except that one –OH group on each monomer unit is replaced by a $–NHCOCH_3$ group.

- The extensive intramolecular and intermolecular hydrogen bonding in chitin makes it hard and insoluble in water. It is also biodegradable.

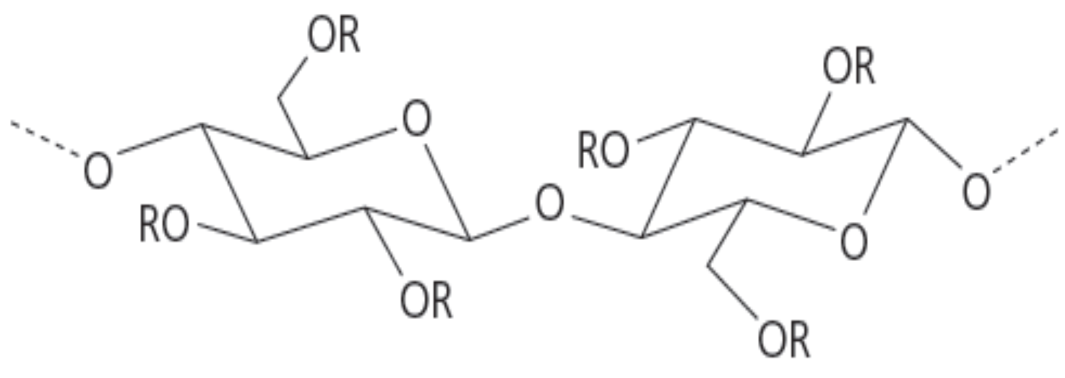
The structure of chitin can also be represented as:



47.4 Chitin (p.9)

Practice 47.1

Methyl cellulose is a polymer synthesised from cellulose. A part of the structure of methyl cellulose is shown below.



(In this structure, R can be H or CH_3.)

The solid softens upon heating. The heat absorbed helps the polymeric molecules to overcome the intermolecular forces. The molecules can have relative translational motion. At very high temperatures, the glue chars.

Methyl cellulose is commonly used as the active ingredient of wallpaper glue. The glue is a white solid when dried.

State and explain the behaviour of the white solid when it is gradually heated to a very high temperature.

47.5 Synthetic polymers (p.11)

- Synthetic polymers can be classified into two categories according to what happens to them when they are heated to high temperatures.

Thermoplastics (熱塑性塑膠)

- are synthetic polymers that soften and flow upon heating, and become hard again when cooled. This cycle can be repeated many times, which makes reprocessing during manufacture or recycling after consumer use possible.

Thermosetting plastics(熱固性塑膠)

- become permanently hard during their formation, and do not soften upon heating. If they are exposed to enough heat, they will crack or become charred.
- 80% of the synthetic polymers produced are thermoplastics and of these polythene, polypropene, polyvinyl chloride and polystyrene are the most commonly used.

47.6 Addition polymerisation(p.12)

- There are two broad types of polymerisation reactions, i.e. the **addition polymerisation** and the **condensation polymerisation**.
- In addition polymerisation, the molecules of the same monomer or different monomers join together repeatedly to form polymer molecules. The monomers used are unsaturated compounds, such as alkenes and their derivatives. The polymer so formed is an addition polymer.

➢ Addition polymerization is a reaction in which monomer molecules join together repeatedly to form polymer molecules. No atoms are lost from the monomer molecules during the reaction.

- Addition polymerisation occurs most frequently by a free radical mechanism.

47.6 Addition polymerisation(p.12)

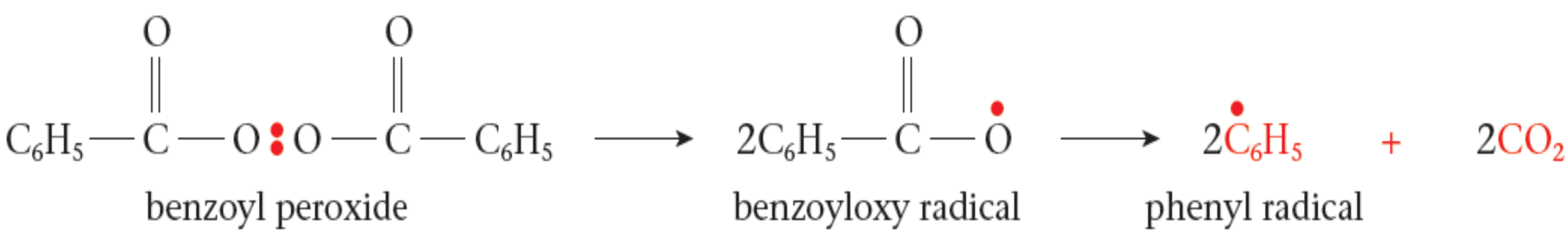
Free radical mechanism

- A variety of alkenes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, etc.
- For example, the polymerisation of ethene to low density polythene is carried out at 147–297 °C and under a pressure of 1 000–3 000 atmospheres in the presence of a small amount of benzoyl peroxide.
- The **three** stages of this reaction to focus on are
  - **initiation;**
  - **propagation; and**
  - **termination**.

47.6 Addition polymerisation(p.12)

Initiation

- When heated, benzoyl peroxide can produce benzoyloxy radicals by cleaving at an oxygen-oxygen bond. The benzoyloxy radicals can break down further to give phenyl radicals and carbon dioxide.



- A new and larger free radical is generated when a phenyl radical adds to an ethene molecule.

$$\dot{C}_6H_5 + CH_2{=}CH_2 \longrightarrow C_6H_5{-}CH_2{-}\dot{C}H_2$$

47.6 Addition polymerisation(p.12)

Propagation

- As this radical reacts with another molecule of ethene, another bigger radical is formed.

$$C_6H_5-CH_2-\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$$

- By repeating this step, the carbon chain of the radical grows in length.

$$C_6H_5-\left[CH_2-CH_2\right]_n-CH_2-\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow C_6H_5-\left[CH_2-CH_2\right]_{n+1}-CH_2-\dot{C}H_2$$

47.6 Addition polymerisation(p.12)

Termination

- When two radicals combine to form a stable molecule, the chain reactions carried by these radicals are terminated.
- One mode of termination of chain reaction is shown below:

$$C_6H_5{-}\!\left[CH_2{-}CH_2\right]_n\!{-}CH_2{-}\dot{C}H_2 + C_6H_5{-}\!\left[CH_2{-}CH_2\right]_n\!{-}CH_2{-}\dot{C}H_2$$

$$\longrightarrow C_6H_5{-}\!\left[CH_2{-}CH_2\right]_n\!{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\!\left[CH_2{-}CH_2\right]_n\!{-}C_6H_5$$

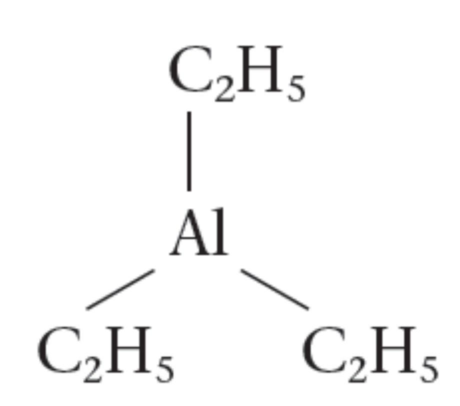
47.6 Addition polymerisation(p.12)

Ziegler-Natta catalysts

- An efficient addition polymerisation procedure was developed by Karl Ziegler and Giulio Natta in the 1950s. Their findings permitted, for the first time, the synthesis of unbranched high density polythene. The production occurs at 60–70 °C and under a pressure of 6–7 atmospheres.

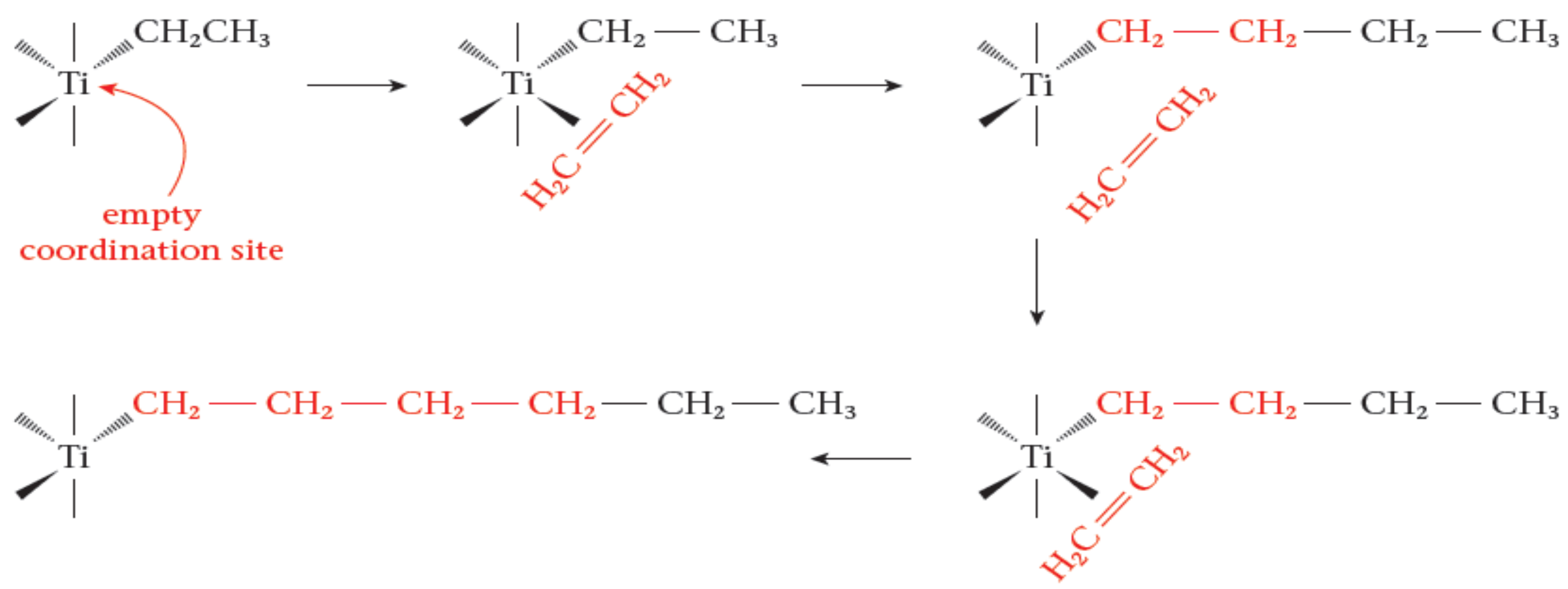
- A typical Ziegler-Natta catalyst can be prepared from titanium(IV) chloride and triethylaluminium

Triethylaluminium



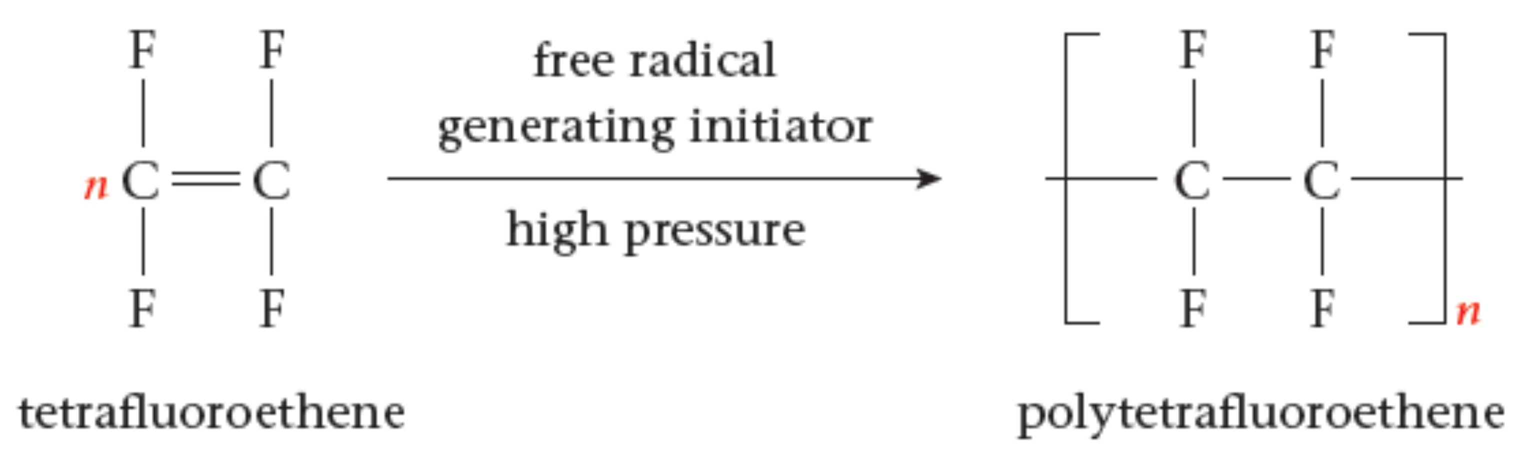
47.6 Addition polymerisation(p.12)

- An empty coordination site on the titanium atom.
- The ethene molecule attaches itself to the empty site and this molecule then inserts itself into the carbon-titanium bond to extend the carbon chain.
- This process then continues, thereby forming a linear polymer, high density polythene.



47.7 Polytetrafluoroethene (p.16)

- Polytetrafluoroethene (PTFE) is a thermoplastic produced by addition polymerisation of tetrafluoroethene via a free radical mechanism. The polymerisation is carried out under high pressure in the presence of a free radical generating initiator such as a peroxide.



47.7 Polytetrafluoroethene (p.16)

Properties of polytetrafluoroethene

- Polytetrafluoroethene is distinguished by its high melting point, non-sticky property and resistance to attack by almost all chemicals.

Melting point

- The melting point of polytetrafluoroethene is quoted as 327 °C. The molecules in polytetrafluoroethene pack very closely together in a regular way, producing strong van der Waals' forces and hence a high melting point.

47.7 Polytetrafluoroethene (p.16)

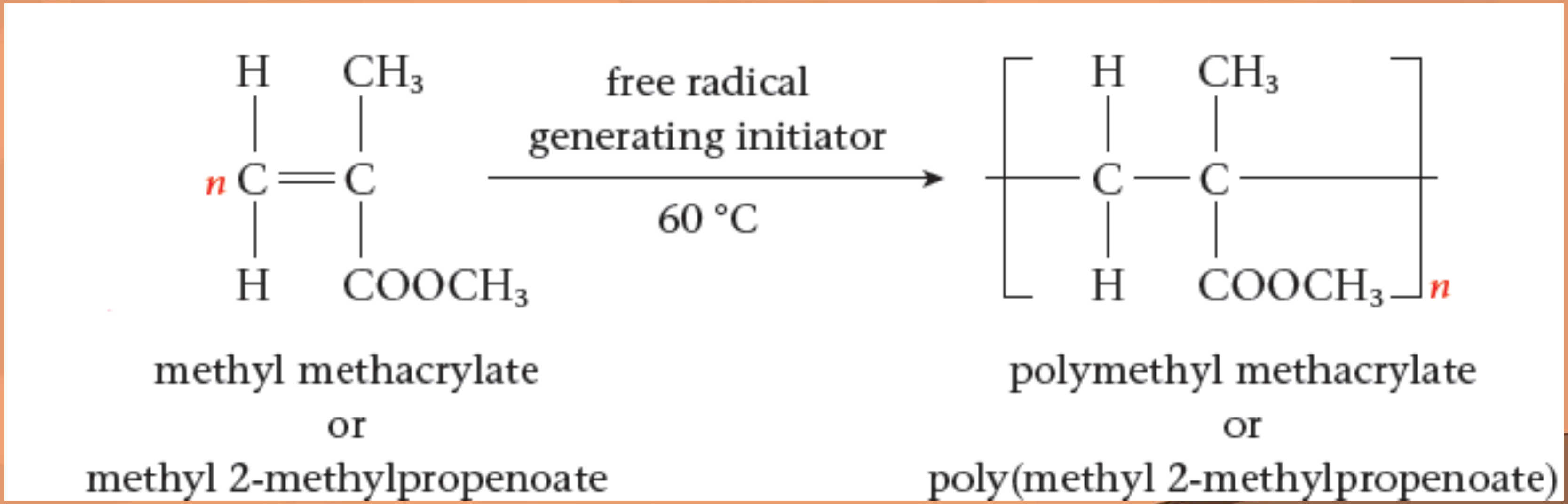
Non-sticky property

- Water and oil do not stick to the surface of polytetrafluoroethene, and you can fry an egg in a PTFE-coated pan without lot of it ending up stuck to the pan.
- Fluorine is the most electronegative element.
- C–F bonds in polytetrafluoroethene are strongly polar.
- There is an evenly distributed layer of partial negative charge on the surface of polytetrafluoroethene.
- This layer of fluorine atoms almost repels all other materials, preventing them from adhering to polytetrafluoroethene.
- Polytetrafluoroethene has a slippery and non-sticky surface.

47.8 Polymethyl methacrylate (PMMA) (p.19)

- Polymethyl methacrylate (PMMA) is a commonly used thermoplastic with boundless applications.

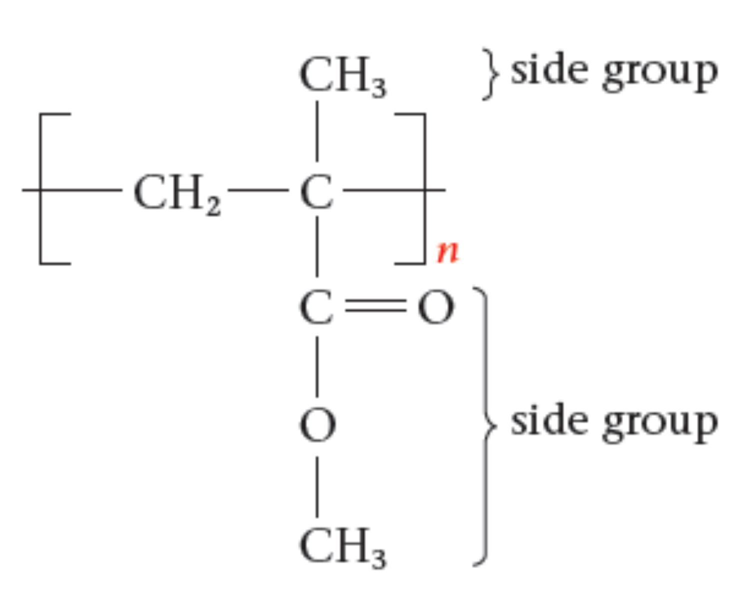
- It is produced from the free radical addition polymerisation of **methyl methacrylate (甲基丙烯酸甲酯)** at about 60 °C in the presence of a free radical generating initiator such as a peroxide.



47.8 Polymethyl methacrylate (PMMA) (p.19)

- The presence of bulky side groups attached to the main chain of a molecule of polymethyl methacrylate prevents the molecules from packing closely in a regular way.
- These side groups also make the molecules unable to slide past each other easily. As a result, polymethyl methacrylate is a tough and rigid polymer.

Bulky side groups on the structure of PMMA



47.8 Polymethyl methacrylate (PMMA) (p.19)

Uses of polymethyl methacrylate

- Polymethyl methacrylate is a **highly transparent synthetic polymer**.
- The sheets are used in baths and other sanitary ware. This application, along with illuminated signs, is the largest use of the polymer.
- Because of its high transparency, polymethyl methacrylate is often used as a lightweight and shatter-resistant replacement for glass like covers for car lights. The windows of many aircraft and many motorcycle helmet visors.

47.8 Polymethyl methacrylate (PMMA) (p.19)

Medicine:

- It has a good compatibility with human tissue and has been used for replacement of intraocular lenses in eyes. Hard contact lenses are often composed of polymethyl methacrylate.
- Bone cement containing polymethyl methacrylate is used to connect bone implants and remodel lost bone.

Artistic uses:

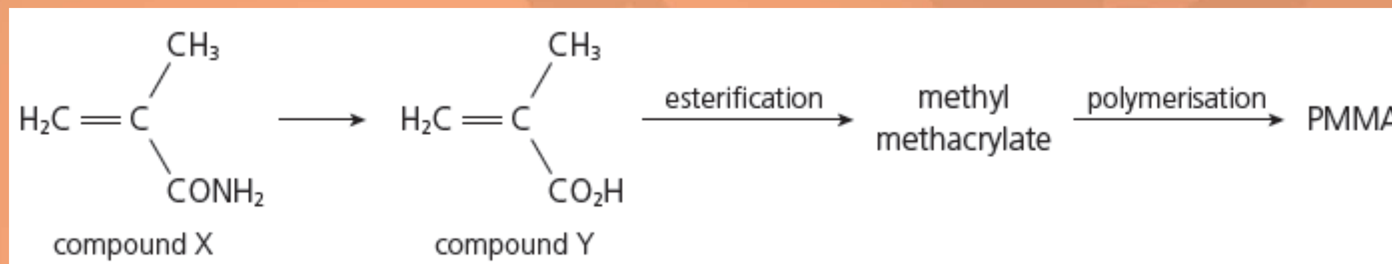
- Acrylic paints are largely polymethyl methacrylate suspended in water

Preparing Perspex *Ref.*

47.8 Polymethyl methacrylate (PMMA) (p.19)

Practice 47.2

Polymethyl methacrylate (PMMA) can be obtained from compound X via the following route:



a) Give the reagent(s) and conditions required for the conversion of X to Y.

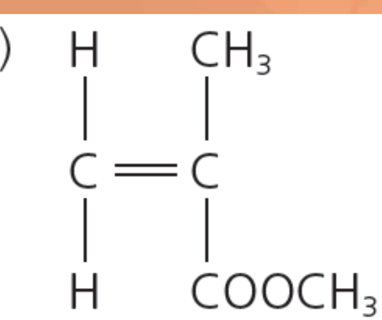
b) Draw the structure of methyl methacrylate.

a) $H^+(aq)$, heat

c) Write the chemical equation for the polymerisation of methyl methacrylate.

d) PMMA of a special grade is used in making contact lenses. State ONE property of PMMA making it suitable for this purpose.

d) • PMMA is transparent.
• PMMA is biocompatible

b)


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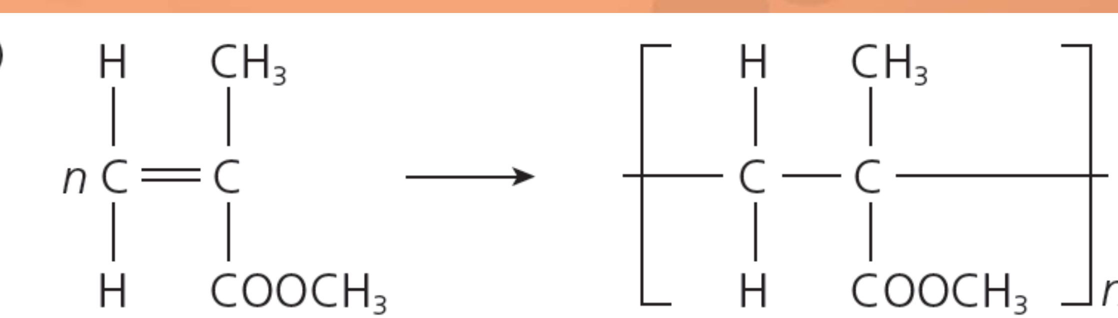
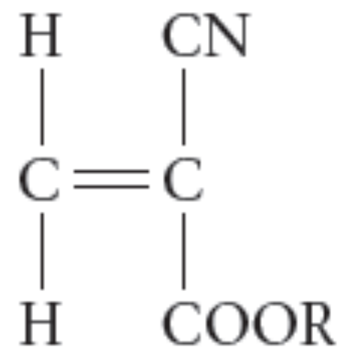


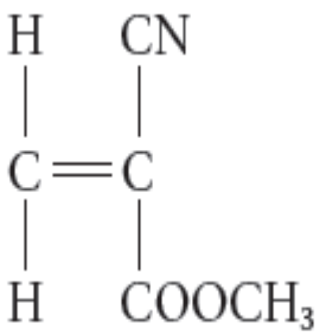
47.9 Cyanoacrylates (Superglue) (p.21)

- **Cyanoacrylates**, with the basic structure shown below, are a family of monomers renowned for their instant adhesive properties and wide-ranging applications.

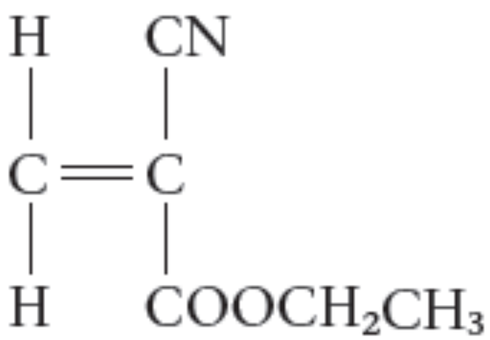


cyanoacrylate

- Short chain cyanoacrylates, such as **methyl 2-cyanoacrylate** and **ethyl 2-cyanoacrylate**, have found great utility as the major components of industrial and household instant adhesives or Superglue



methyl 2-cyanoacrylate



ethyl 2-cyanoacrylate

47.9 Cyanoacrylates (Superglue) (p.21)

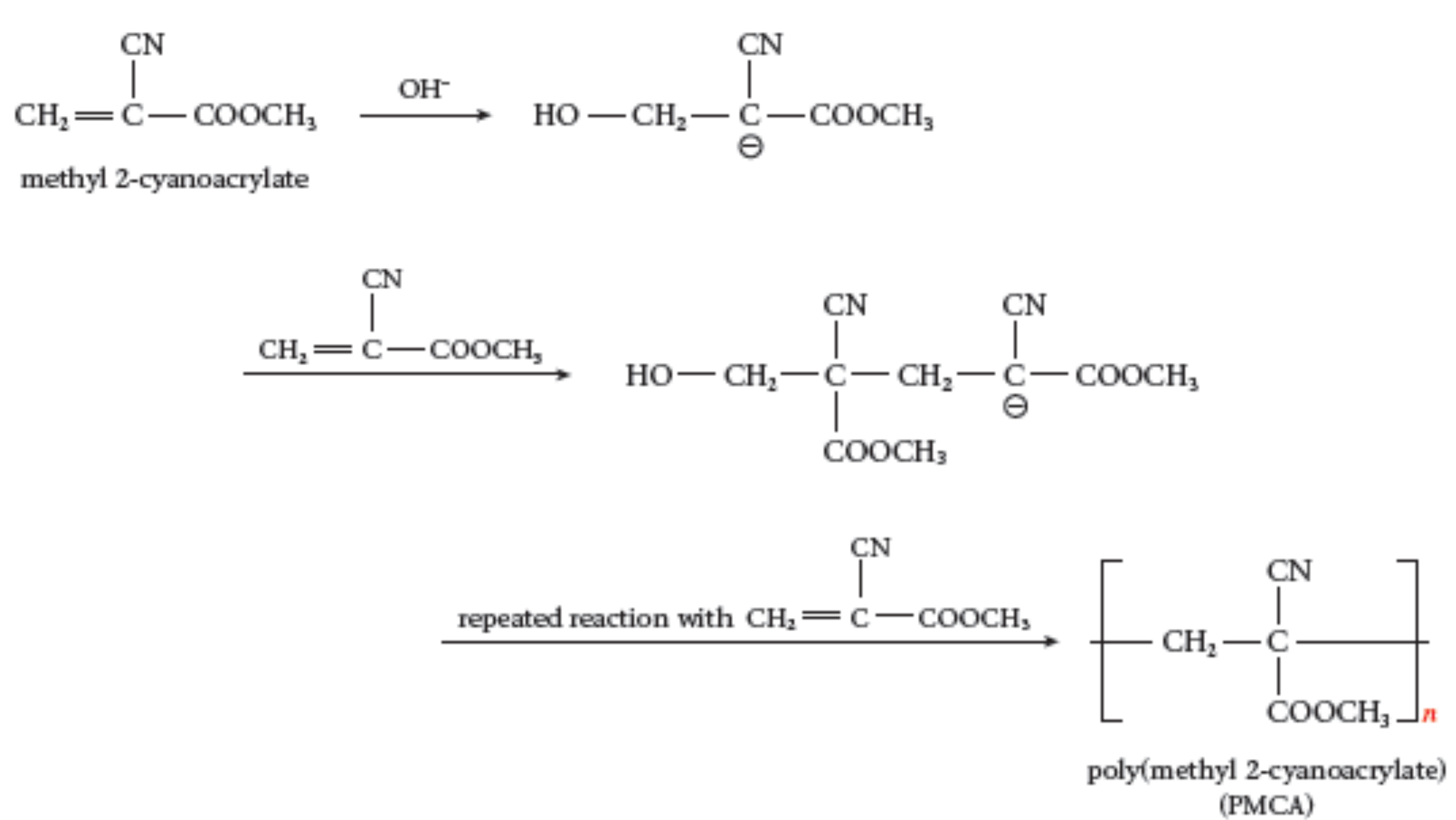
Polymerisation of cyanoacrylate

- Cyanoacrylate can undergo a process called anionic polymerisation rapidly in the presence of water.
- The **cyanoacrylate (氰丙烯酯)** molecules link together to form long and strong polymer chains in between the two surfaces in contact.

- ‘Anionic’ specifically indicates the hydroxide ions here, which come from water. A cyanoacrylate molecule contains a carbon-carbon double bond. Upon reaction with the hydroxide ion, an anion is formed.
- The anion formed then bonds with another cyanoacrylate molecule. This reaction forms another anion, which can then bond with another cyanoacrylate molecule. The reaction continues.
- This polymerisation takes place within seconds to give you the polycyanoacrylate, poly(methyl 2-cyanoacrylate) or simply PMCA

47.9 Cyanoacrylates (Superglue) (p.21)

Methyl 2-cyanoacrylate undergoes anionic polymerisation to give poly(methyl 2-cyanoacrylate)



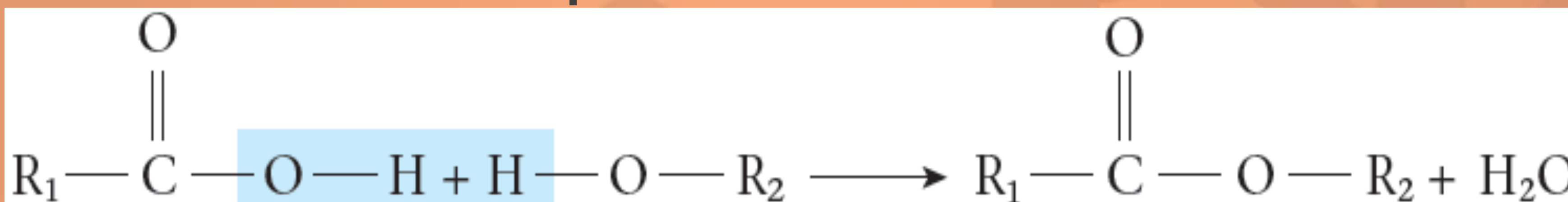
47.9 Cyanoacrylates (Superglue) (p.21)

Advantages and limitations of Superglue

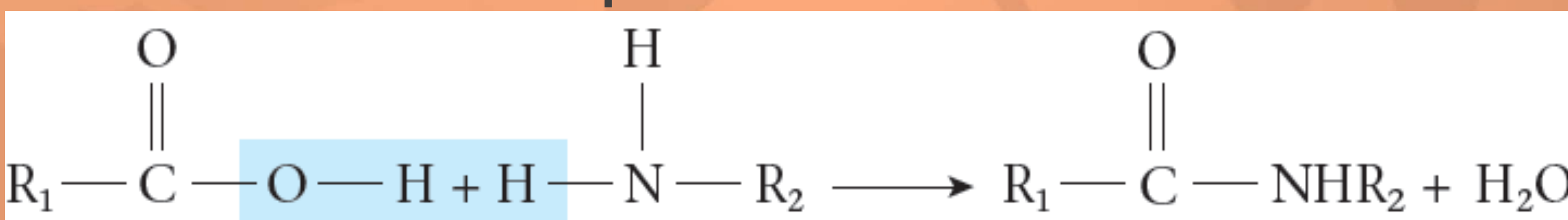
- Superglue dries very quickly, which means there is usually no need to clamp materials together for a long time. It is also extremely strong. It is usually impossible to reposition the materials being glued once the glue has been applied. The glue can be easily dissolved with the help of propanone.
- The human skin is constantly respiring and generates a layer of moisture, creating conditions for the cyanoacrylate to polymerise.
- To increase the usable life of your Superglue, always put back the cap for the glue after use. This prevents moisture in the air that can cause the cyanoacrylate to polymerise. Keeping the Superglue in an air-tight container also helps to extend its usable life.

47.10 Condensation polymerisation (p.23)

- The monomer molecules takes place by a condensation reaction with the elimination of a small molecule like water (HCl and NH_3) are called **condensation polymerisation(縮合聚合作用)**.
- **Ester formation example**



- **Amide formation example**

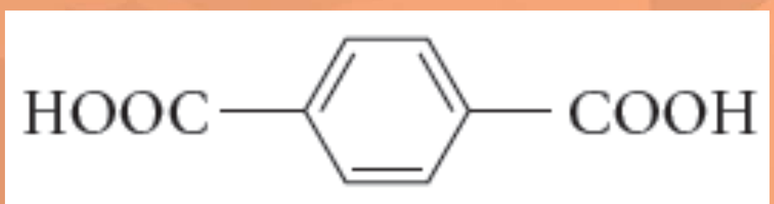


- The condensation can continue to give a polymer if the reactants are having **two functional groups** like diols, dicarboxylicacids

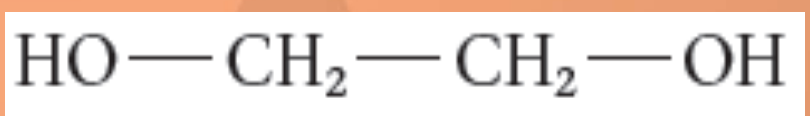
47.11 Polyesters (p.24)

- Polyesters are extremely important thermoplastics. They are condensation polymers made from the reaction of dicarboxylic acid with diol.

- **Poly(ethylene terephthalate) (PET) (聚對苯二甲酸乙二酯)** is the most commonly used polyester. It is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.



benzene-1,4-dicarboxylic acid (terephthalic acid)



ethane-1,2-diol (ethylene glycol)

47.11 Polyesters (p.24)

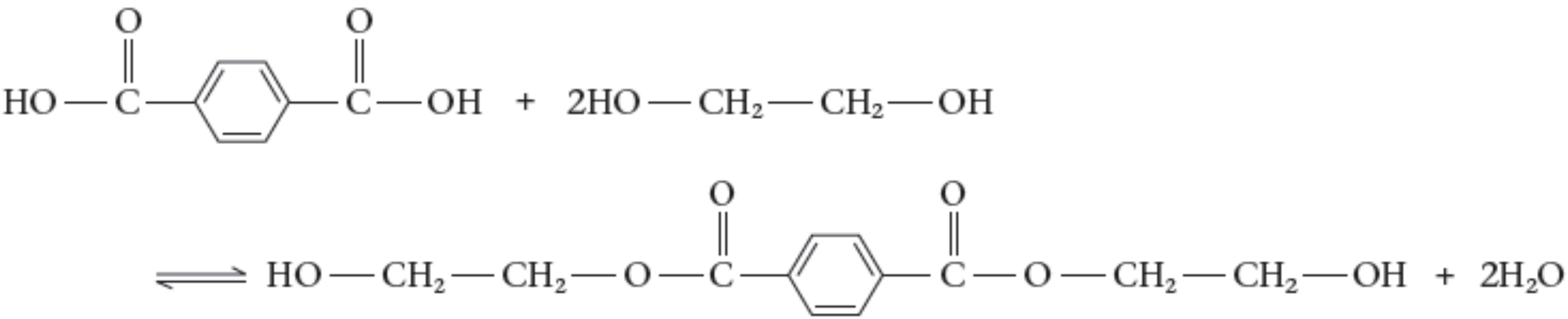
Manufacture of poly(ethylene terephthalate)

- The manufacture of poly(ethylene terephthalate) involves two different starting reactions.
- One is the **esterification reaction** in which ethane-1,2-diol reacts with benzene-1,4 dicarboxylic acid, producing an intermediate.
- In the other reaction, ethane-1,2-diol reacts with the dimethyl ester of benzene-1,4-dicarboxylic acid. This process is known as **transesterification (酯基轉移作用)**, in which one alcohol (ethane-1,2-diol) exchanges for another (methanol).

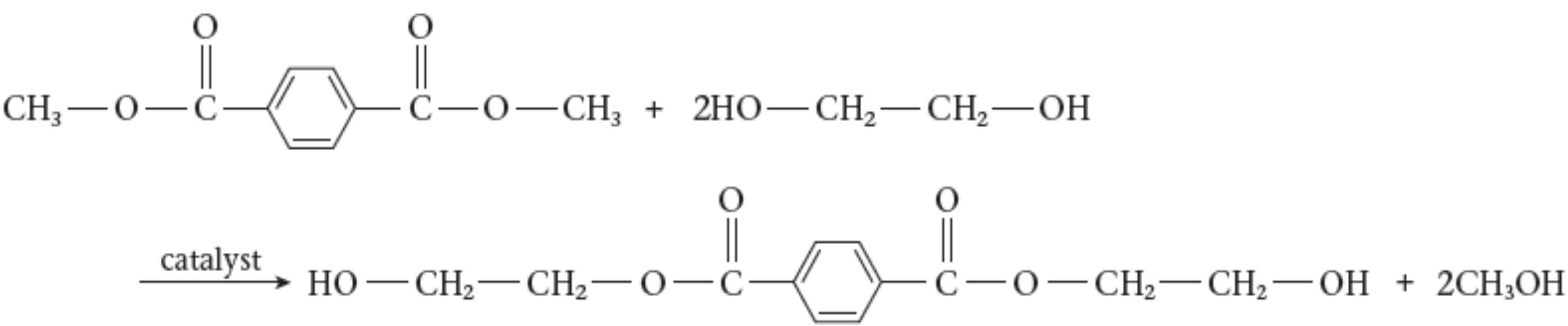
47.11 Polyesters (p.24)

Manufacture of poly(ethylene terephthalate)

Esterification reaction

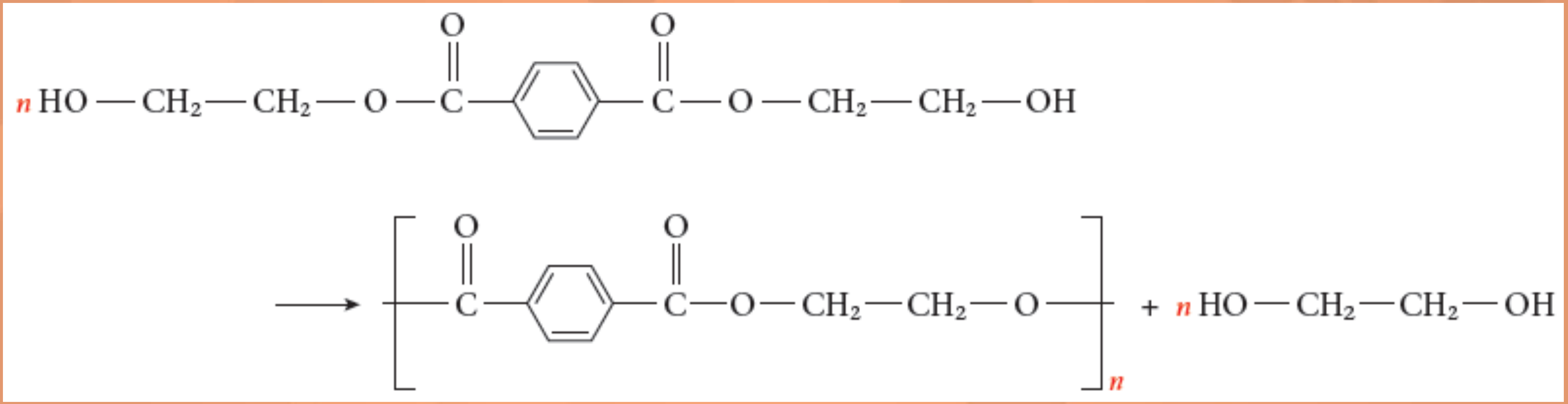


Transesterification reaction



47.11 Polyesters (p.24)

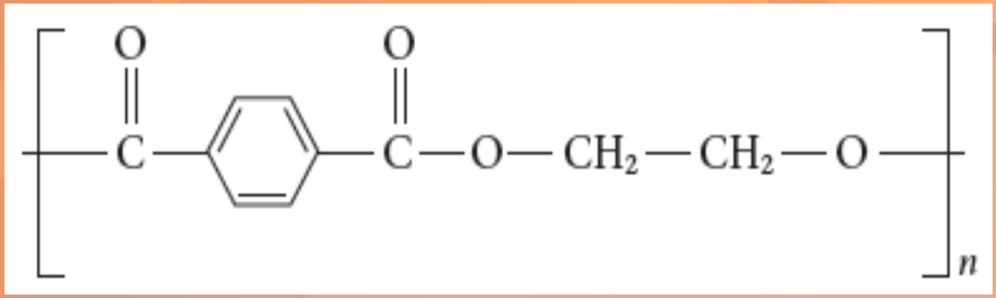
- The intermediate then undergoes polycondensation with the elimination of ethane-1,2-diol.



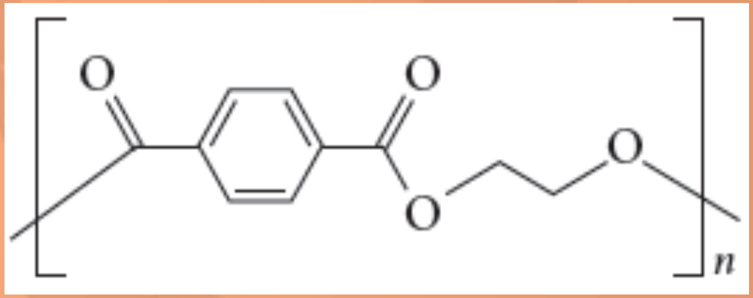
47.11 Polyesters (p.24)

- This process requires a catalyst, and is carried out at high temperatures (260–300 °C). Low pressures are used to favour product formation. Ethane-1,2-diol is recycled.

- The structure of poly(ethylene terephthalate) can be written as:



or



- Poly(ethylene terephthalate) contains ester linkages (–COO–).
- To form a condensation polymer, two functional groups are required on each monomer.

47.11 Polyesters (p.24)

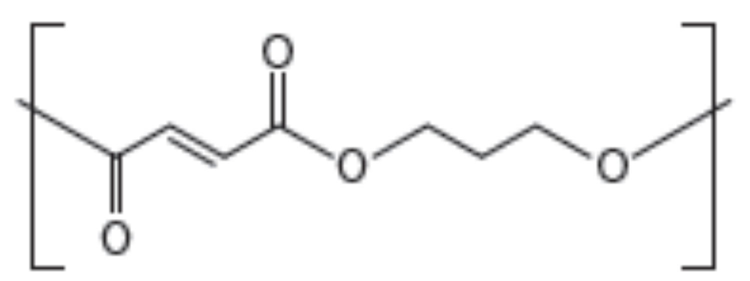
Uses of poly(ethylene terephthalate)

- To produce a fibre, small PET granules are melted and squeezed through fine holes and the resulting filaments spun to form a fibre.
- This fibre is widely used in clothing either alone or in blends with other natural fibres, principally cotton. It is also used for filling **anoraks (厚夾克)** and **bedding duvets (羽絨被)** to give good heat insulation.
- The polyester can be made into thin films which can be used in food packaging, audio and video tapes, electrical insulation, and X-ray films.
- A newer use of poly(ethylene terephthalate) is for packaging, such as for bottling carbonated drinks and water. The polyester has a great strength and a good chemical resistance. It also possesses good gas and moisture barrier properties.

47.11 Polyesters (p.24)

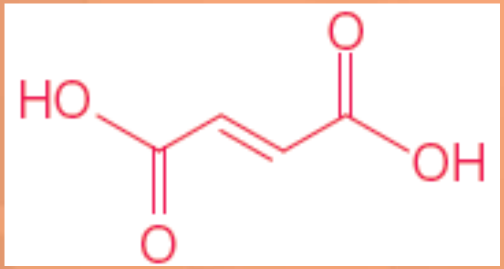
Practice 47.3

1) The repeating unit of a polyester is shown below:



a) Name this type of polymer. Condensation polymer

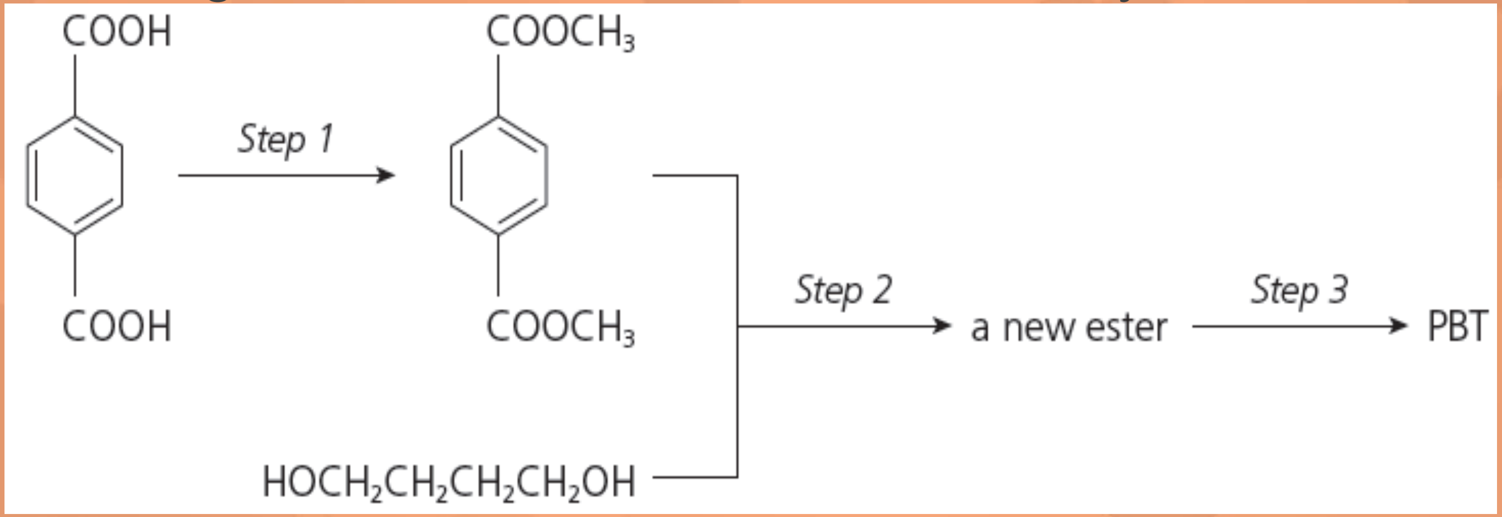
b) Draw the structures of monomers of this polyester.



47.11 Polyesters (p.24)

Practice 47.3

2) Poly(butylene terephthalate) (PBT) is a polyester used in making products in the automotive, electrical and electronics sectors. The flow diagram below shows a route for the synthesis of PBT.



a) Give the reagent(s) and conditions for *Step 1*.

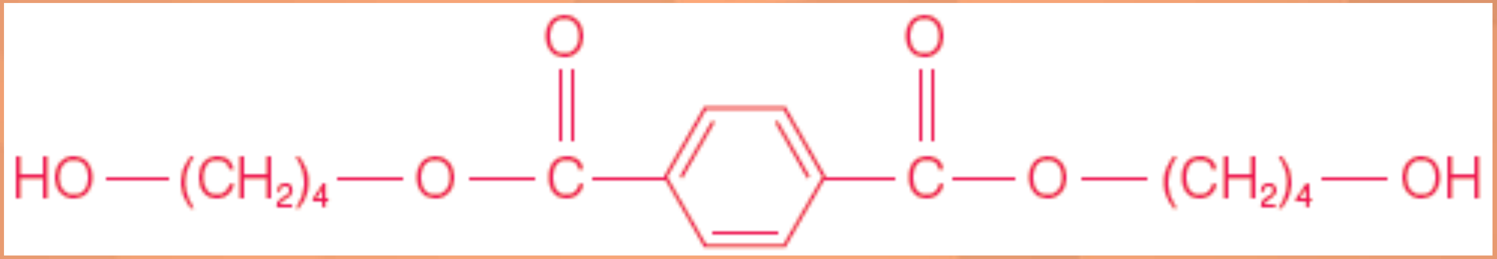
CH_3OH in the presence of concentrated sulphuric acid, heat

47.11 Polyesters (p.24)

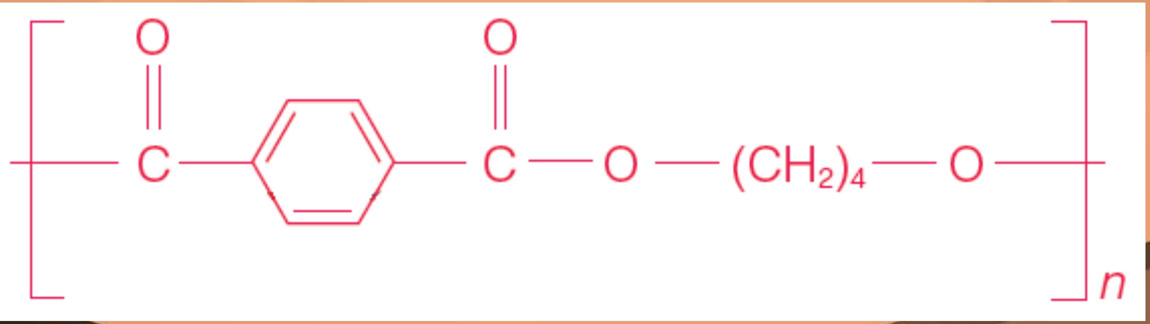
Practice 47.3

2b) Draw the structures of
 i) the new ester formed in *Step 2*; and
 ii) PBT.

bi)



bii)



47.12 Nylons (p.28)

- **Nylons(尼龍)** refers to the group of synthetic polymers known as polyamides. They are condensation polymers made from the reaction of a diamine and a carboxylic acid. They are thermoplastics because there is NO cross-link between polymer chains.

- There are different types of nylons, for example nylon-6,6 and nylon-6,10. The type of nylon depends on the number of carbon atoms in the monomers used. If the diamine used contains six carbon atoms and the dicarboxylic acid contains a chain of ten carbon atoms, then the resulting nylon is referred to as nylon-6,10.

47.12 Nylons (p.28)

Making nylon-6,6 in industry

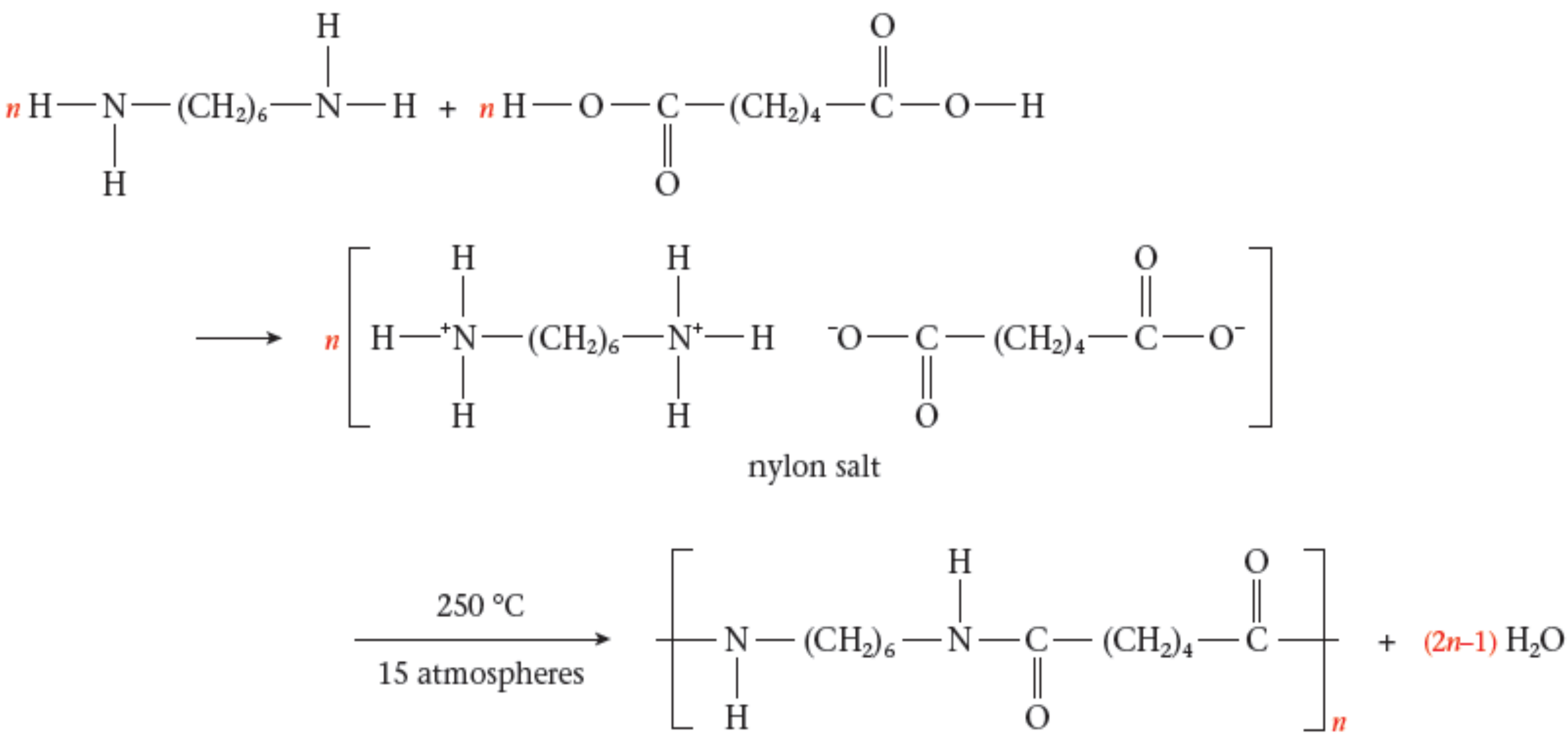
- Nylon-6,6 is made from the two monomers shown below, each of which contains six carbon atoms in their molecules.

Hexane-1,6-diamine: $H_2N—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—NH_2$

Hexanedioic acid: $HOOC—CH_2—CH_2—CH_2—CH_2—COOH$

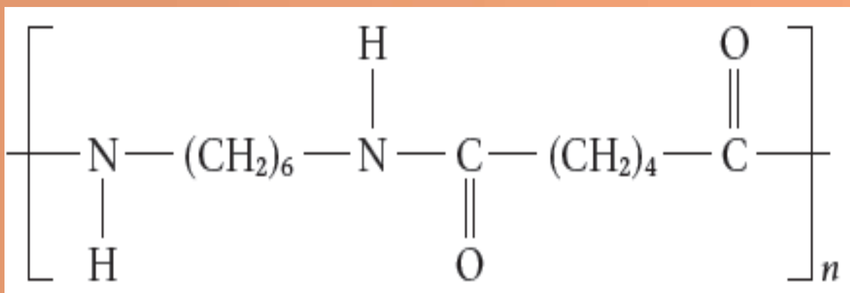
- In the manufacture of nylon-6,6, hexane-1,6-diamine and hexanedioic acid are dissolved in aqueous ethanol where they react to form a salt called nylon salt.
- Nylon salt is then heated to 250 °C where pressure rises to about 15 atmospheres. Under these conditions, $–NH_3^+$ groups from the diamine and $–COO^-$ groups from the dicarboxylic acid react with loss of water to form **amide linkages.(酰胺鍵合)**.

47.12 Nylons (p.28)



47.12 Nylons (p.28)

The structure of nylon-6,6 can be written as:



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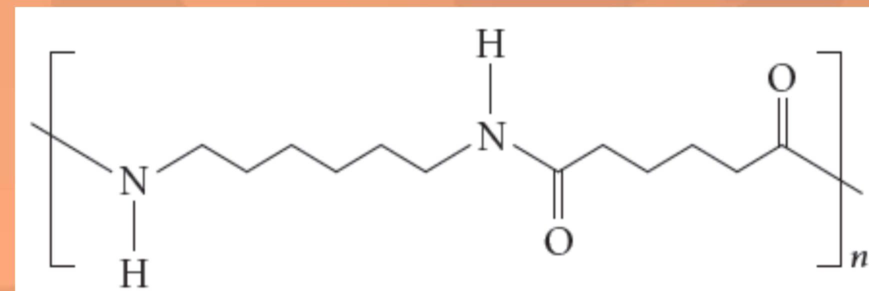
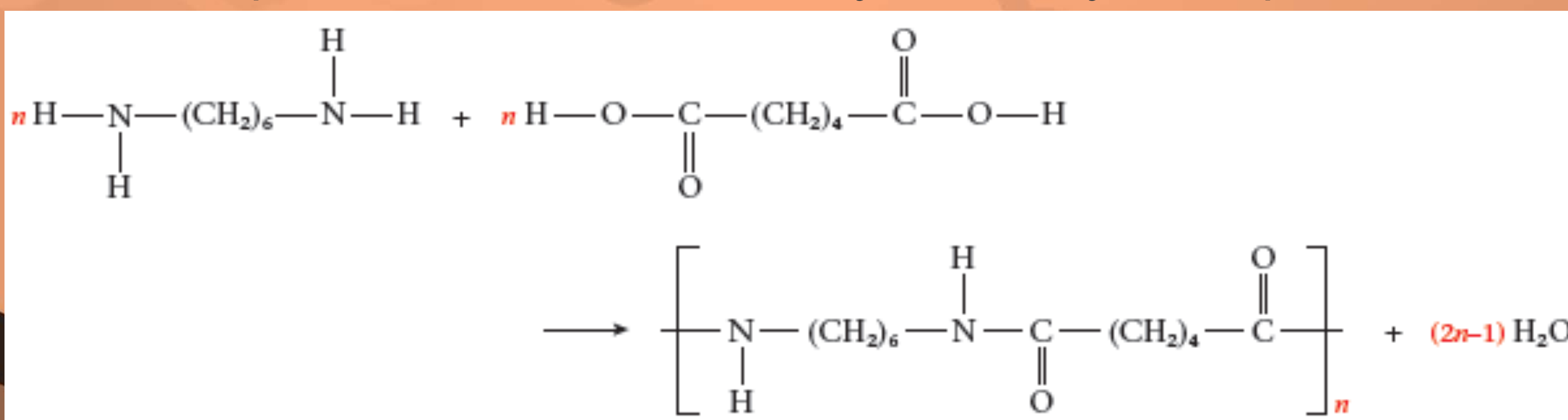


Nylon-6,6 contains amide linkages (–CONH–).

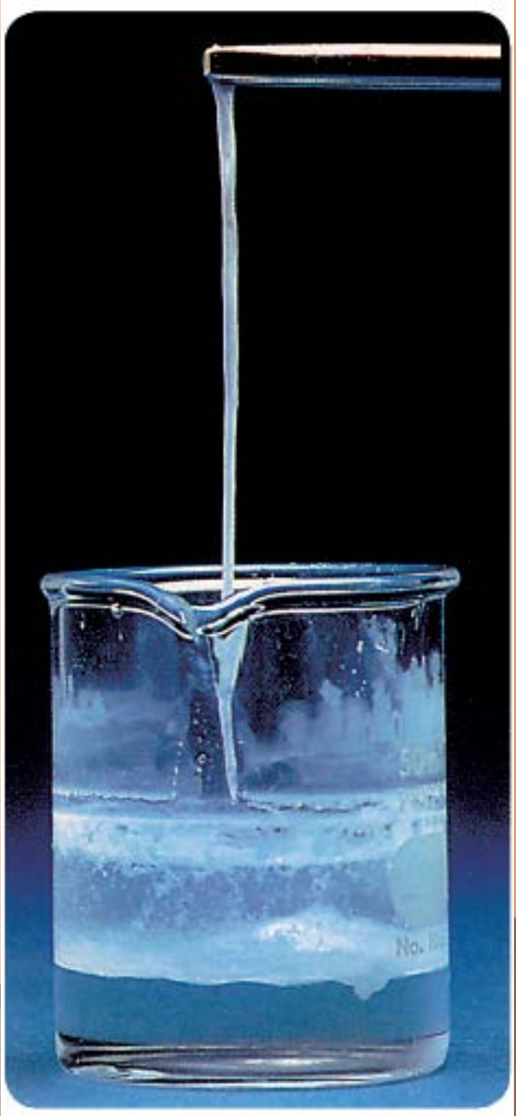
You can represent the formation of nylon-6,6 by the equation below:



47.12 Nylons (p.28)

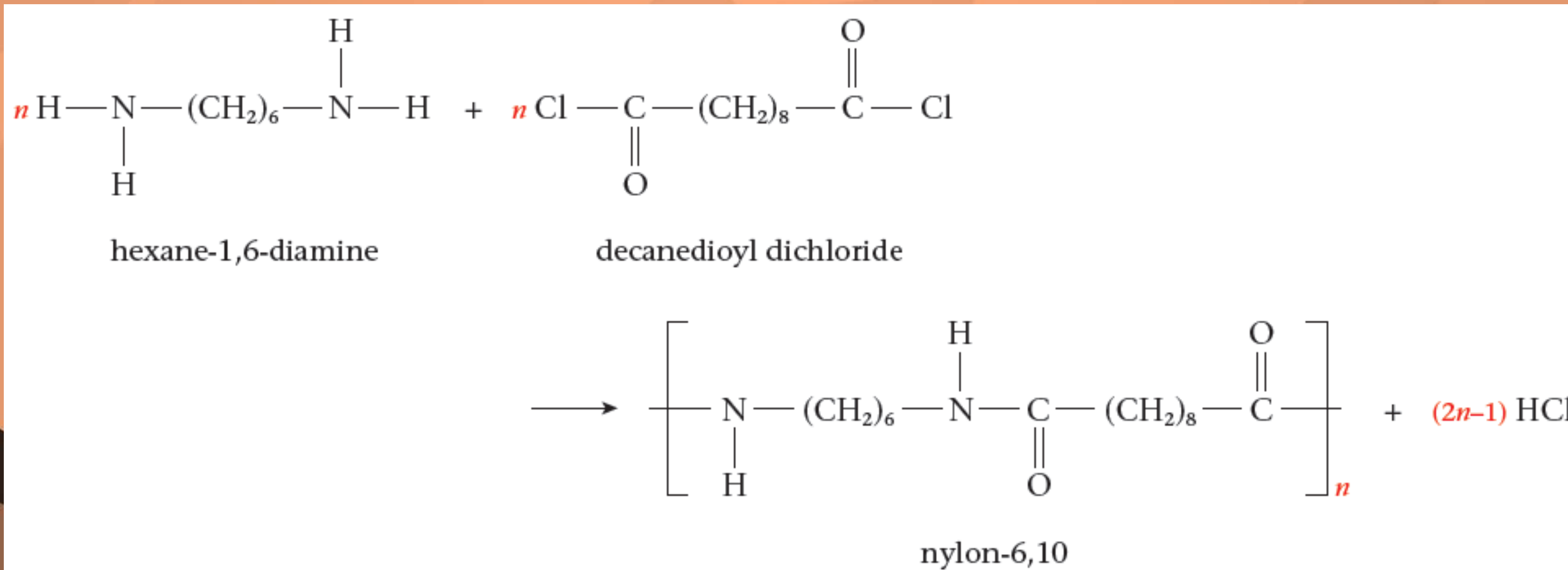
Preparing nylon in the laboratory

- When nylon is prepared by the reaction between a diamine and a dicarboxylic acid, the reaction is actually quite slow. For a demonstration in the laboratory this can be speeded up by reacting a chloride derivative of the acid with a diamine. In this case, the condensation reaction is much faster and hydrogen chloride is eliminated between the monomers instead of water.



47.12 Nylons (p.28)

- To make nylon-6,10 in the laboratory, hexane-1,6-diamine is dissolved in sodium carbonate solution, and a solution of decanedioyl dichloride in cyclohexane is layered carefully on top of the aqueous solution. The reaction takes place at the interface between the two immiscible solutions and the raw nylon can be spooled away as a nylon rope.



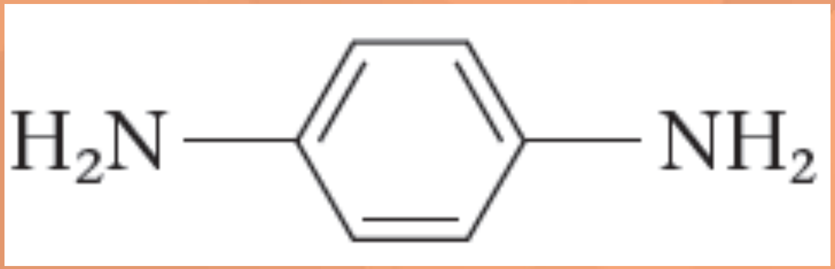
47.12 Nylons (p.28)

Uses of nylons

- Nylon fibres are strong while very lightweight. These properties lead to a wide variety of uses, such as fishing nets and ropes. Nylon films are used for food packaging.
- Nylon is also used to make fabrics in textile industry. Nylon dries rather quickly and retains its shape rather well after laundering, which ensures longevity of the garment.
- Nylon finds many applications as replacements for metals, for example in car engine components. Nylon intake manifolds in engines for air distribution of the air/fuel mixture to cylinders are tough, corrosion resistant, light and cheap. The self-lubricating properties of nylon make it useful for gears and bearings.

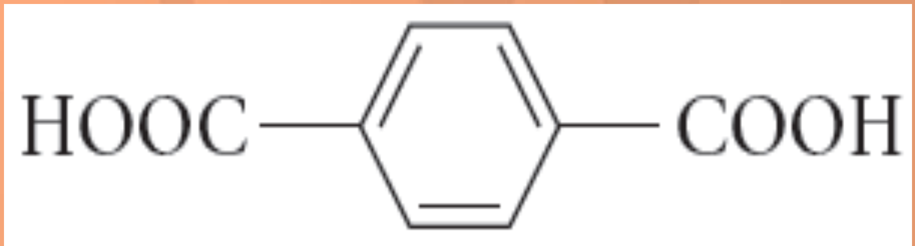
47.13 Kevlar (p.32)

- Kevlar is similar in structure to nylon-6,6 except that instead of the amide linkages joining chains of carbon atoms together, they join benzene rings. The two monomers of Kevlar are 1,4-diaminobenzene and benzene-1,4-dicarboxylic acid. **Kevlar(凱庫勒)** is a thermoplastic.



1,4-diaminobenzene

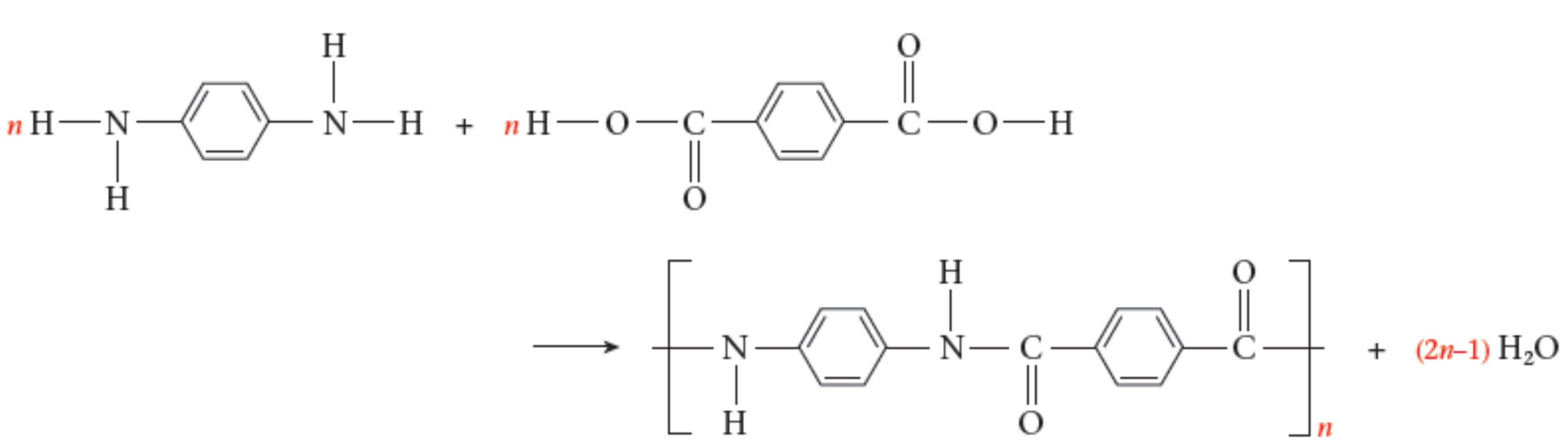
or



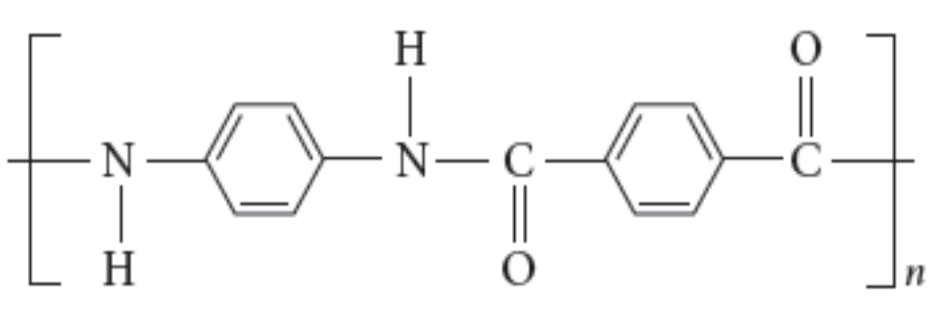
Benzene-1,4-dicarboxylic acid

47.13 Kevlar (p.32)

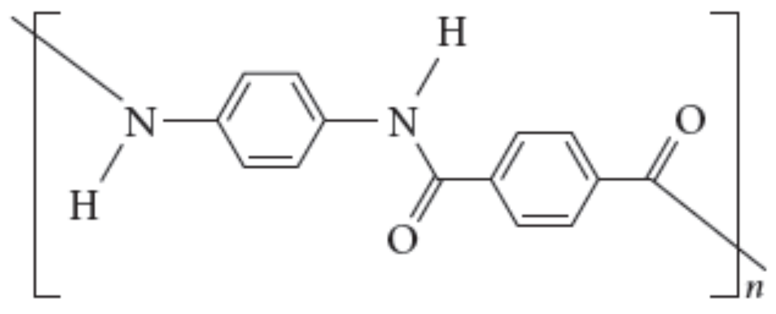
The formation of Kevlar by the equation below



The structure of Kevlar can be written as:



or



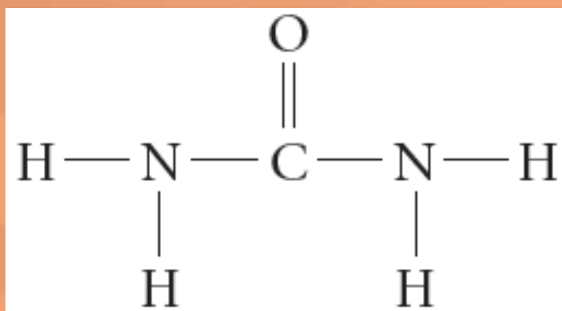
47.13 Kevlar (p.32)

Use of Kevlar

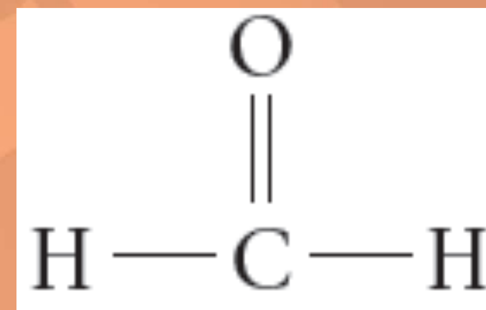
- Kevlar is very strong but relatively light. It is about five times as strong as steel on an equal weight basis.
- Unlike most synthetic polymers, Kevlar does not melt. It is reasonably good at withstanding temperatures and decomposes only at about 450 °C. Kevlar can resist attacks from many different chemicals.
- Kevlar is used in a huge range of demanding applications ranging from deep sea umbilical lines and premium sports goods to high performance structural composites in boat hulls, aircraft components and high-performance cars, also used to make bullet-proof vests, ropes and fire-protective clothing.

47.14 Urea-methanal (p.33)

- Urea-methanal is a thermosetting plastic formed from the two monomers shown below:

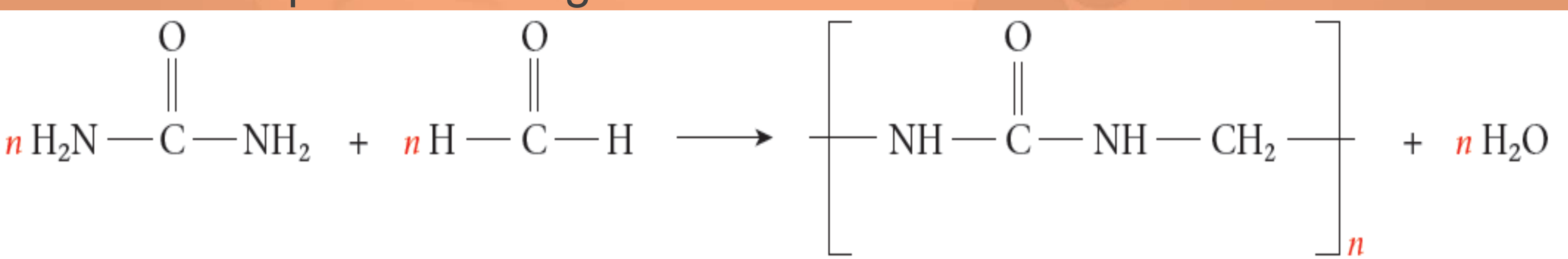


Urea (carbamide)



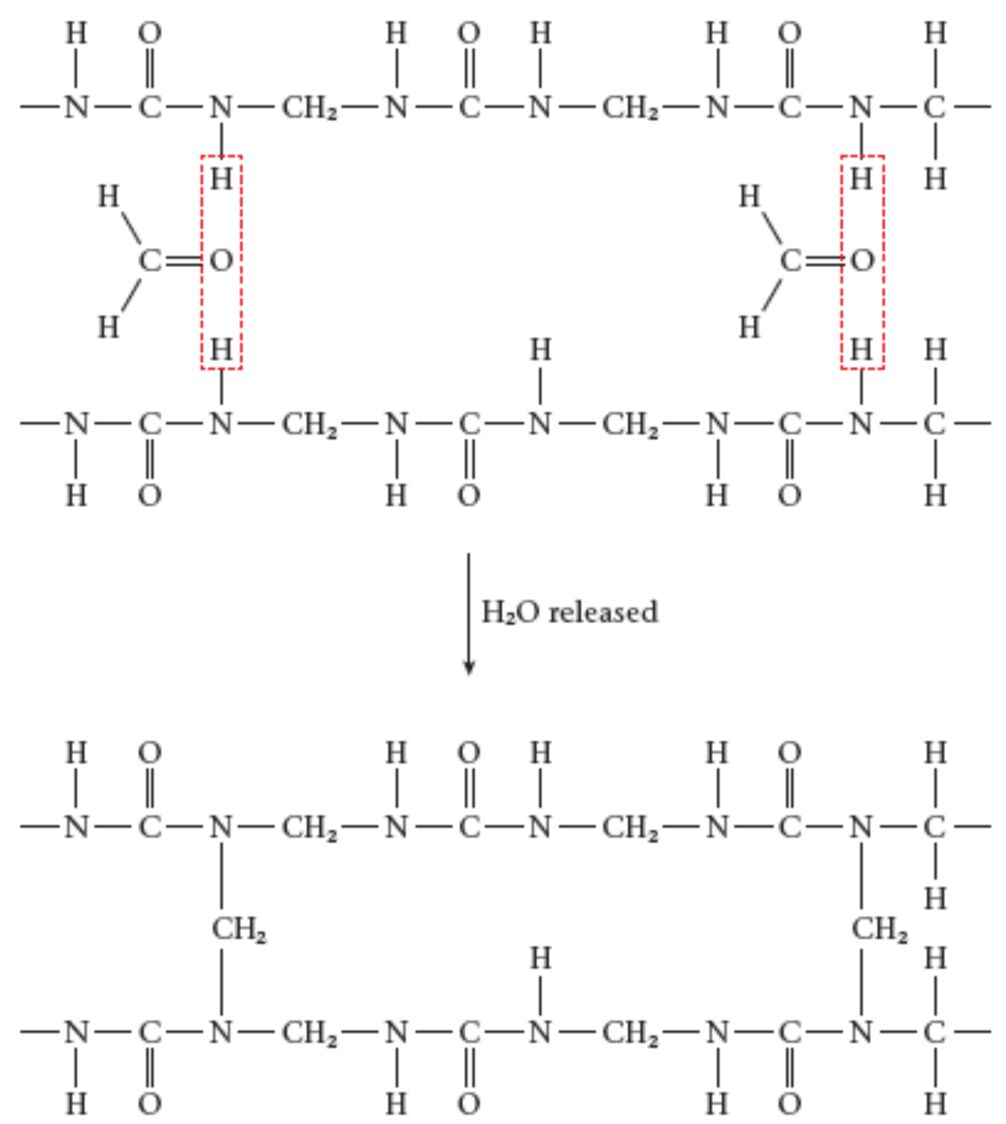
Methanal

- Heating urea and methanal in the presence of ammonia produces urea-methanal. The initial condensation reaction between urea and methanal produces long chain molecules.



47.14 Urea-methanal (p.33)

- If there are excess methanal molecules, cross-links (covalent bonds) can form between the polymer chains, resulting in a thermosetting plastic.



47.14 Urea-methanal (p.33)

Uses of urea-methanal

- As urea-methanal has a giant covalent network structure, it does not melt upon heating.
- Urea-methanal is hard and strong. It is an excellent electrical insulator and also resistant to chemical attacks.

Urea-methanal can be used to make
- electric switches;
- lamp fittings;
- handles of kitchenware (e.g. pots and pans).

Preparing Perspex *Ref.*

47.14 Urea-methanal (p.33)

Practice 47.4

Differentiate between thermoplastics and thermosetting plastics.

Thermoplastics	Thermosetting plastics
They go soft and melt on heating	They do not go soft on heating
They are less brittle	They are more brittle
They have linear structures	They have three-dimensional cross-linked structures

47.15 Deductions involving structures of polymers and monomers (p.36)

1. Deducing the type of polymerisation for a given monomer or a pair of monomers;
2. Deducing the repeating unit of a polymer obtained from a given monomer or a pair of monomers;
3. Deducing the type of polymerisation from a given part of a polymer chain;
4. Deducing the monomer(s) from a given part of a polymer chain.

47.15 Deductions involving structures of polymers and monomers (p.36)

1. Deducing the type of polymerisation for given monomer(s)

a) Addition polymerisation

- A monomer containing the carbon-carbon double bond is likely to undergo addition polymerisation. Many addition polymers are made using one particular monomer, for example, polypropene from propene.

- You might be given two different compounds containing carboncarbon double bonds as a pair of monomers, for example, $H_2C{=}CH_2$ and $H_2C{=}CHCOOH$. They will still undergo addition polymerization to form a copolymer.

47.15 Deductions involving structures of polymers and monomers (p.36)

b) Condensation polymerisation

- Monomers undergoing condensation polymerisation contain two different functional groups that will react with each other. These two functional groups can be in the same monomer, or at either end of two different monomers, as in the monomers of nylon-6,6.

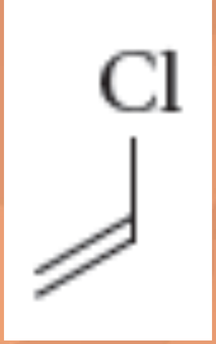
- Examples of functional groups involved in condensation polymerisation included:
  - –COOH groups in a dicarboxylic acid and –OH groups in a diol;
  - –COCl groups in the chloride derivative of a dicarboxylic acid and –OH groups in a diol;
  - –COOH groups in a dicarboxylic acid and $–NH_2$ groups in a diamine.

47.15 Deductions involving structures of polymers and monomers (p.36)

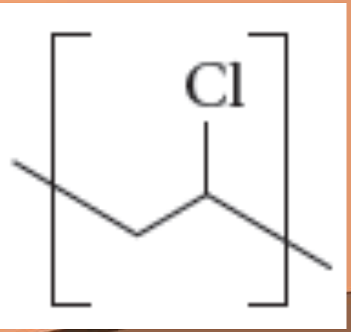
2. Deducing the repeating unit of a polymer obtained from given monomer (s)

a) Addition polymerisation

- Given a monomer with a carbon-carbon double bond, simply turn the carbon-carbon double bond into a carbon-carbon single bond and show the bonds that will continue on either side of the two carbon atoms. This gives the repeating unit.
- For example, the monomer of polyvinyl chloride and the repeating unit are shown below.



monomer of polyvinyl chloride

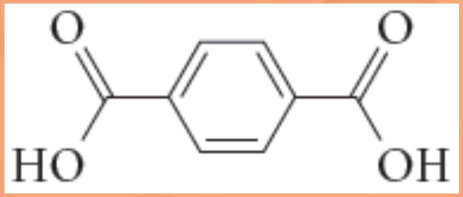


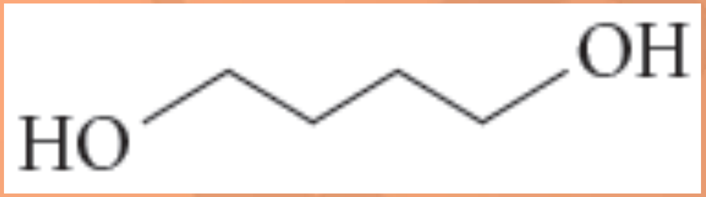
repeating unit of polyvinyl chloride

47.15 Deductions involving structures of polymers and monomers (p.36)

b) Condensation polymerisation

- In condensation polymerisation, the monomers join together and small molecules get lost.
- For example, a polyester is made by a reaction involving a dicarboxylic acid with two –COOH groups and a diol with two –OH groups.

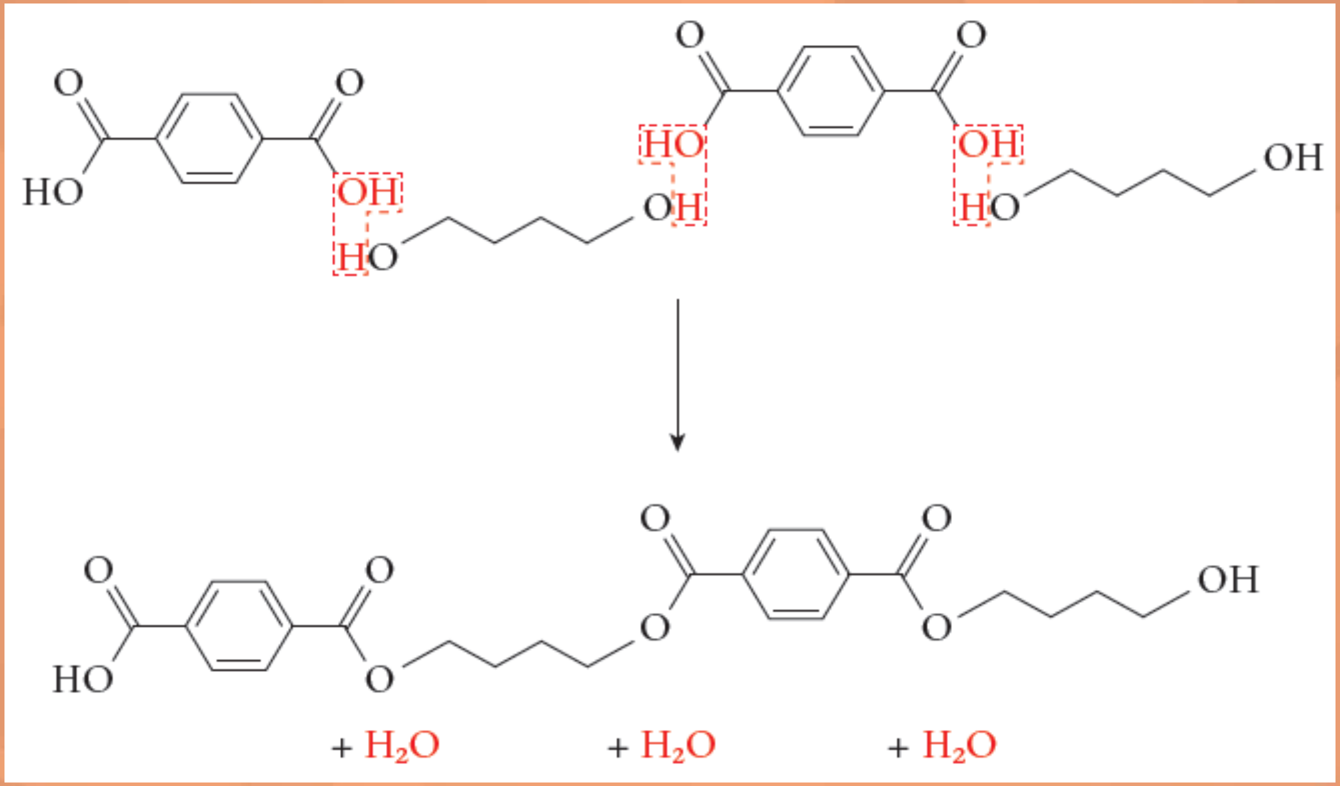




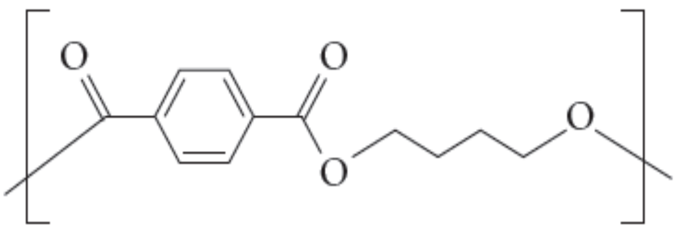
- Imagine lining molecules of these monomers up alternately and condensation reactions occur between the –COOH groups of the dicarboxylic acid molecules and the –OH groups of the diol molecules to form ester linkages.

47.15 Deductions involving structures of polymers and monomers (p.36)

b) Condensation polymerisation



The repeating unit of the polyester is:

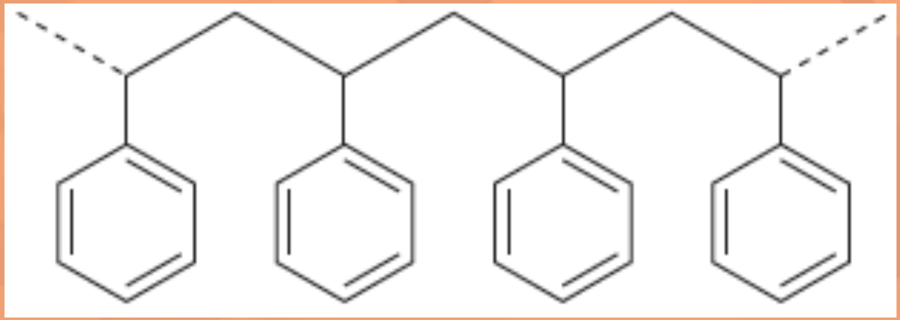


47.15 Deductions involving structures of polymers and monomers (p.36)

3. Deducing the type of polymerisation from a given part of a polymer chain

a) Addition polymerisation

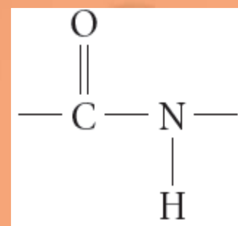
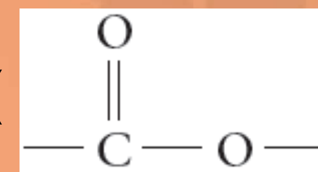
- Polymers resulting from addition polymerisation will have no functional groups in the chain of carbon atoms that forms the ‘backbone’ of the polymer. Polystyrene is an example.

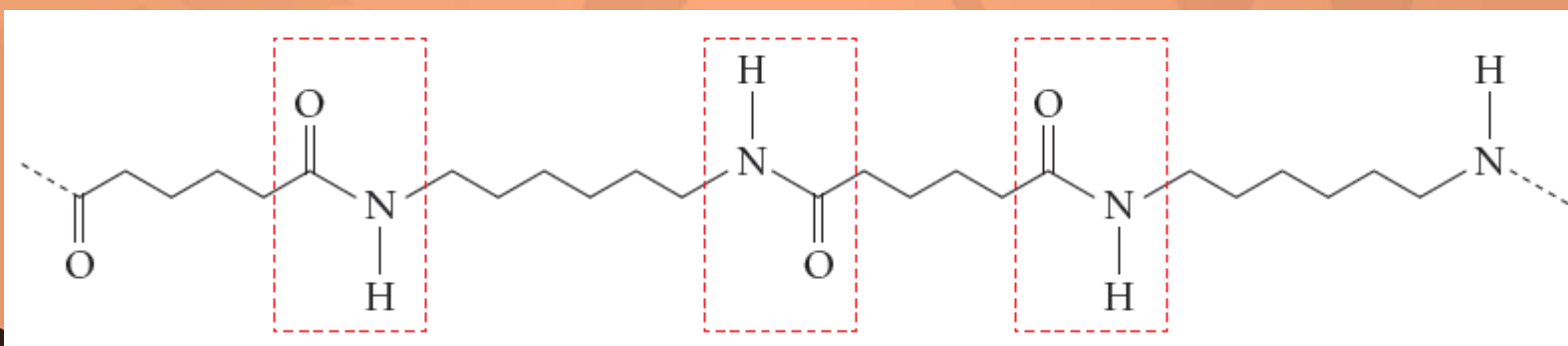


A part of a polymer chain of polystyrene

47.15 Deductions involving structures of polymers and monomers (p.36)

b) Condensation polymerisation

Polymers resulting from condensation polymerisation will have amide linkages() or ester linkages () in the 'backbone' of the polymer chain. Nylon-6,6 is an example.



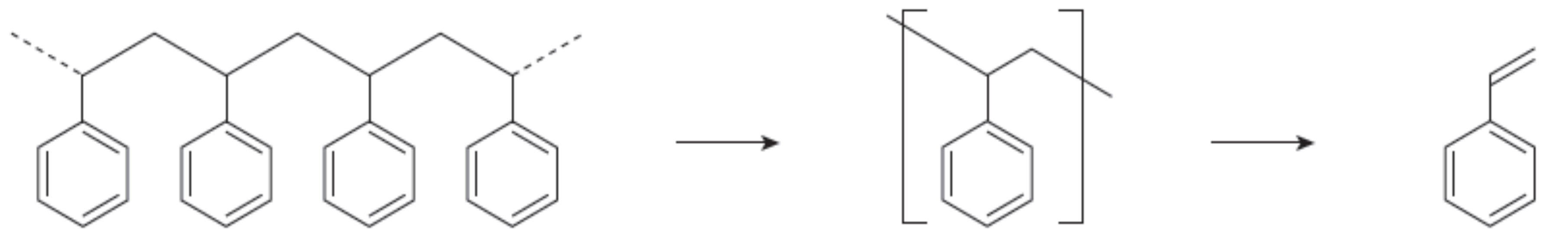
A part of a polymer chain of nylon-6,6

47.15 Deductions involving structures of polymers and monomers (p.36)

4. Deducing the monomer(s) from a given part of a polymer chain

a) Addition polymerisation

- With an addition polymer, identify the repeating unit — this will be two carbon atoms in the chain and the four atoms or groups joined to them. Put the carbon-carbon double bond back so as to obtain the monomer.

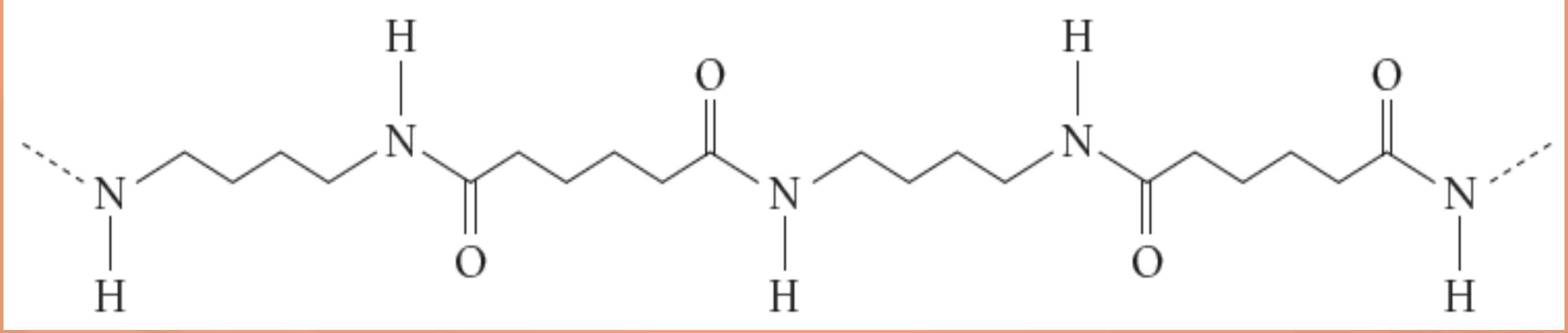


A part of polymer chain of an addition polymer (polystyrene) | Repeating unit | Monomer

47.15 Deductions involving structures of polymers and monomers (p.36)

b) Condensation polymerisation

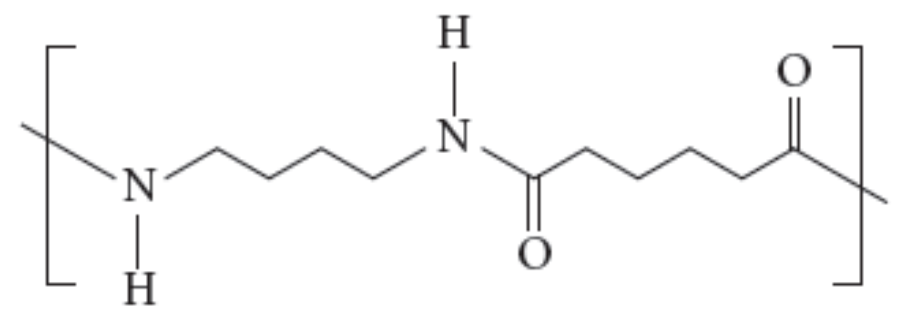
- With a condensation polymer, identify the repeating unit. Identify the atoms from the small molecules given off in the polymerization reaction and replace them on the functional groups in the monomers.



A part of a polymer chain of a condensation polymer

47.15 Deductions involving structures of polymers and monomers (p.36)

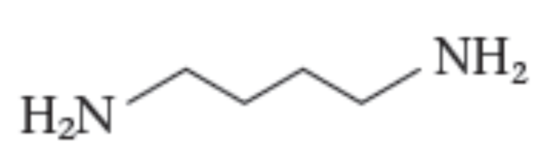
b) Condensation polymerisation



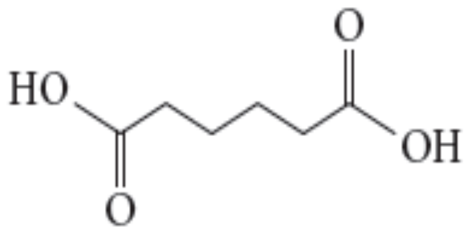
repeating unit

↓

monomers



and



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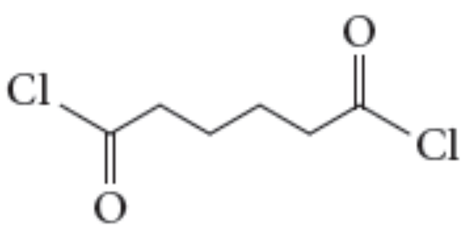
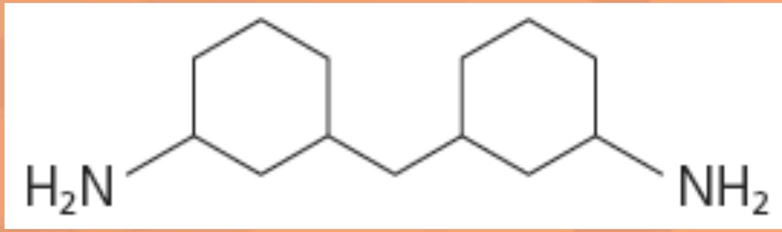
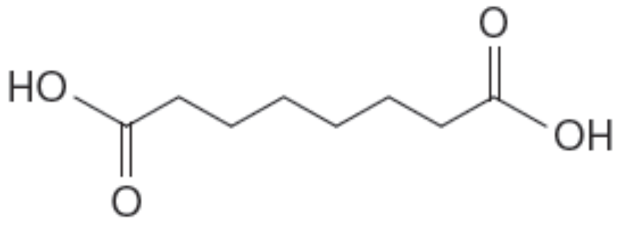


47.15 Deductions involving structures of polymers and monomers (p.36)

Practice 47.5

1) Quiana is a synthetic polymer that can be spun into a soft, silky fabric. The monomers used to make Quiana are shown below.

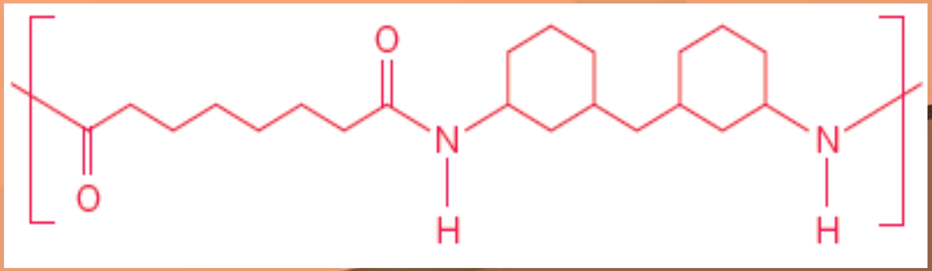




a) Name the type of polymerisation involved in the production of Quiana.

Condensation polymerisation

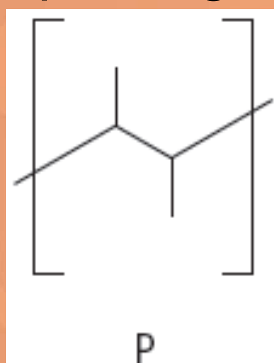
b) Draw the repeating unit of Quiana.

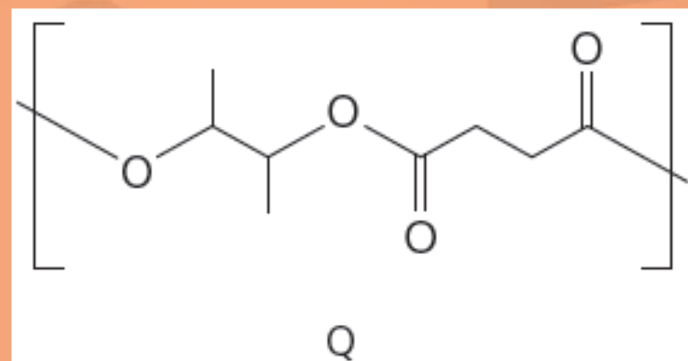


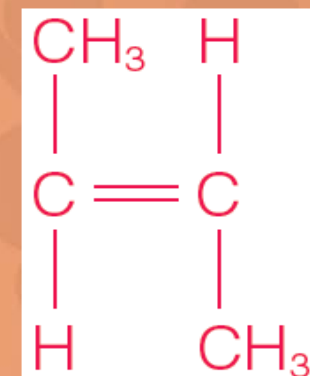
47.15 Deductions involving structures of polymers and monomers (p.36)

Practice 47.5

2) The repeating units of two polymers, P and Q are shown below.





aii) 

but-2-ene

a) i) Name the type of polymerisation involved when forming polymer P. ai) Addition polymerisation

ii) Draw the structure of monomer of polymer P. Name the monomer.

iii) State a structural characteristic of monomers which can undergo the type of polymerisation stated in (i).

aiii) The monomer molecule has C=C bond.

47.15 Deductions involving structures of polymers and monomers (p.36)

Practice 47.5 (Continued)

b) i) Name the type of polymerisation involved when forming polymer Q.

bi) Condensation polymerisation

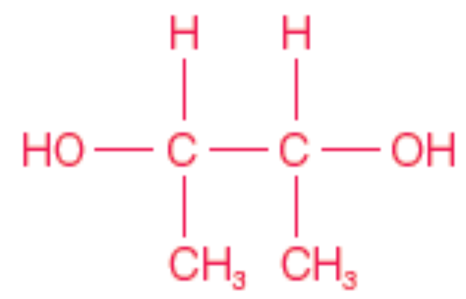
ii) Draw the structures of monomers of polymer Q. Name these two monomers.

biii) The monomer molecule has two functional groups.

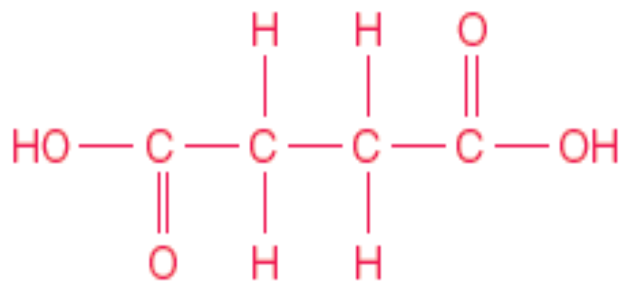
iii) State a structural characteristic of monomers which can undergo the type of polymerisation stated in (i).

bii)

butane-2,3-diol

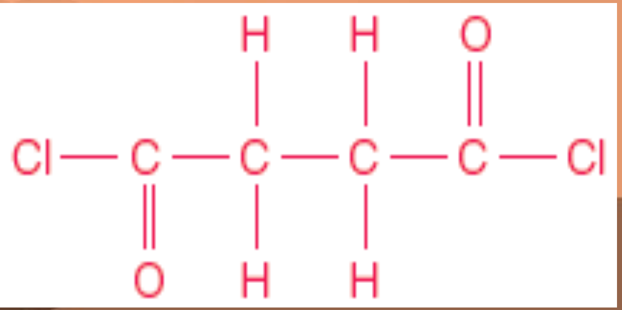


butanedioic acid



or

butanedioyl dichloride



Key terms (p.43)

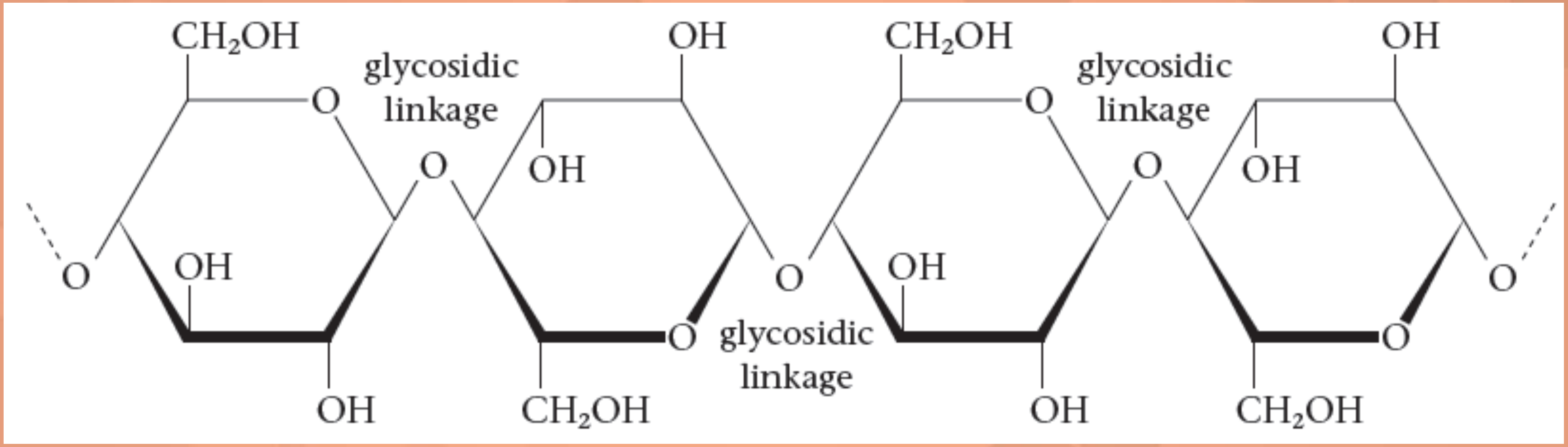
polymer	聚合物	ceramic	陶瓷
composite material	複合材料	cellulose	纖維素
glycosidic linkage	糖苷鍵合	chitin	甲殼素
thermoplastic	熱塑性塑膠	thermosetting plastic	熱固性塑膠
methyl methacrylate	甲基丙烯酸甲酯	cyanoacrylate	氰丙烯酯
condensation polymerisation	縮合聚合作用	poly(ethylene terephthalate)	聚對苯二甲酸乙二酯
transesterification	酯基轉移作用	nylon	尼龍
amide linkage	酰胺鍵合	Kevlar	凱庫勒
urea-methanal	脲甲醛		

Summary (p.44)

1. Materials are classified into four main categories: metals, polymers, ceramics and composite materials. Polymers may be natural or synthetic.

Summary (p.44)

2a) Cellulose is the most abundant natural polymer on Earth. It is an unbranched condensation polymer of β-glucose.



Summary (p.44)

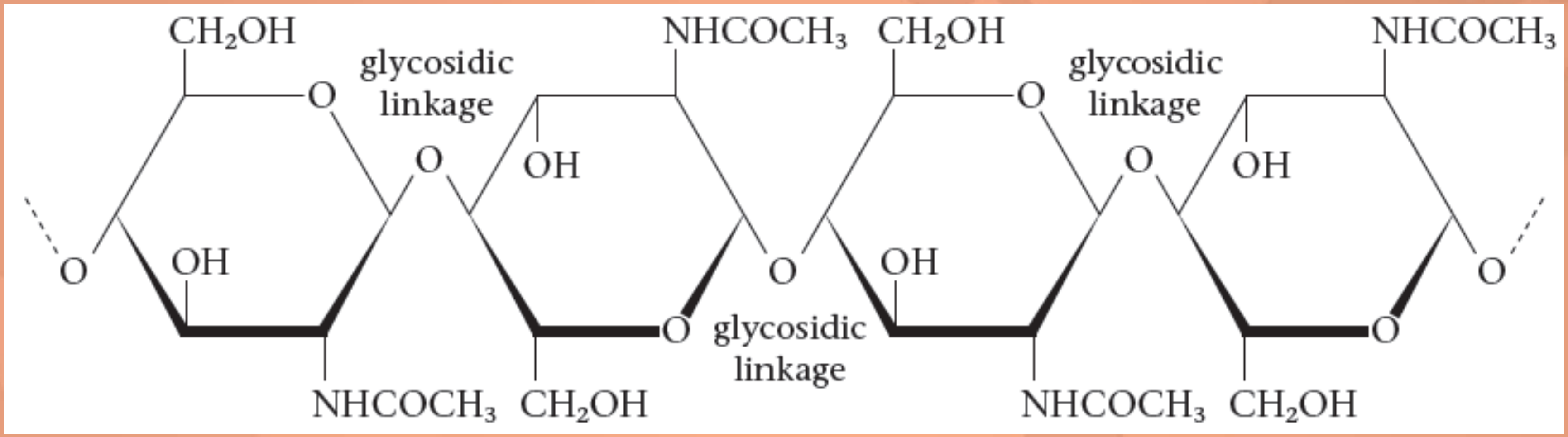
2b) Cellulose is insoluble in water. The –OH groups in cellulose molecules can form extensive intramolecular and intermolecular hydrogen bonding. Hence the –OH groups are less available to form hydrogen bonds with water molecules.

c) A cellulose molecule has a linear structure. The –OH groups of one molecule can form hydrogen bonds with –OH groups of other molecules lying parallel to it, this gives rise to the high strength of cellulose.

d) Cellulose is biodegradable.

Summary (p.44)

3a) Chitin is the second most abundant natural polymer on Earth.



b) The extensive intramolecular and intermolecular hydrogen bonding in chitin makes it hard and insoluble in water.

c) Chitin is also biodegradable.

Summary (p.44)

4. Thermoplastics and thermosetting plastics are synthetic polymers.

a) Thermoplastics soften and flow upon heating, and become hard again when cooled. This cycle can be repeated many times.

b) Thermosetting plastics become permanently hard during their formation, and do not soften upon heating.

Summary (p.44)

5.

Polymerisation

a reaction in which monomer molecules join together repeatedly to form polymer molecules

Addition polymerisation

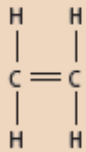
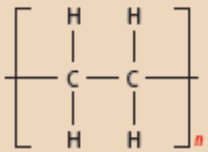
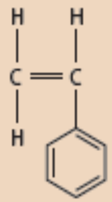
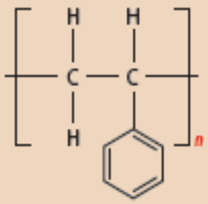
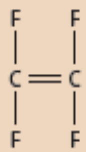
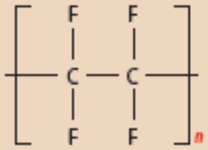
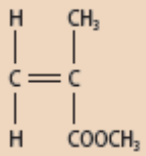
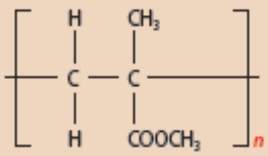
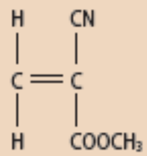
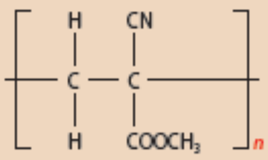
- monomers used are unsaturated compounds
- addition polymerisation occurs most frequently by a free radical mechanism

Condensation polymerisation

- small molecules are formed during the reaction
- each monomer molecule has two functional groups

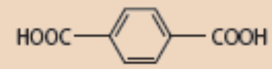
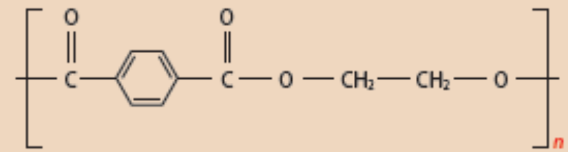
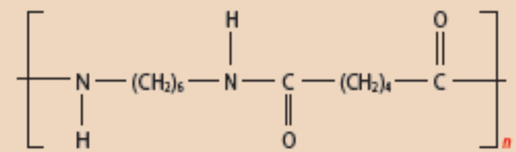
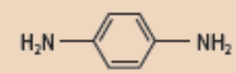
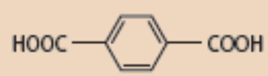
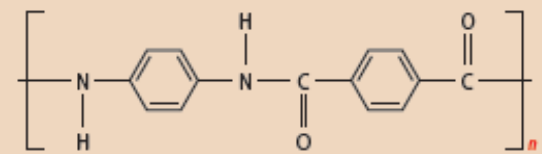
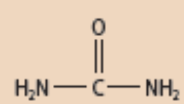
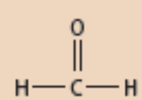
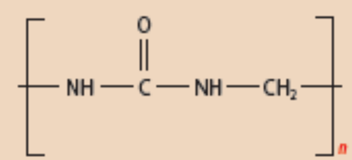
Summary (p.44)

6. The table below gives examples of addition polymers. All are thermoplastics.

Name	Monomer	Structure of polymer
Polythene (PE)		
Polystyrene (PS)		
Polytetrafluoroethene (PTFE)		
Polymethyl methacrylate (PMMA)		
Poly(methyl 2-cyanoacrylate) (PMCA)		

Summary (p.44)

7. The following table gives examples of condensation polymers.

Name	Monomers	Structure of polymer
Poly(ethylene terephthalate) (PET) (a thermoplastic)	 terephthalic acid $HO-CH_2-CH_2-OH$ ethylene glycol	
Nylon-6,6 (a thermoplastic)	$H_2N-(CH_2)_6-NH_2$ hexane-1,6-diamine $HOOC-(CH_2)_4-COOH$ hexanedioic acid	
Kevlar (a thermoplastic)	 1,4-diaminobenzene  benzene-1,4-dicarboxylic acid	
Urea-methanal (a thermosetting plastic)	 urea  methanal	

Unit Exercise (p.48)

Note: Questions are rated according to ascending level of difficulty (from 1 to 5):

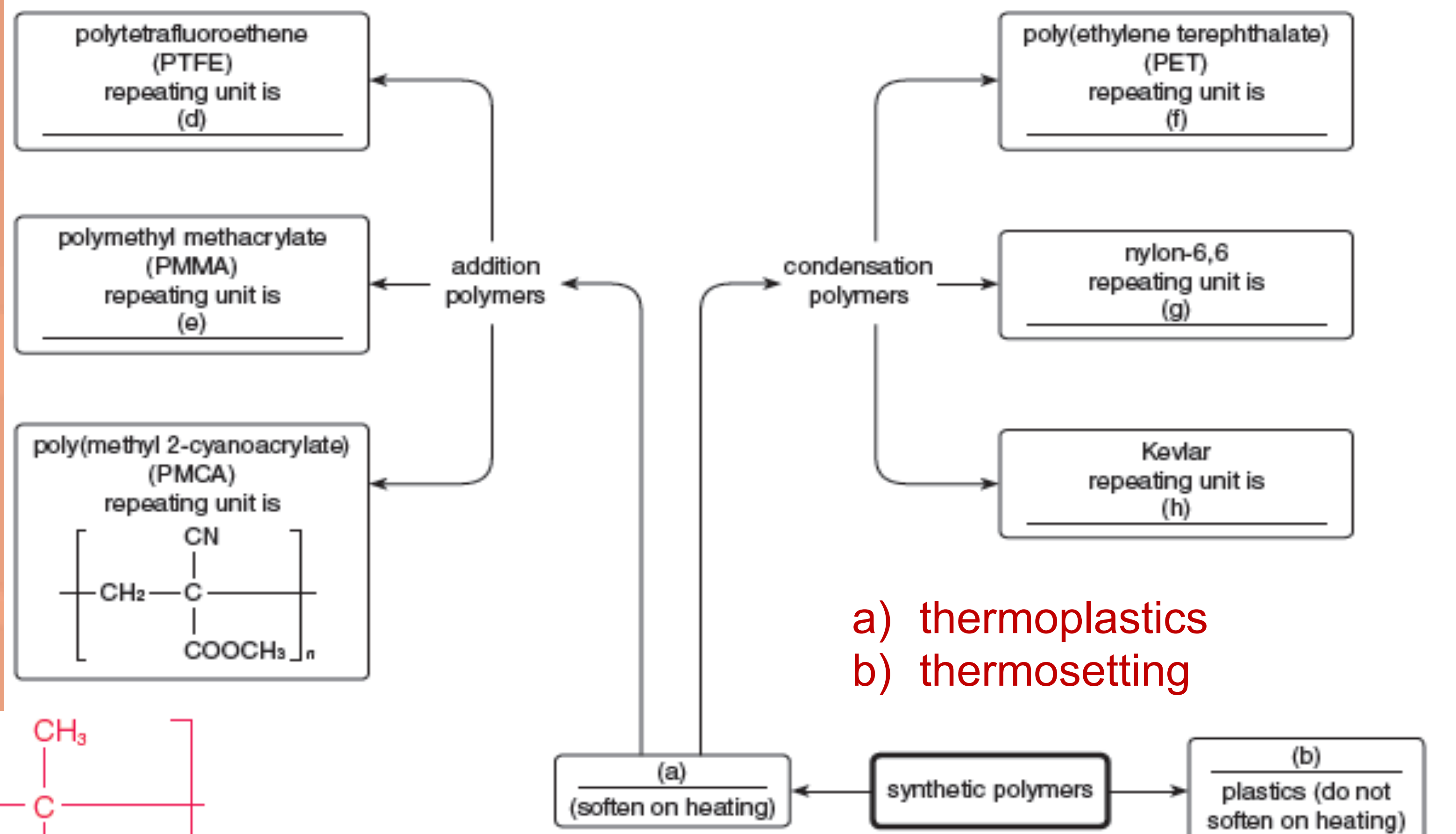
👍 **question targeted at level 3 and above;**
👍👍 **question targeted at level 4 and above;**
👍👍👍 **question targeted at level 5.**
‘ * ’ indicates 1 mark is given for effective communication.

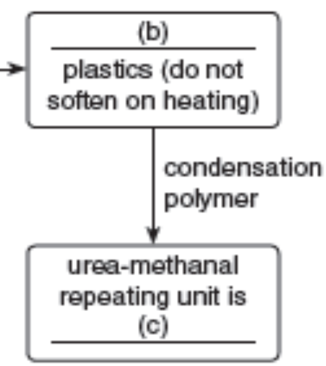
Unit Exercise (p.48)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept map.

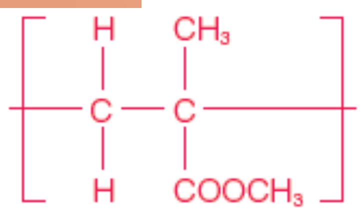
Unit Exercise (p.48)



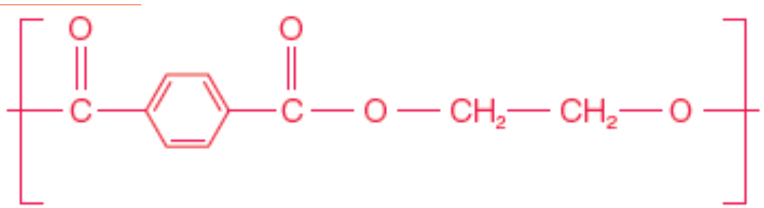


a) thermoplastics
b) thermosetting

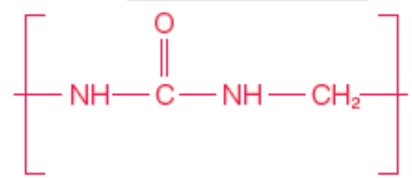
e)



f)



c)

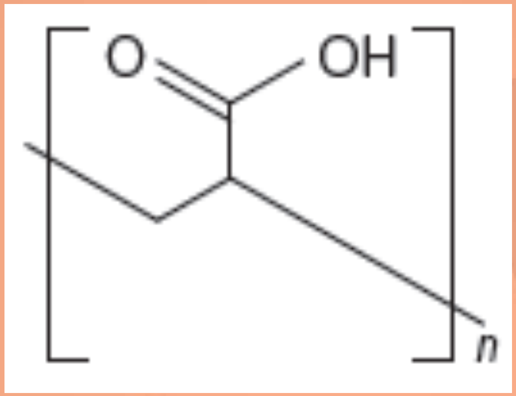


d)

Unit Exercise (p.48)

PART II MULTIPLE CHOICE QUESTIONS

The structure of a polymer made from acrylic acid (CH_2=CHCOOH) is shown below.



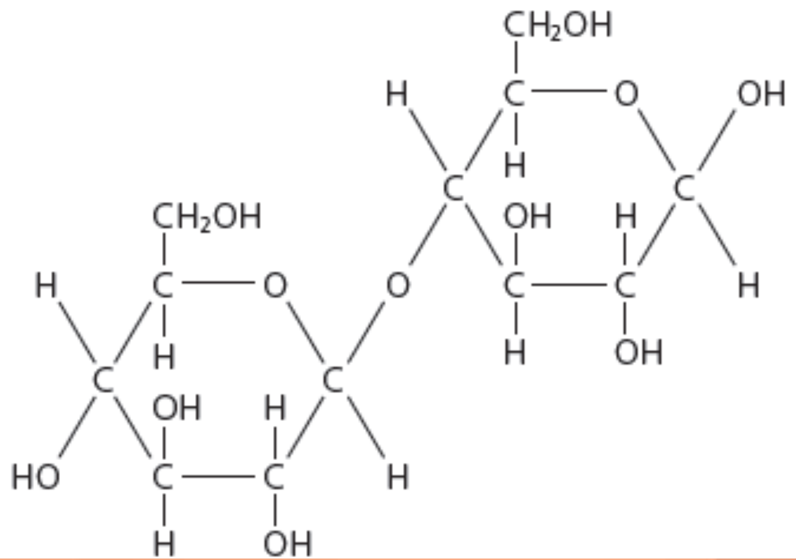
Which type of reaction results in the formation of this polymer?

A Addition
B Condensation
C Hydration
D Oxidation

Answer: A

Unit Exercise (p.48)

3 Cellobiose is formed by partial hydrolysis of cellulose. The structure of cellobiose is shown below:



What type of reaction forms the link between the two monomer units that make up cellobiose?

A Condensation

B Oxidation

C Reduction

D Substitution

Answer: A

Unit Exercise (p.48)

4 Condensation polymerisation differs from addition polymerisation in that

A it involves the elimination of small molecules.
B it must involve two different monomers.
C thermosetting plastics are always formed in the process.
D covalent bonds are formed between polymer chains.

Answer: A

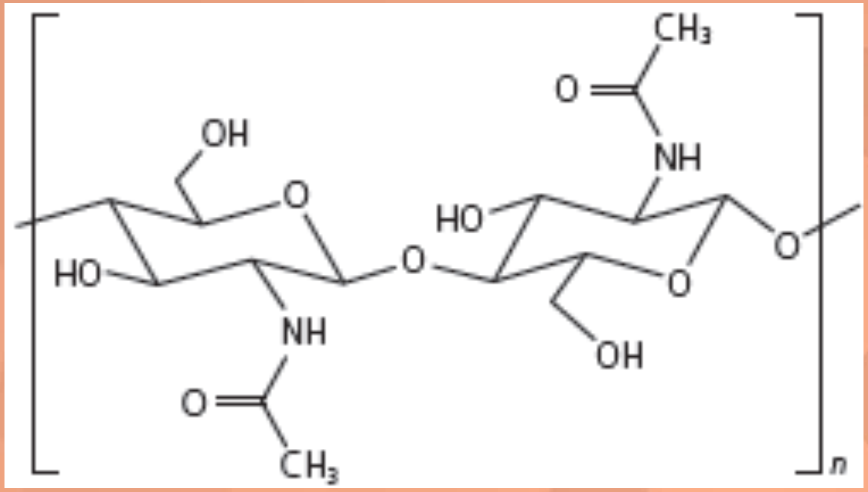
Unit Exercise (p.48)

5

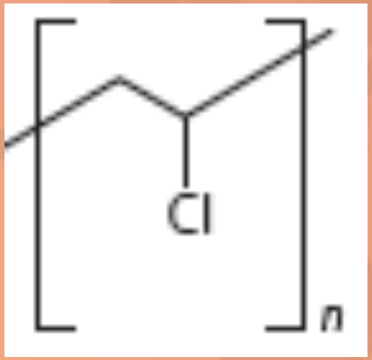
What is the structure of the polymer most likely to have been used in the manufacture of the cup shown?

Unit Exercise (p.48)

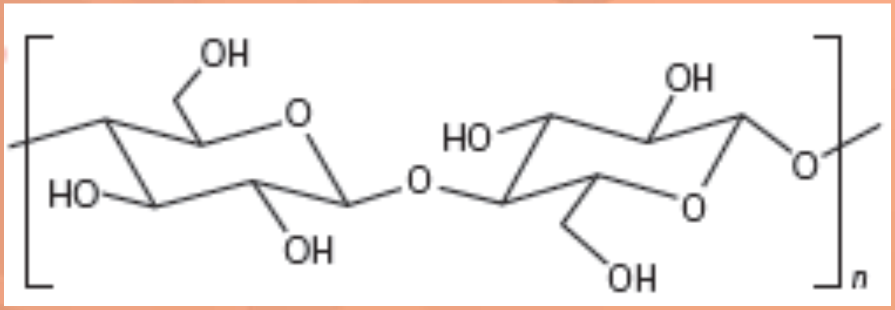
A



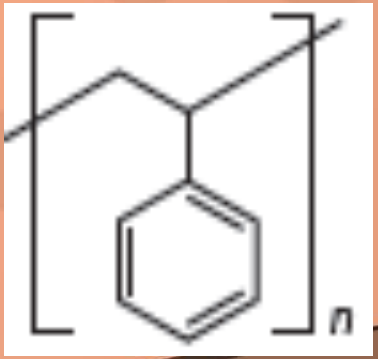
C



B



D

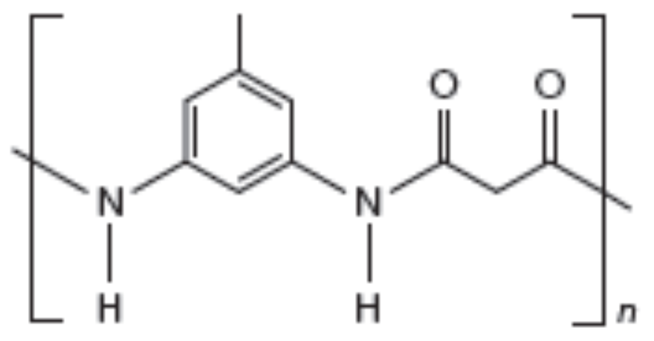


The cup is made of cellulose.

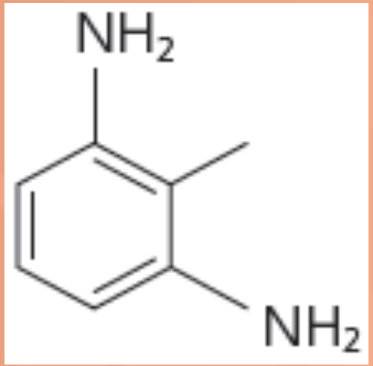
Answer: B

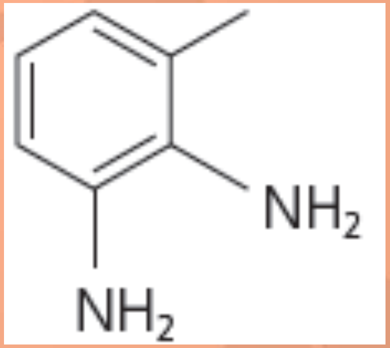
Unit Exercise (p.48)

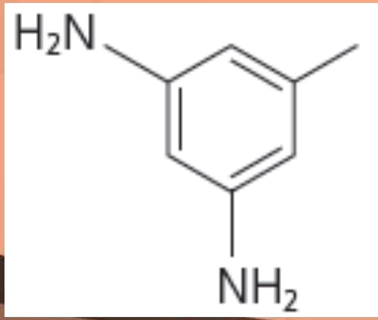
6 Which isomer reacts with propanedioyl dichloride to form the polymer shown?

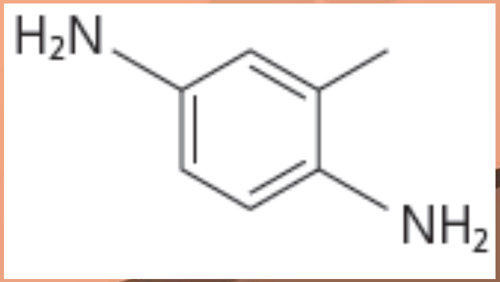


Answer: B

A


C


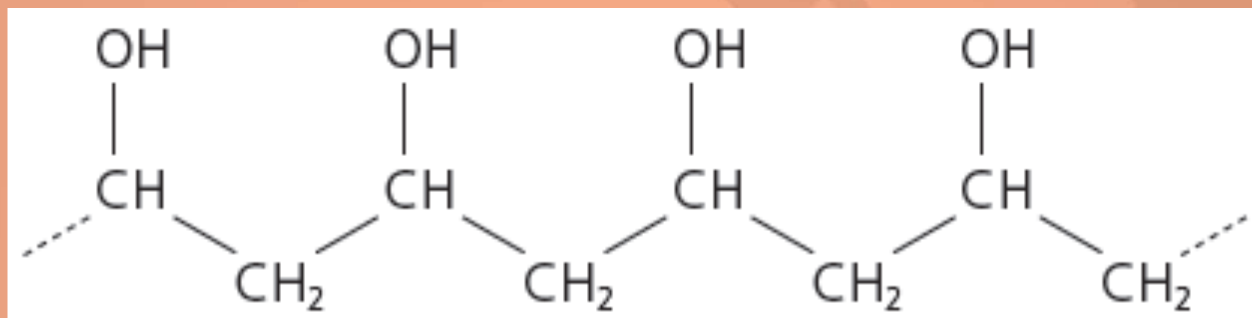
B


D


(Edexcel International Advanced Level, Unit 5, WCH05, Jun. 2017, 17)

Unit Exercise (p.48)

Directions: Questions 7 and 8 refer to the polymer shown below. Chains of the polymer can be ‘crosslinked’.



Answer: C

7 Which of the following molecules would be the most suitable for cross-linking?

A $HOCH_2CH_2OH$
B $HOOCCH_2CH_2COOH$
C $H_2NCH_2CH_2NH_2$
D $H_2NCH_2CH_2COOH$

$HOOCCH_2CH_2COOH$ can cross-link chains of the polymer via ester linkages.

Unit Exercise (p.48)

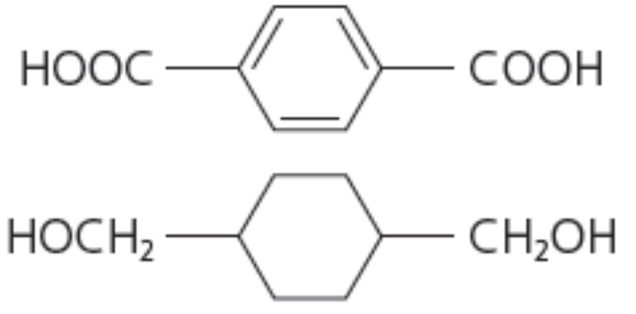
8 What type of linkage would form during the crosslinking?

A Amine linkage
B Amide linkage
C Ester linkage
D Glycosidic linkage

Answer: C

Unit Exercise (p.48)

9 The polymer Kodel is made using the two monomers shown below:

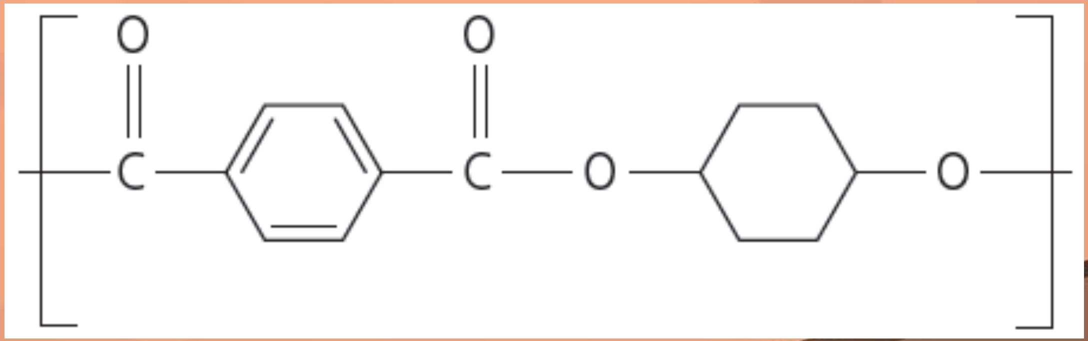


Which of the following statements about Kodel is / are correct?

(1) It is a thermoplastic.

(2) Hydrogen bonds exist between its polymer chains.

(3) Its repeating unit is as shown below:



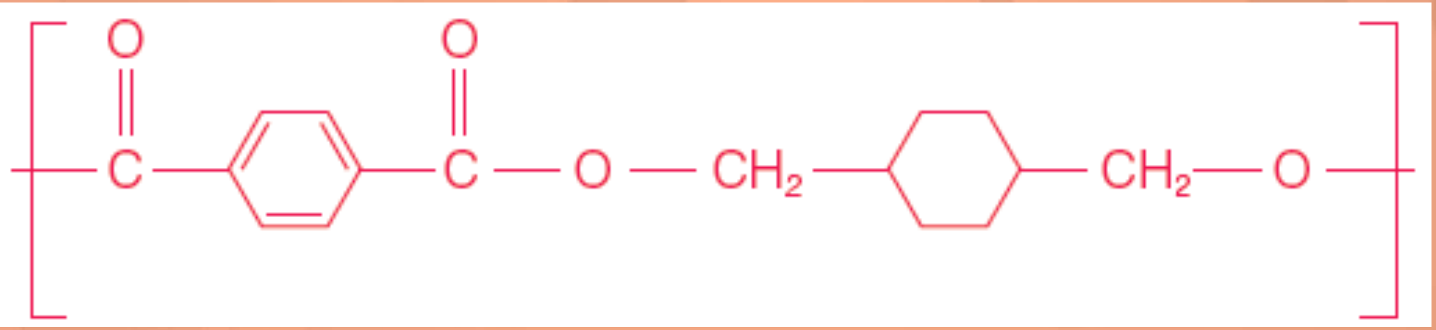
Unit Exercise (p.48)

9

A (1) only
B (2) only
C (1) and (3) only
D (2) and (3) only

Answer: A

9 The repeating unit of Kodel is shown below:



Hydrogen bonds do NOT exist between the polymer chains.

Unit Exercise (p.48)

10 Which of the following statements concerning plastics is / are correct?
(1) Nylon-6,6 is a thermoplastic formed by condensation polymerisation.
(2) Polystyrene is a thermosetting plastic formed by addition polymerisation.
(3) Urea-methanal is a thermosetting plastic formed by condensation polymerisation.

A (1) only
B (2) only
C (1) and (3) only
D (2) and (3) only

Answer: C

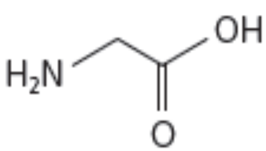
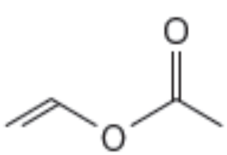
(2) Polystyrene is a thermoplastic.

Unit Exercise (p.48)

PART III STRUCTURED QUESTIONS

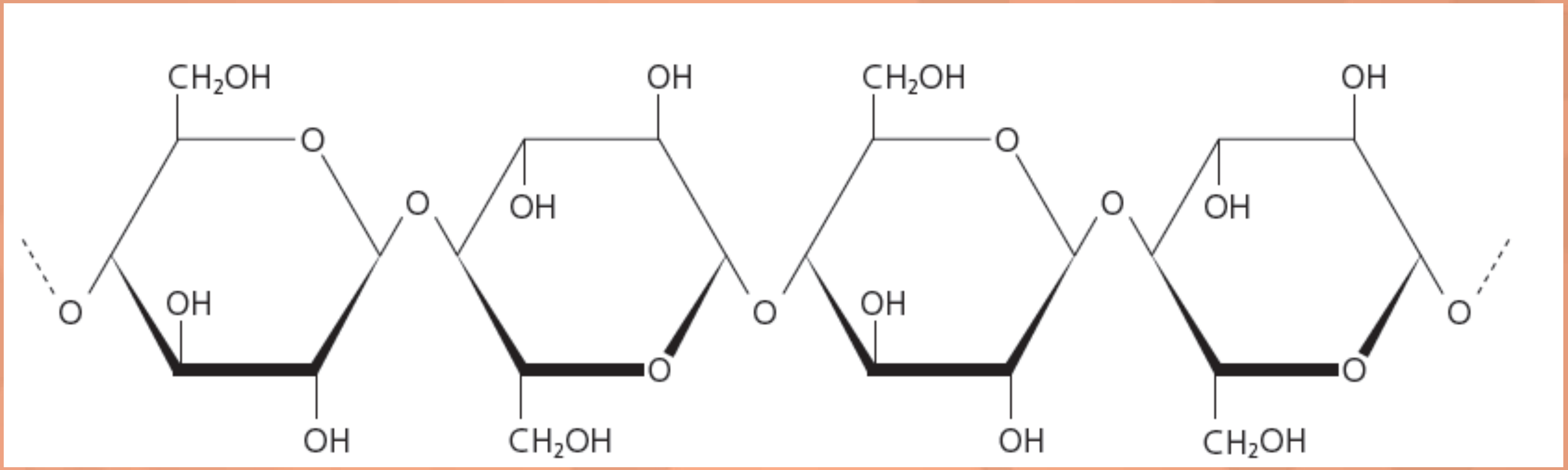
11 Polymers consist of monomer molecules joined together by addition or condensation polymerisation.

Complete the table by placing a tick (4) in the correct column to indicate the type of polymerisation that would polymerise each of the monomer molecules.

Monomer	Addition polymerisation	Condensation polymerisation	Both
		✔ (1)	
	✔ (1)		
	✔ (1)		

Unit Exercise (p.48)

12 A part of the structure of a cellulose molecule is shown below.



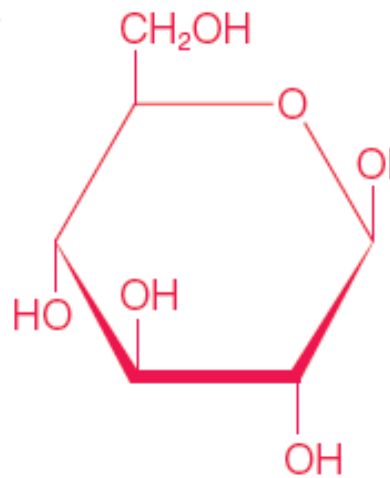
a) Cellulose is a condensation polymer of glucose.

i) Explain why cellulose is classified as a condensation polymer.

When the monomer molecules join together to form cellulose, small water molecules are eliminated. (1)

Unit Exercise (p.48)

ii) Draw the structure of a glucose molecule.



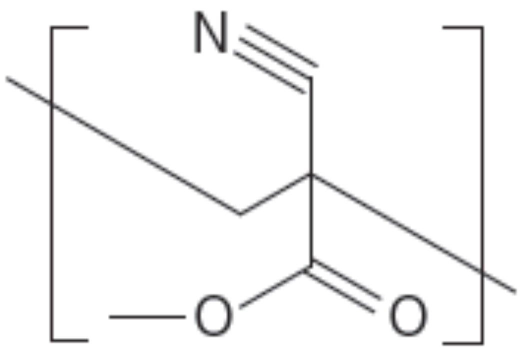
(1)

b) Explain why cellulose is insoluble in water.

The –OH groups in a cellulose molecule can form extensive hydrogen bonding with other cellulose molecules. Hence the –OH groups are less available to form hydrogen bonds with water molecules. (1)

Unit Exercise (p.48)

13 Poly(methyl 2-cyanoacrylate) is commonly used as the active ingredient of Superglue. The repeating unit of poly(methyl 2-cyanoacrylate) is shown below:

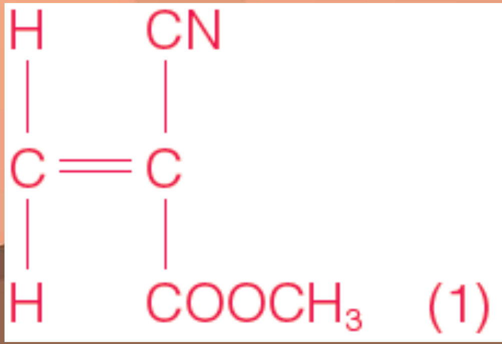


a) Draw the structure of the monomer of poly(methyl 2-cyanoacrylate).

b) Name a gas which could be produced when the polymer burns.

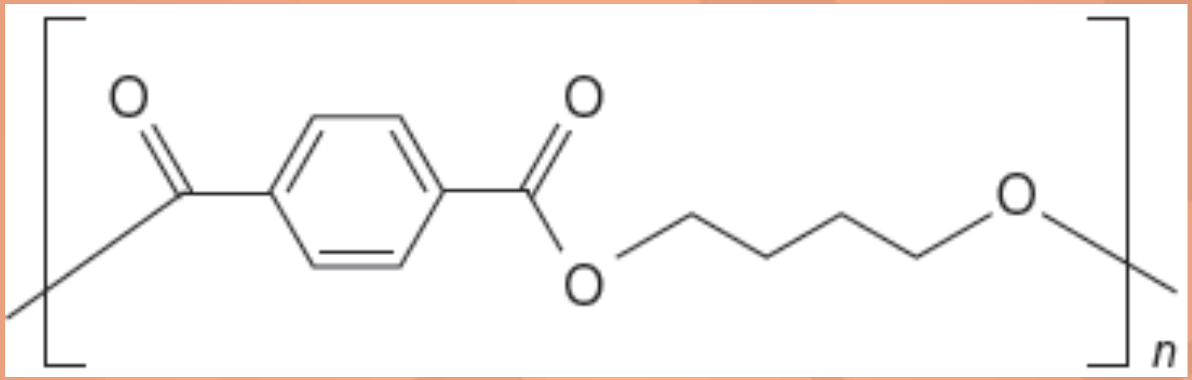
Hydrogen cyanide / carbon monoxide (1)

a)



Unit Exercise (p.48)

14 The keycap of a computer keyboard is made of PBT. The structure of PBT is shown below:

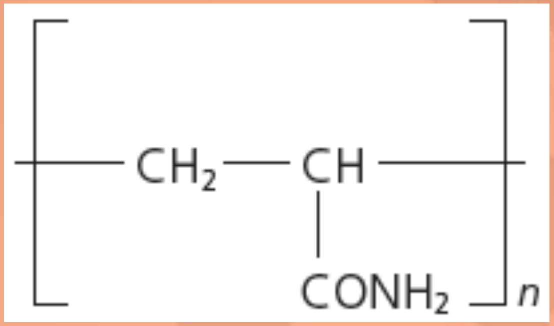


a) Draw the structures of the various monomers of PBT.
b) Name the type of polymerisation involved in the formation of PBT.

(HKDSE, Paper 2, 2016, 2(c)(i)(1)–(2))

Unit Exercise (p.48)

15 A brand of baby diaper uses polyacrylamide as the water absorbing material. The structure of polyacrylamide is shown below.



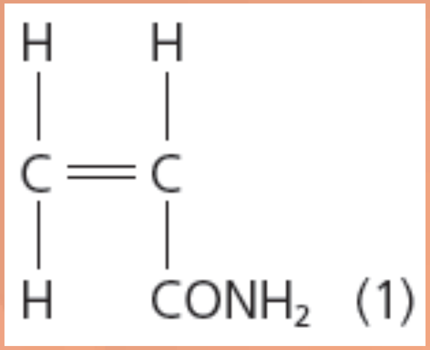
a) Draw the structure of the monomer of polyacrylamide.

b) Suggest a synthetic route, with NOT MORE THAN THREE STEPS, for the transformation of propenoic acid to the monomer of polyacrylamide.

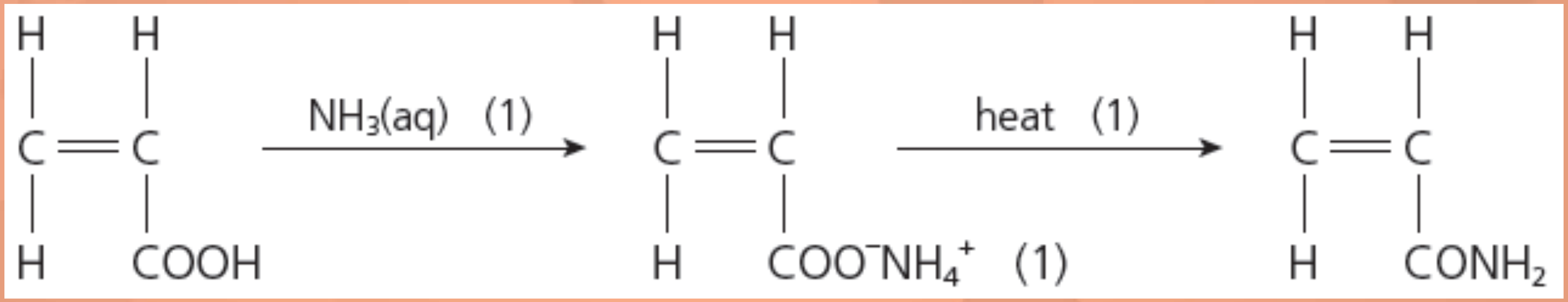
c) Account for the water absorbing property of polyacrylamide.

Unit Exercise (p.48)

a)



b)



c) Polyacrylamide contains a large number of amide groups.
These amide groups can form hydrogen bonds with water molecules. (1)

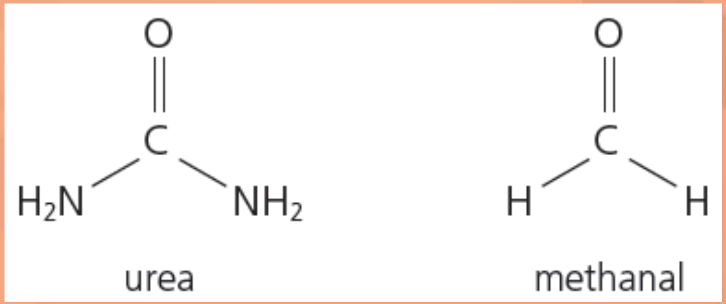
Unit Exercise (p.48)

16 The diagrams below show some items.

a) The lamp holder is made of a thermosetting plastic — urea-methanal.

i) What is meant by the term 'thermosetting plastic'?

ii) Urea and methanal undergo condensation to give urea-methanal.

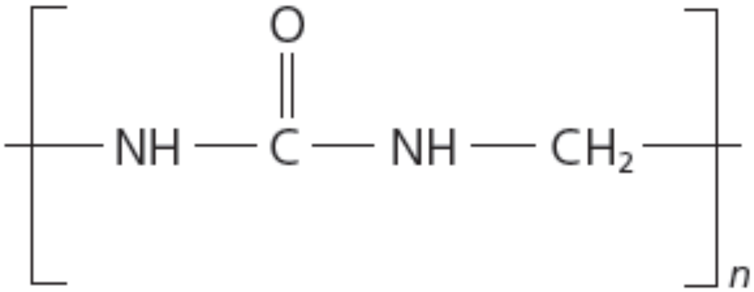


Draw the structure of urea-methanal.

Unit Exercise (p.48)

i) A thermosetting plastic becomes permanently hard during its formation, and does not soften upon heating. (1)

ii)



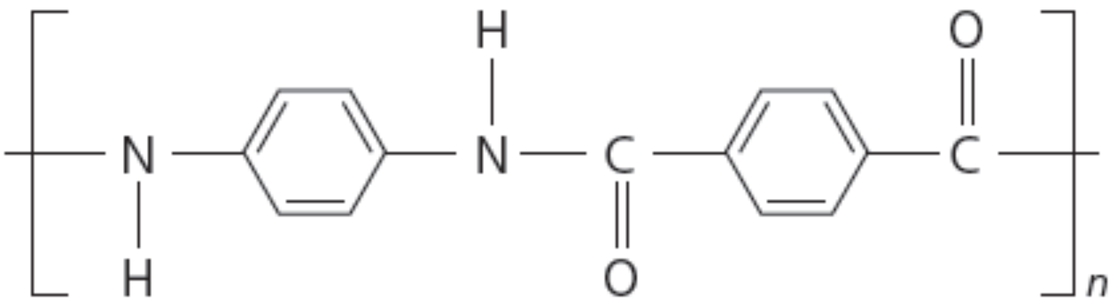
(1)

b) Kevlar is used to make the bullet-proof vest.

i) Draw the structure of Kevlar.

ii) Name the type of polymerisation involved in the production of Kevlar.

i)



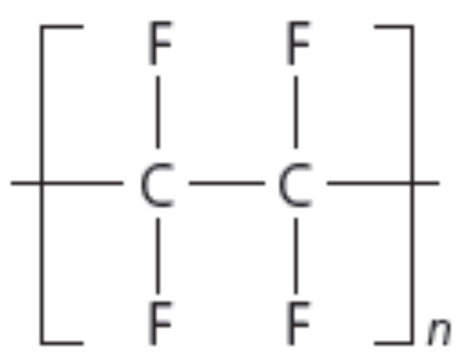
(1)

ii) Condensation polymerisation (1)

Unit Exercise (p.48)

c) Polytetrafluoroethene (PTFE) is used as the coating of the non-sticky pan.

i) Draw the repeating unit of PTFE.



(1)

ii) Explain why PTFE has a non-sticky surface.

Fluorine is the most electronegative element. Hence the C–F bonds in polytetrafluoroethene are strongly polar. (1)

There is an evenly distributed layer of partial negative charge on the surface of polytetrafluoroethene.

This layer of fluorine atoms almost repels all other materials, preventing them from adhering to polytetrafluoroethene. (1)

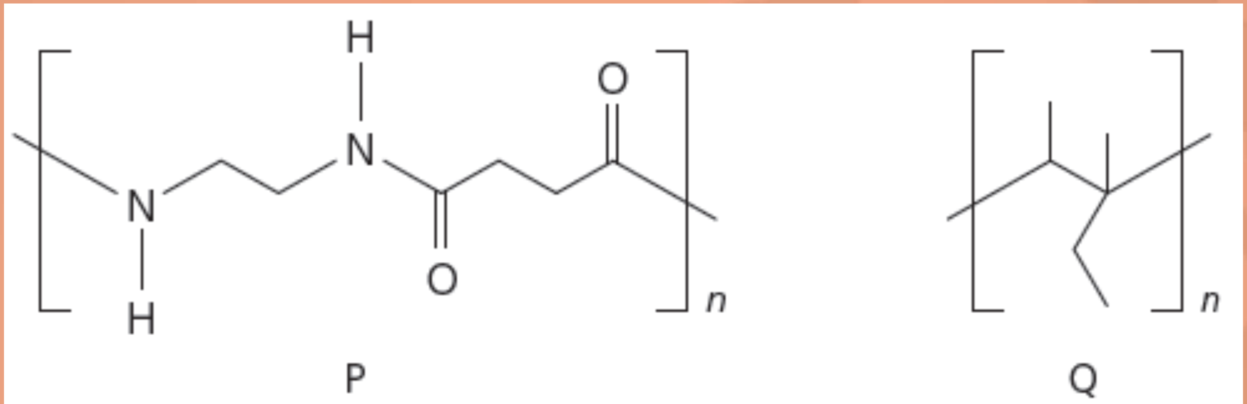
Unit Exercise (p.48)

17 Polymerisation can take place by addition polymerisation or condensation polymerisation.
Give TWO differences between the two processes.

Addition polymerisation	Condensation polymerisation	
Molecule of monomer has carbon-carbon double bond	Molecule of monomer has two functional groups	(1)
Same empirical formula as monomer	Different empirical formula	(1)
No loss of small molecule	Small molecule is formed	(1)
Usually requires an initiator	Does not require an initiator	(1)

Unit Exercise (p.48)

18 The structures of polymers P and Q are shown below.



a) i) Name the type of polymerisation involved in the formation of P.

Condensation polymerisation (1)

ii) Draw the structures of monomers of polymer P. Name the monomers.

$H_2N–(CH_2)_2–NH_2$ (1) ethane-1,2-diamine (1)

$HOOC–(CH_2)_2–COOH$ (1) butanedioic acid (1)

iii) What is the name given to polymers containing the same functional group as polymer P?

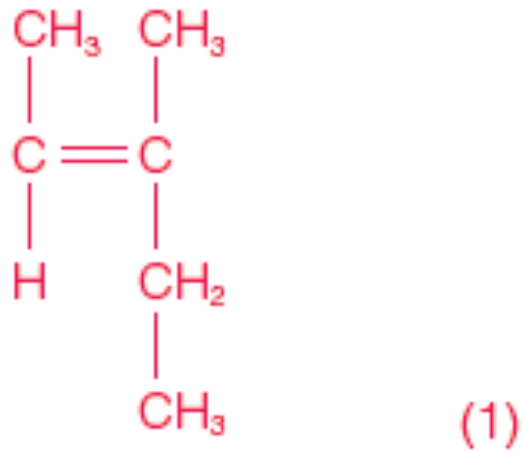
Polyamides (1)

Unit Exercise (p.48)

b) i) Name the type of polymerisation involved in the formation of Q.

Addition polymerization. (1)

ii) Draw the structure of the monomer of polymer Q. Name the monomer.



3-methylpent-2-ene (1)

iii) Polymer Q is a thermoplastic.

What is meant by the term ‘thermoplastic’?

A type of plastic that becomes soft when heated; becomes hard when cooled. (1)

Unit Exercise (p.48)

19 Consider the information below concerning the production of low density polythene from ethene.

$$n\ CH_2{=}CH_2 \xrightarrow[\text{high pressure}]{\text{benzoyl peroxide}} \left[-CH_2-CH_2- \right]_n$$

a) Outline the steps involved in the production of low density polythene.

b) Is the product a single compound? Explain.

a) The initiator produces phenyl radicals.

A phenyl radical adds to an ethene molecule, producing a larger radical. (1)

$$\dot{C}_6H_5 + CH_2{=}CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$$ (1)

This radical reacts with another ethene molecule. The carbon chain of the radical grows in length. (1)

$$C_6H_5-CH_2-\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$$ (1)

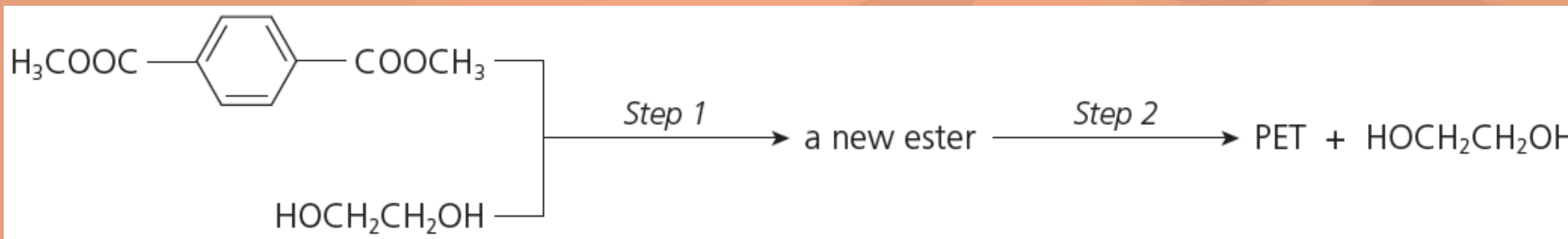
The length of the carbon chain of the radical continues to grow until two radicals combine to form a stable molecule.

b) No

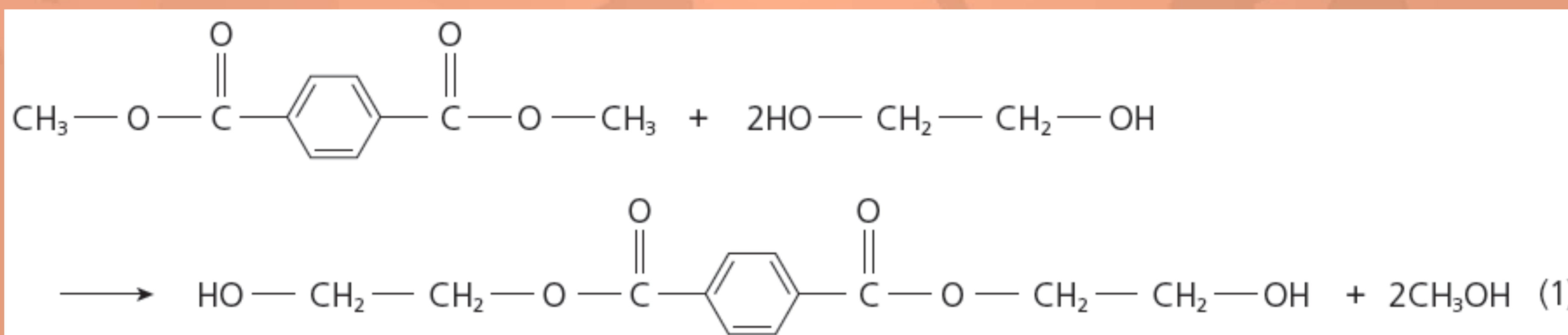
A mixture of products with different chain lengths is obtained. (1)

Unit Exercise (p.48)

20 The flow diagram below shows a route for the synthesis of PET.

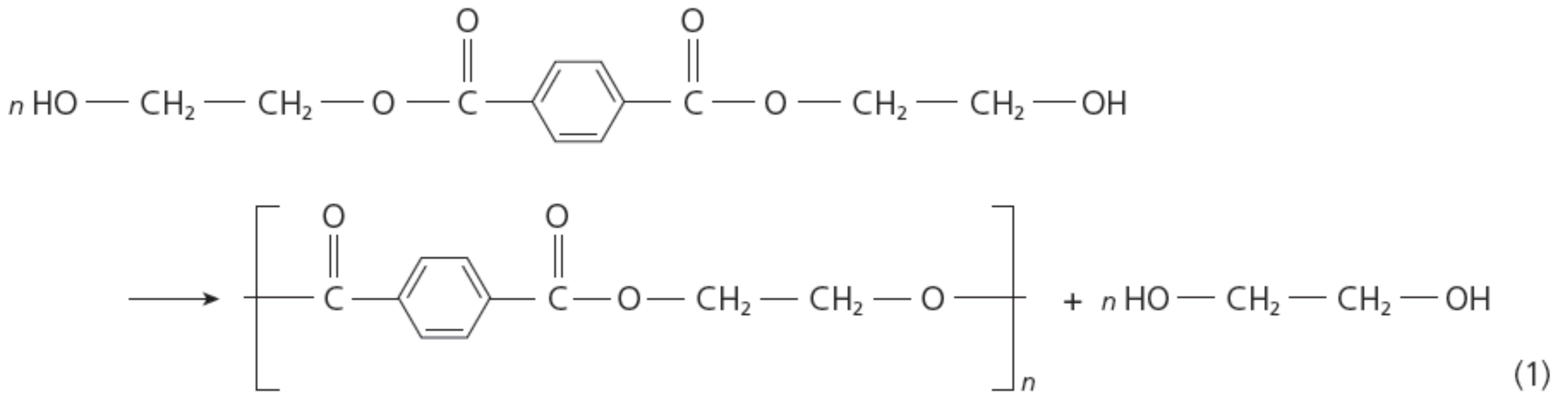


a) Write the chemical equation to represent the reaction in *Step1*.



Unit Exercise (p.48)

b) Write the chemical equation to represent the reaction in *Step 2*.



c) What is the name given to polymers containing the same functional group as PET?

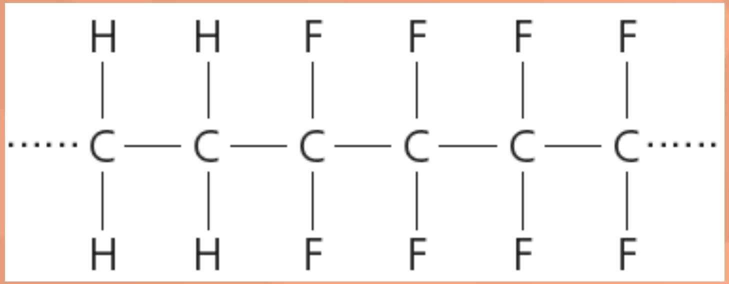
Polyesters (1)

Unit Exercise (p.48)

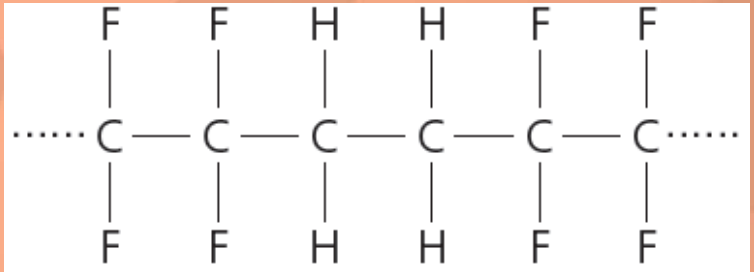
21 At the Eden Project, plants grow in transparent domes that are made from ETFE. ETFE is a polymer made by reacting ethene with tetrafluoroethene.

a) Draw a section of the ETFE chain that includes ONE unit from ethene and TWO units from tetrafluoroethene.

Any one of the following:



(1)



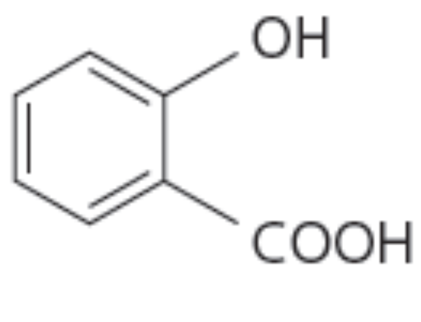
(1)

b) One property of ETFE is that it is insoluble in water. This makes ETFE a suitable material for the domes at the Eden project.
Explain why ETFE is insoluble in water.
ETFE does NOT form hydrogen bonds with water. (1)

(OCR Advanced Subsidiary GCE, Chem. B (Salters), F332, Jun. 2016, 2(b)–(d))

Unit Exercise (p.48)

22 Salicylic acid is a naturally occurring carboxylic acid, widely used in organic synthesis.



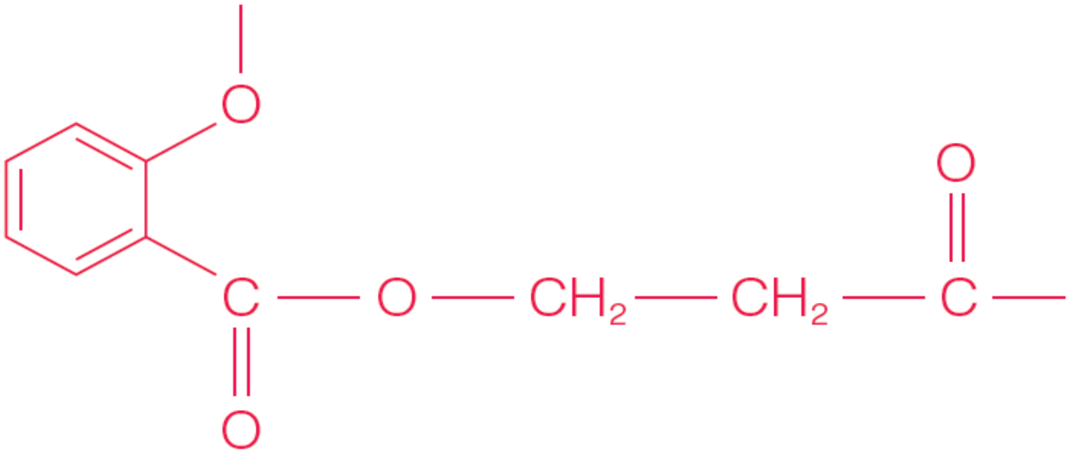
salicylic acid

Salicylic acid reacts with 3-hydroxypropanoic acid ($HO–CH_2–CH_2–COOH$) to form a mixture of condensation polymers.
To form one polymer, the two monomers react in equal quantities.
Draw the repeating unit of this polymer, displaying the linkage between the monomer units.

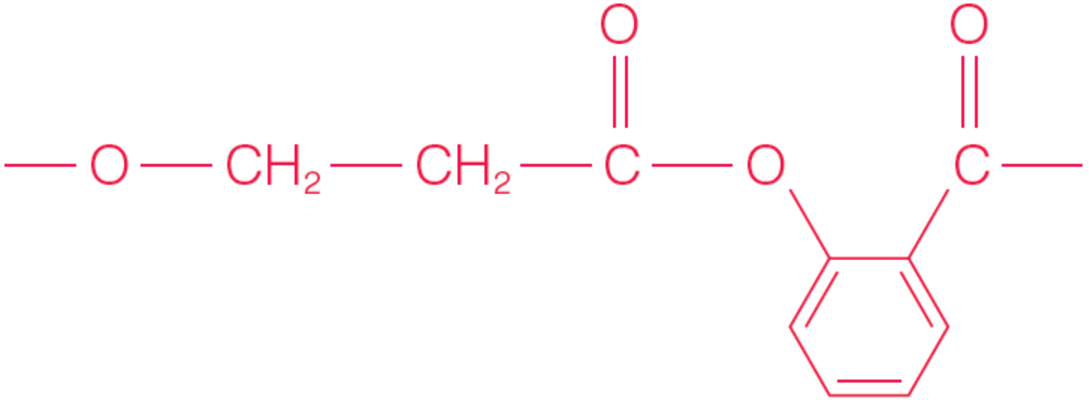
(OCR Advanced GCE, Chem. A, F324, Jun. 2014, 1(d)(iii))

Unit Exercise (p.48)

22 Any one of the following:



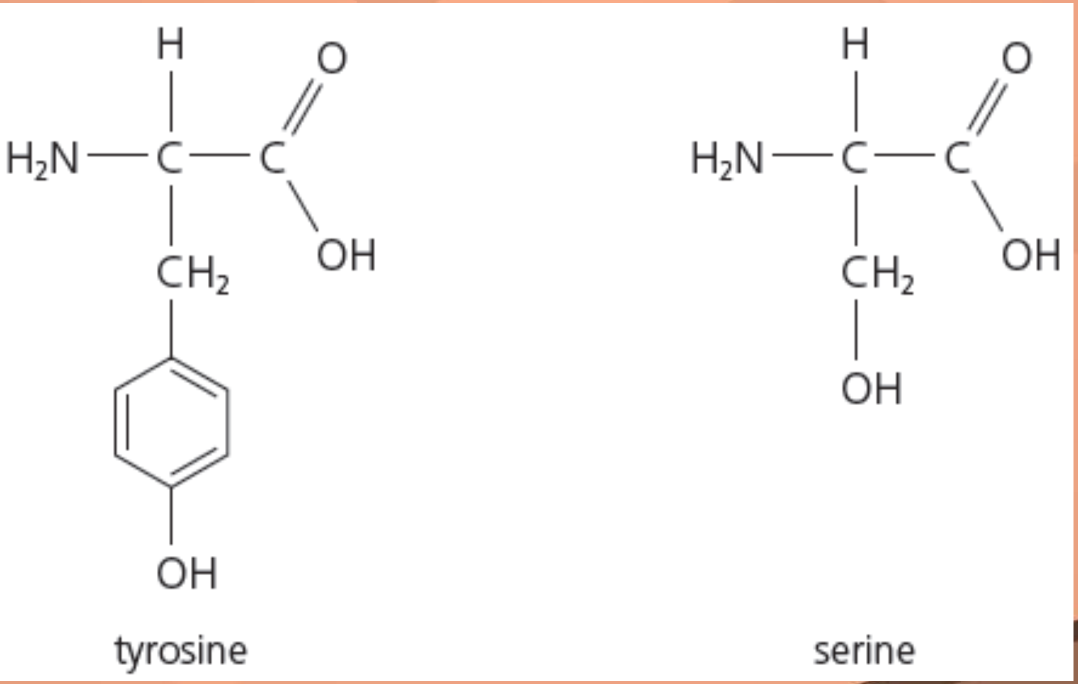
(1)



(1)

Unit Exercise (p.48)

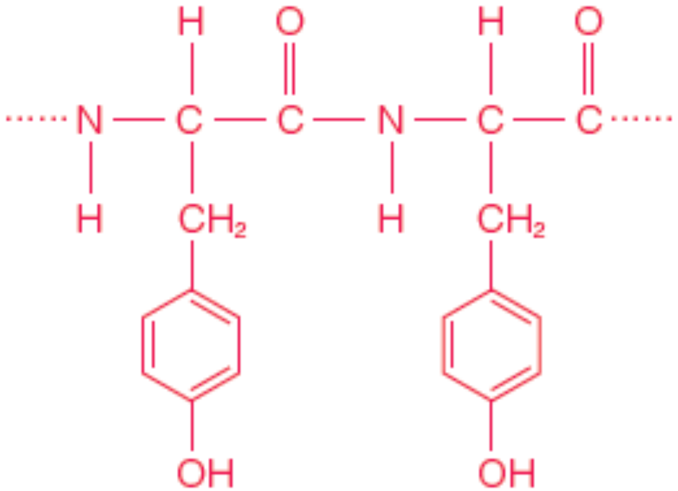
23 Amino acids contain both amine and carboxylic acid functional groups. Tyrosine and serine can form different types of condensation polymers. Draw TWO repeating units of the polyamide formed from tyrosine only and TWO repeating units of the polyester formed from serine only. The polymer linkages must be displayed.



(Edexcel International Advanced Level, Unit 5, WCH05, Jan. 2017, 23(b)(iii))

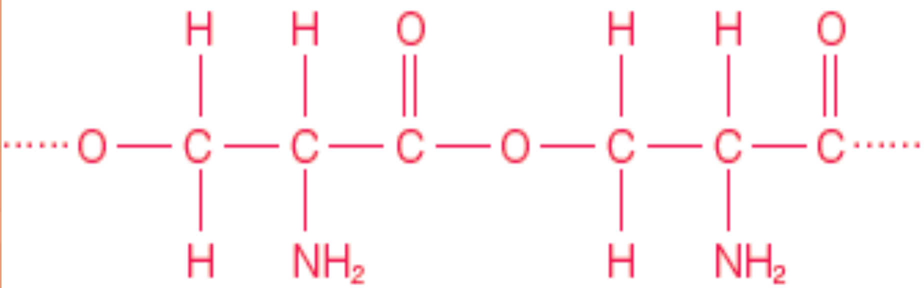
Unit Exercise (p.48)

23 Polyamide



(1)

Polyester



(1)