11 Petrochemicals and polymers

In this chapter, you will find out about:

- fossil fuels
- the formation and fractional distillation of petroleum (crude oil)
- catalytic cracking
- S alternative transport fuels
- S biogas
- S addition polymerisation
- S condensation polymerisation
- S the disposal and recycling of plastic waste
- S biological condensation polymers
  - proteins
  - carbohydrates.

Sheets and tubes of carbon – new technology

Industry based on organic chemistry has given us a vast range of new fuels and materials that have revolutionised our lives. As we explore the virtuosity of carbon as an element, novel materials continue to be discovered. In 2010, the Nobel Prize was awarded to Andre Geim and Konstantin Novoselov for their work on graphene sheets (Figure 11.1a).

Graphene is a flat sheet of carbon atoms arranged in a hexagonal pattern – atomic-scale carbon 'chicken wire'. Stacks of graphene sheets make up the graphite in the pencils you use every day. However, the individual sheets are providing many new ideas for their use. Graphene is very strong and flexible. It allows electrons to flow very efficiently across its surfaces. Its electrical conductivity is high and it may eventually replace silicon in computer chips.

Graphene sheets are also the starting point for making carbon nanotubes (Figure **11.1b**). The discovery of nanotubes has suggested, among other things, new methods of medical drug delivery and conducting materials. Chemical polymerisation reactions have been carried out in miniature within nanotubes, with the carbon tubes being used as linear reaction vessels.

This chapter will focus on some of the ways we exploit the rich chemistry of carbon. The future holds the prospect of even more incredible adaptations and technological developments.

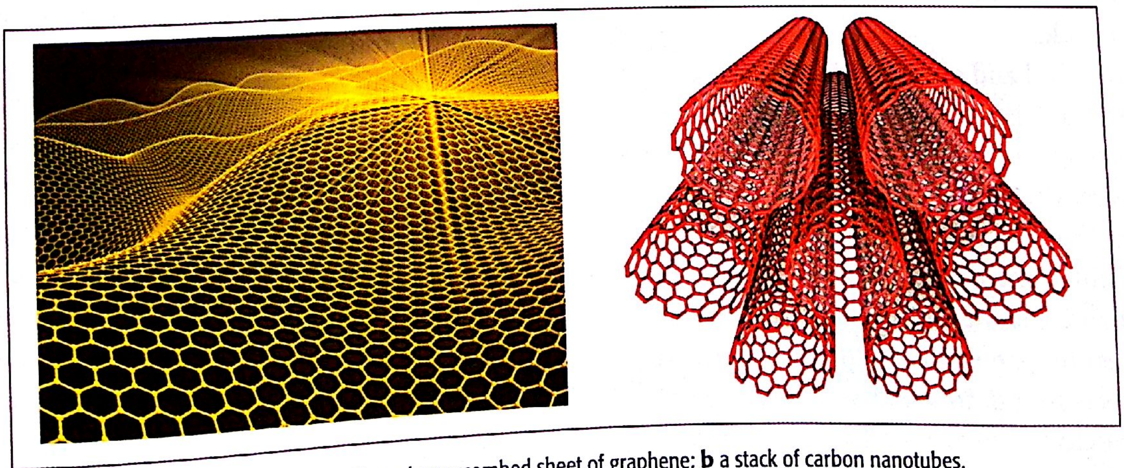


Figure 11.1 Computer graphics of the structures of: **a** a honeycombed sheet of graphene; **b** a stack of carbon nanotubes.

11.1 Petroleum

Fossil fuels were formed in the Earth's crust from material that was once living. **Coal** comes from fossil plant material. **Petroleum** (or **crude oil**) and **natural gas** are formed from the bodies of marine microorganisms. The formation of these fuels took place over **geological periods of time** (many millions of years). These fuels are therefore a **non-renewable** and **finite resource**.

There are three major **fossil fuels**:

- **coal**
- **petroleum (crude oil)**
- **natural gas.**

The formation of petroleum

Petroleum (or **crude oil**) is one of the Earth's major natural resources, the result of a process that began up to 400 million years ago. When prehistoric marine creatures died, they sank to the seabed and were covered by mud. The change into petroleum and natural gas was brought about by high pressure, high temperature and bacteria acting over millions of years. The original organic material broke down into hydrocarbons. Compression of the mud above the hydrocarbon mixture transformed it into shale. Then geological movements and pressure changed this shale into harder rocks, squeezing out the oil and gas. The oil and gas moved upwards through the porous rocks, moving from high-pressure to low-pressure conditions. Sometimes they reached the surface, but often they became trapped by a layer of non-porous rock.

Reservoirs of oil and gas were created. These reservoirs are **not** lakes of oil or pockets of gas. Instead, the oil or gas is spread throughout the pores in coarse rocks such as sandstone or limestone, in much the same way as water is held in a sponge.

Oilfields and gasfields are detected by a series of geological and seismic surveys. Promising areas are then drilled to gain more geological information or, if oil or gas is found, to see how extensive the oilfield or gasfield is. Once a field is established, production oil rigs can be set up, on land or at sea (Figure 11.2).

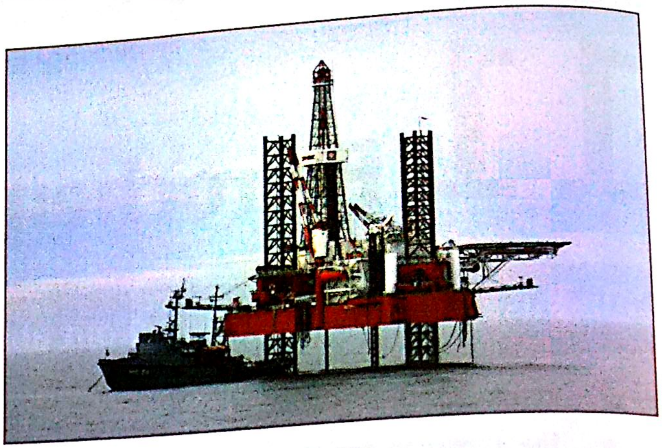


Figure 11.2 An oil rig in the Caspian Sea.

Recently, novel approaches for the exploitation of shale gas- and oilfields have added new and abundant availability of fossil fuel resources. The 'fracking' techniques involved in shale gas extraction are proving controversial, however, particularly in countries with large population density.

Fractional distillation

Petroleum is a mixture of many different hydrocarbon molecules. Most of the petroleum that is extracted from the ground is used to make fuel, but around 10% is used as a **feedstock**, or raw material, in the chemical industry. Before it can be used, the various hydrocarbon molecules are separated by refining. This is done by fractional distillation at an **oil refinery**.

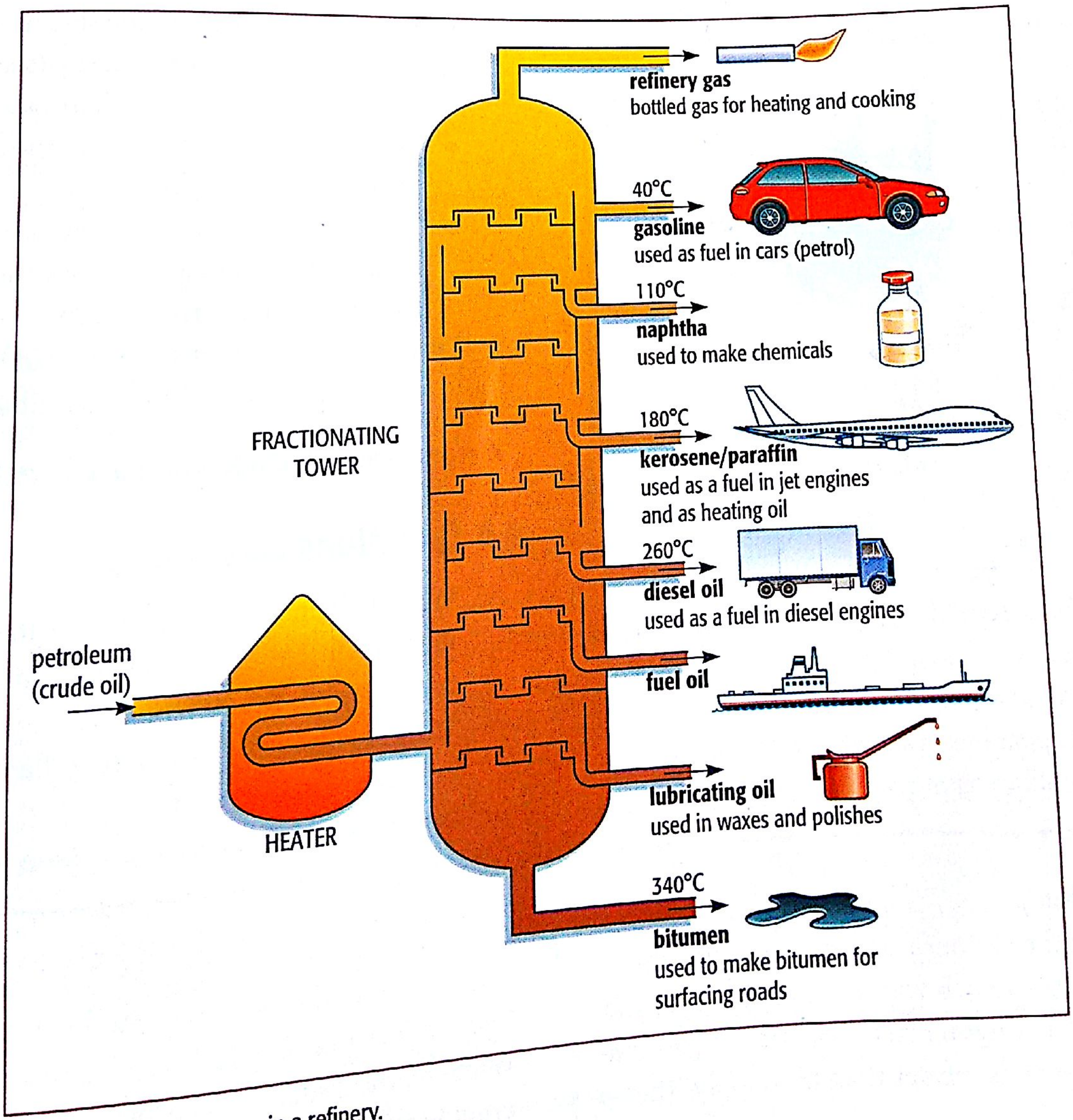
At a refinery, petroleum is separated into different fractions – groups of hydrocarbons that have different boiling points. These different boiling points are roughly related to the number of carbon atoms in the hydrocarbons (Table 11.1).

Separation of the hydrocarbons takes place by **fractional distillation** using a **fractionating column** (or tower). At the start of the refining process, petroleum is preheated to a temperature of 350–400 °C and pumped in at the base of the tower. As it boils, the vapour passes up the tower. It passes through a series of bubble caps, and cools as it rises further up the column. The different fractions cool and condense at different temperatures, and therefore at different heights in the column. The fractions condensing at the different levels are collected on trays. Fractions from the top of the tower are called 'light' and those from the bottom 'heavy'. Each fraction contains a number of different hydrocarbons. The individual single hydrocarbons can then be obtained by further distillation. Figure 11.3 shows the separation into different fractions and some of their uses.

Fraction	Approximate number of carbon atoms in hydrocarbons		Approximate boiling range / °C	
refinery gas	1–4	C_1–C_4	below 25	↓ b.p. and viscosity increasing
gasoline/petrol(a)	4–12	C_4–C_{12}	40–100	
naphtha	7–14	C_7–C_{14}	90–150	
kerosene/paraffin(a)	12–16	C_9–C_{16}	150–240	
diesel oil/gas oil	14–18	C_{14}–C_{18}	220–300	
fuel oil	19–25	C_{19}–C_{25}	250–320	
lubricating oil	20–40	C_{20}–C_{40}	300–350	
bitumen	over 70	$> C_{70}$	above 350	

(a)Different terms are used in the UK and the USA. Note that 'crude oil' (UK) is the same as 'petroleum' (USA), 'petrol' (UK) is the same as 'gasoline' (USA), and 'paraffin' (UK) is the same as 'kerosene' (USA).

Table 11.1 Various petroleum(a) fractions.



ure 11.3 Fractional distillation of petroleum in a refinery.

Study tip

Take care over names for the different fractions in different parts of the world. Note that the syllabus uses 'petroleum' as the name of the crude oil drilled from the ground.

Study tip

Make sure you know the order of the fractions as they are produced from the fractionating tower, and a use for each of the fractions.

Activity 11.1
Fractional distillation of petroleum

Skills

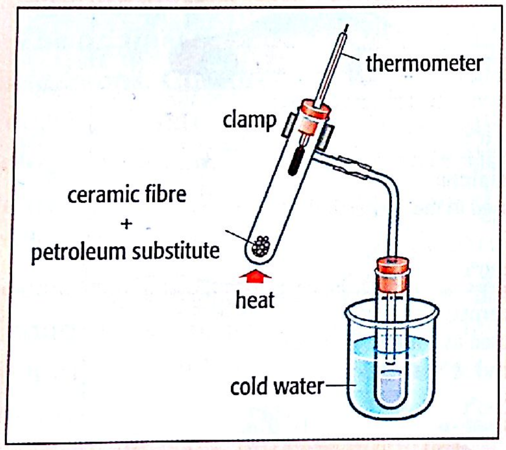
A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate)

A03.3 Make and record observations, measurements and estimates

A03.4 Interpret and evaluate experimental observations and data

⚠ **Wear eye protection. The petroleum is highly flammable and harmful.**

This experiment simulates the industrial fractional distillation of petroleum (crude oil) in the laboratory.



1 Place about a 2 cm^3 depth of ceramic fibre in the bottom of a side-arm test tube. Add about 2 cm^3 of petroleum substitute to this, using a teat pipette.

2 Set up the apparatus as shown in the diagram. The beaker of cold water around the collecting tube helps to condense the low boiling point fraction. The bulb of the thermometer should be level with, or just below, the side arm. Heat the bottom of the side-arm test tube gently, with the lowest Bunsen flame. Watch the thermometer carefully.

3 When the temperature reaches 100 °C, replace the collection tube with another empty one. The beaker of water is no longer necessary and can be removed.

4 Collect three further fractions, to give the fractions as follows:

A Room temperature to 100 °C
B 100–150 °C
C 150–200 °C
D 200–250 °C

5 A black residue remains in the side-arm test tube. Test the four fractions for viscosity (see how easily they pour), colour, smell and flammability.

- To test the smell, **gently** waft the smell towards you with your hand.
- To test for flammability, pour a small quantity on to a hard-glass watch glass and light the fraction with a burning splint.

6 Keep one set of fractions and see that they combine to form a mixture very like the original sample.

A worksheet is included on the CD-ROM.

Questions

A1 What differences did you observe in the viscosity of the fractions? What molecular property would you suggest causes this difference?

A2 What differences were there in flammability between the fractions?

Catalytic cracking

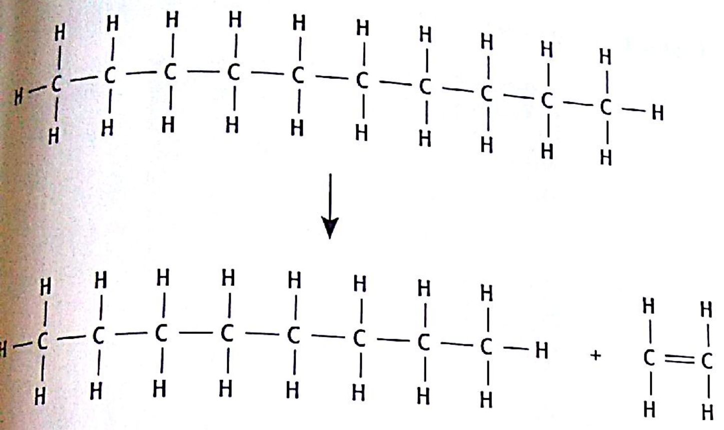
The demand for the various fractions from the refinery does not necessarily match with their supply from the oil (Figure 11.4). For lighter fractions such as gasoline (petrol), the demand is greater than the supply. The opposite is true for heavier fractions such as kerosene (paraffin) and diesel. Larger molecules from these heavier fractions can be broken into smaller, more valuable, molecules. This process is called **catalytic cracking** ('cat cracking').

Cracking takes place in a huge reactor (Figure 11.5). In this reactor, particles of catalyst (made of powdered minerals such as silica, alumina and zeolites) are mixed with the hydrocarbon fraction at a temperature around 500 °C. The cracked vapours containing smaller molecules are separated by distillation.

The shortened hydrocarbon molecules are produced by the following type of reaction:

$$\text{decane} \xrightarrow[\text{catalyst}]{\text{heat}} \text{octane} + \text{ethene}$$

$$C_{10}H_{22} \longrightarrow C_8H_{18} + C_2H_4$$



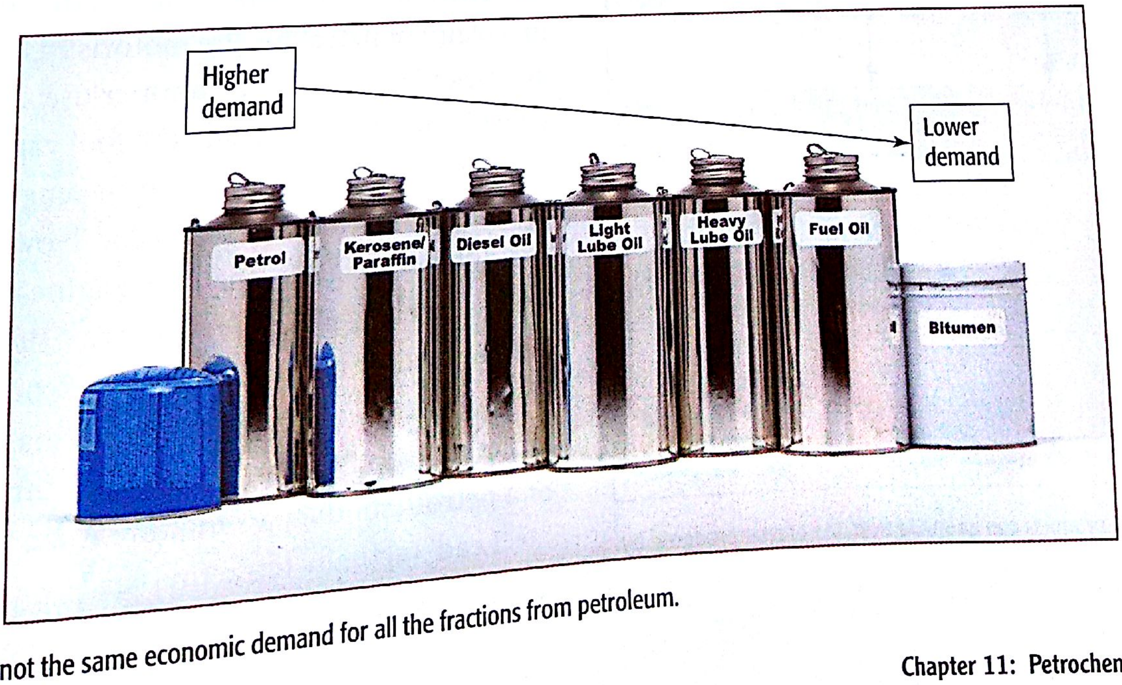
his is just one of the possible reactions when decane cracked. The molecules may not all break in the me place. The alkene fragment is not always ethene: opene and but-1-ene may also be produced.

ll cracking reactions give:
- an **alkane** with a shorter chain than the original, and a short-chain **alkene**
- or two or more **alkenes** and **hydrogen**.

Both products are useful. The shortened alkanes can be blended with the gasoline fraction to enrich the petrol. The alkenes are useful as raw materials for making several important products. Figure 11.6 shows the various uses for the ethene produced.

Propene polymerises to poly(propene) (trade name 'polypropylene'), while butene polymerises to produce synthetic rubber. The cracking reaction can be carried out in the laboratory using paraffin oil (Figure 11.7).

Figure 11.5 A cracking plant in an oil refinery.



11.4 There is not the same economic demand for all the fractions from petroleum.

Activity 11.2
Cracking hydrocarbons

Skills

- A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate)
- A03.3 Make and record observations, measurements and estimates
- A03.4 Interpret and evaluate experimental observations and data

The exact composition of petroleum varies depending on where it comes from, but most oil contains more of the larger molecules than the smaller ones. The smaller ones, however, are more useful and therefore more economically important. To increase the profit that can be made from a barrel of oil, the larger hydrocarbons are broken down into smaller ones. This activity involves a small-scale version of this conversion, which is performed in industry every day.

A worksheet is included on the CD-ROM.

Details of a scaled-up version of this experiment are given in the Notes on Activities for teachers/technicians.

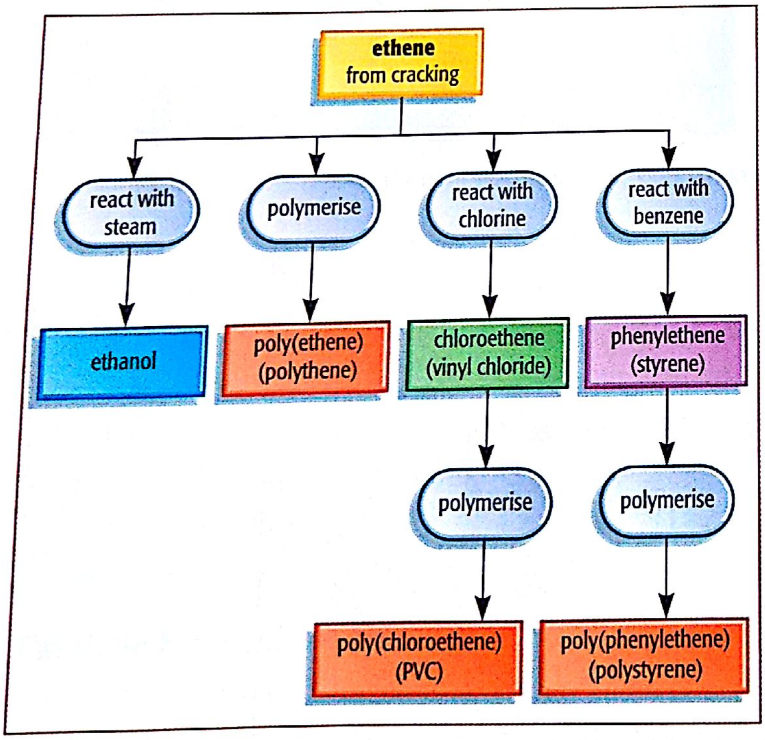


Figure 11.6 Important products can be made from the ethene produced by catalytic cracking.

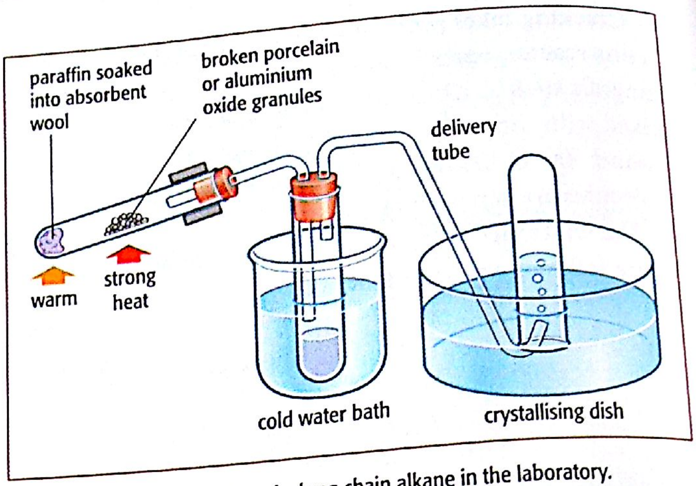


Figure 11.7 The cracking of a long-chain alkane in the laboratory.

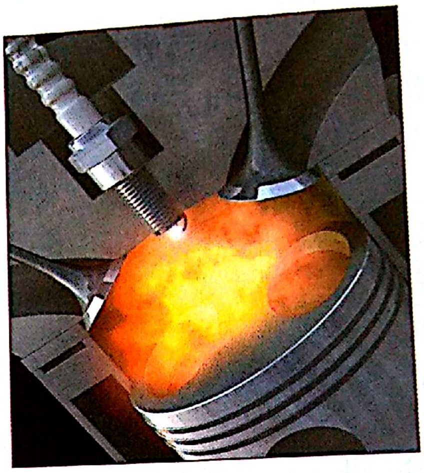


Figure 11.8 Computer image of an internal combustion engine cylinder. The piston (lower right) is moved up and down by the combustion (burning) of fuel. This image shows the fuel/air mixture being ignited by the spark plug.

Blending gasoline

Some of the products from cracking are added to the gasoline fraction to improve the quality of the petrol. As many as 12 different components (containing over 300 different hydrocarbons and additives) may be used in a blend of petrol for the motorist. Different blends are made for winter and summer use. An important consideration is how easily the fuel vapour ignites. If the fuel ignites too easily, then the engine will not run smoothly – 'knocking' will occur. However, if the fuel i too difficult to ignite, then the engine will be difficult t start, especially on cold mornings. High-quality petrol contains many branched-chain hydrocarbons, made i a process known as re-forming, so that the fuel does n ignite too soon (Figure 11.8). The ignition temperatur of a petrol/[solidus] air mixture is around 550 °C.

'Lead' (actually tetraethyl-lead) was added to gasoline to prevent 'knocking'. But this caused high levels of lead in the air, particularly in large cities. This led to concern over the link with brain damage in young children. Unleaded fuel is now almost universally available and has to be used in modern cars fitted with catalytic converters (the lead would poison the catalyst and so prevent it working).

The removal of sulfur from gasoline fractions is now very efficient. Car exhaust emissions contain very little sulfur dioxide. The carbon monoxide (CO), unburnt hydrocarbons (HC) and oxides of nitrogen (NO_x) in exhaust fumes do continue to cause concern. The levels of emission of these compounds are reduced by fitting a catalytic converter to the exhaust.

Gasoline vapour also escapes into the air at petrol stations. Modern pumps now have hoods on the nozzles to cut down the escape of fumes.

Activity 11.3
Comparing fuels

Skills

A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate)

A03.2 Plan experiments and investigations

A03.3 Make and record observations, measurements and estimates

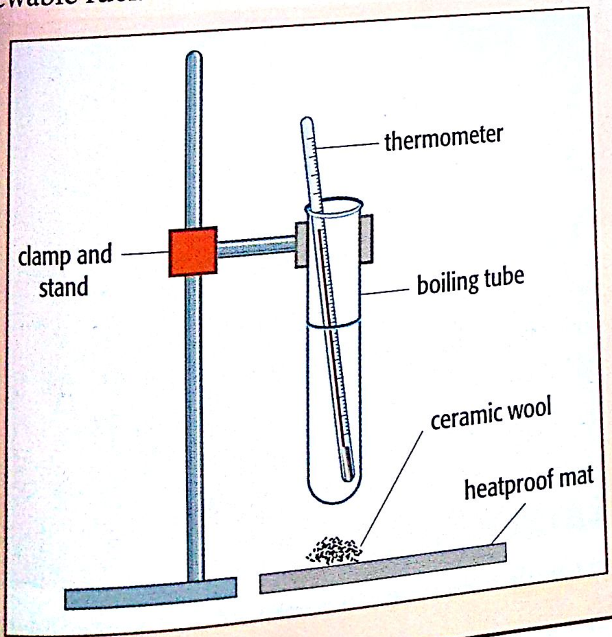
A03.4 Interpret and evaluate experimental observations and data

A03.5 Evaluate methods and suggest possible improvements

⚠ **Wear eye protection.**

There is concern that fossil fuels will run out. There is also concern that burning fossil fuels is causing global warming because of all the carbon dioxide which is released into the atmosphere.

You are asked to design an experiment to compare two fuels: one a fossil fuel and the other a renewable fuel.



The apparatus shown could be used to discover how much heat a fuel produces. A small quantity of the fuel is placed on the 'ceramic wool' and ignited. The temperature change of the water in the boiling tube is then recorded.

1 You are asked to compare paraffin, a fossil fuel obtained from petroleum (crude oil), and ethanol, a renewable fuel which can be made by fermenting sugar from plants. You will need to use a relatively small amount of fuel (around 1 cm^3).

2 When you have planned your investigation, you should carry it out and record all your observations and measurements.

3 You should then write a reasoned conclusion that states which fuel you think is better, together with your reasons.

A worksheet is included on the CD-ROM.

The Notes on Activities for teachers/technicians contain details of how the experiment can be used as an assessment of skills AO3.2 and AO3.5.

Questions

11.1 Put the following fractions in order of increasing boiling point: kerosene, diesel, petrol, refinery gas, bitumen, naphtha.

11.2 Name **three** fossil fuels.

11.3 Explain what is meant by 'cracking', and write word and balanced symbol equations to show how ethene can be formed from decane by this method.

11.4 State a use for the following fractions from the distillation of petroleum (crude oil): bitumen, fuel oil, diesel, kerosene.

11.2 Alternative fuels and energy sources

Alternative transport fuels

There is growing interest and a great deal of development work taking place on alternative transport fuels in order to reduce dependence on fossil fuels and find 'greener' forms of transport.

Diesel

High-speed diesel engines in cars, buses and trucks use a fuel (DERV – diesel engine road vehicle) that contains hydrocarbon molecules consisting of between 6 and 20 carbon atoms (in short this is written as C_6–C_{20} molecules). Slower-speed diesel engines for ships, etc., use a slightly heavier fuel. Diesel engines are compression ignition engines (the fuel ignites spontaneously **without** a spark). Diesel engines are more efficient than petrol engines and produce much less carbon monoxide. However, because their working temperature is higher, they produce more oxides of nitrogen. The major problems are smoke, and the particles it contains, and odour.

Gasoline from methanol

New Zealand has large reserves of natural gas (mainly methane) but very little petroleum. The problem of producing petrol has been transformed by a catalyst known as zeolite ZSM-5. (A zeolite is one of a large group of alumino-silicates of sodium, potassium, calcium and barium.) Methane is first converted into methanol. The methanol produced is then turned into hydrocarbons using the ZSM-5 catalyst:

$$\begin{array}{lcccc} \text{methanol} & \rightarrow & \text{hydrocarbons} & + & \text{water} \\ nCH_3OH & \rightarrow & (CH_2)_n & + & nH_2O \end{array}$$

ZSM-5 is an artificial zeolite composed of aluminium, silicon and oxygen. It was first made by two chemists working for the US Mobil Oil company.

LPG and CNG

Liquid petroleum gas (LPG or 'autogas') is composed of propane and butane. Compressed natural gas (CNG) is 90% methane. These products already have a significant market in some countries. For example, all the taxis in Japan use LPG. In India, many of the motorised rickshaws in the major cities run on CNG (Figure **11.9**).

Biofuels

There have been significant developments in the use of fuels based on ethanol (see page **267**) and vegetable oils such as rapeseed or sunflower oil. The potential for adding plant oils to diesel fuel is being investigated worldwide. The future use of these fuels will depend on economic factors. Some countries grow oil-producing crops but do not have their own reserves of petroleum. Recently there has been controversy about the use of land to grow crops for these fuels and the

Figure 11.9 In India, many of the motorised rickshaws ('tuk-tuks') run on CNG.

fact that this diverts farmland from food production. The consequent decrease in food availability and increase in prices have been sources of concern. These have led to other sources of ethanol being explored, including, for instance, using sawdust from sawmills as a starting point for production (Figure 11.10).

Vegetable oils from crops such as rape and sunflowers are also being developed as fuels. Recycled cooking oil is being used as a component of biodiesel. Biodiesel contains esters, which are made from vegetable oils such as rapeseed or animal fats. The continual growth of new oil-producing plants, which absorb carbon dioxide from the air through photosynthesis, means that biodiesel contributes less to global warming than fossil fuels do. Motor manufacturers have all developed cars with engines adapted to run on these new fuels.

Others

We discussed the use of ethanol- and hydrogen-powered cars on pages 89 and 267. Electric and solar-powered cars are also being investigated as alternatives to gasoline, and many manufacturers now have hybrid cars that run on a combination of power systems (Figure 11.11).

Alternative energy sources

Alternative energy sources are very much under discussion. Nuclear energy, wind farms and solar energy are some of the areas being explored. In terms of chemical systems, those based around our use of waste offer an opportunity for development, particularly at local level.

Biogas

Methane gas is formed naturally in a number of different circumstances. Anaerobic bacteria helped to decompose organic matter under geological conditions to produce natural gas. Methane accumulates in coalmines, where it can cause explosions. Marsh gas, which bubbles up through the stagnant water of marshes, swamps and rice paddy fields, is also methane. Methane produced in this way contributes to the **greenhouse effect.**

Figure 11.10 The sawdust from sawmills can be used as a starting point in making ethanol for biofuels.

Methane is produced from organic waste **(biomass)** when it decays in the absence of air. This can be exploited as a source of energy. In countries such as India and China, biomass digesters are important sources of fuel for rural villages (Figure 11.12). The methane is useful for heating and cooking, and the solid residue is used as a fertiliser.

Industrialised countries produce large amounts of waste, much of which is deposited in landfill sites. Biogas forms as the rubbish decays (Figure 11.13). This gas can be used as a fuel for local industry. On Merseyside in the UK, biogas is used to heat the ovens in a Cadbury's biscuit factory.

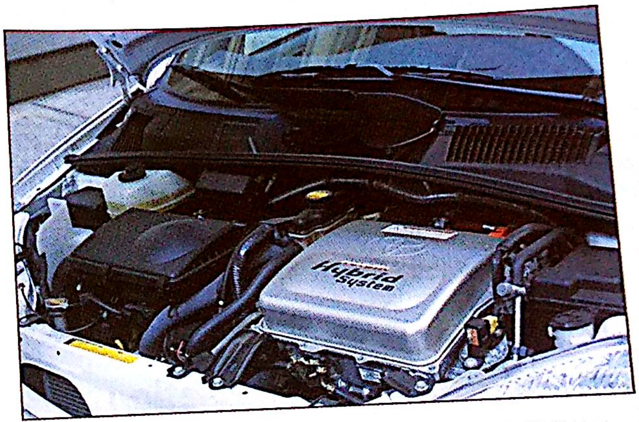


Figure 11.11 The Toyota Prius is a hybrid gas/electric car with low emissions. The battery charges while running on petrol and an on-board computer switches when petrol is low.

Figure 11.12 A small-scale biogas generator uses animal waste to produce methane for a village's needs.

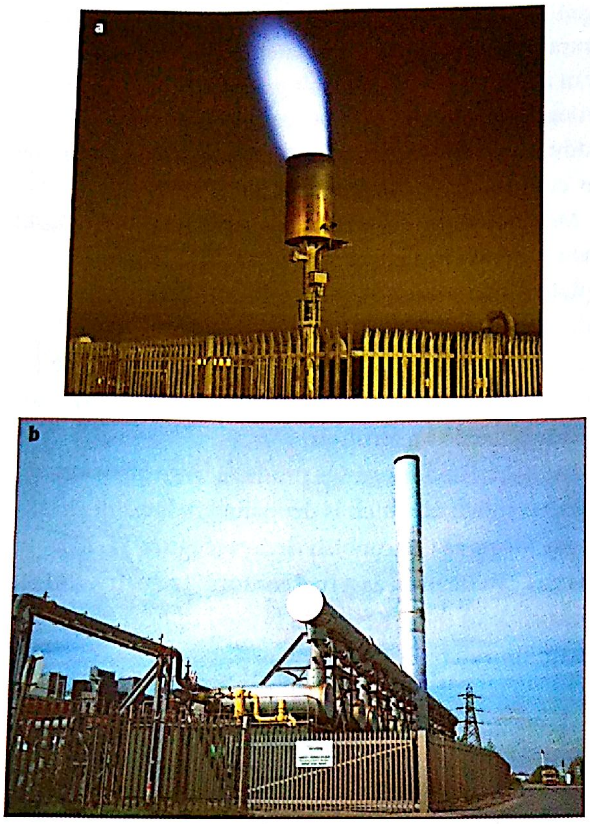


Figure 11.13 **a** Deep in the waste of landfill sites, methane gas accumulates and must be burnt off or it could become dangerous – a landfill flare-off. **b** Alternatively, a power-generating plant can be set up at a landfill site to generate power for the local area.

11.3 Addition polymerisation

All living things contain **polymers**. Proteins, carbohydrates, wood and natural rubber are all polymers. What nature first invented, chemists have learned to copy, alter and use successfully. Synthetic polymers, often called **plastics**, are to be found everywhere in modern technological societies, made into bulky objects, films and fibres. They have properties to suit particular needs, ranging from car and aircraft components to packaging and clothing.

Polymers are large organic **macromolecules**. They are made up of small repeating units known as **monomers** (Figure 11.14) joined together by **polymerisation**. These units are repeated any number of times from about a hundred to more than a million. Some are **homopolymers**, containing just one monomer. Poly(ethene), poly(propene) and poly(chloroethene) are three examples of homopolymers. Other macromolecules are **copolymers**, made of two or more different types of monomer. For example, nylon is made from two monomers, and biological proteins are made from 20 different monomers, the **amino acids**.

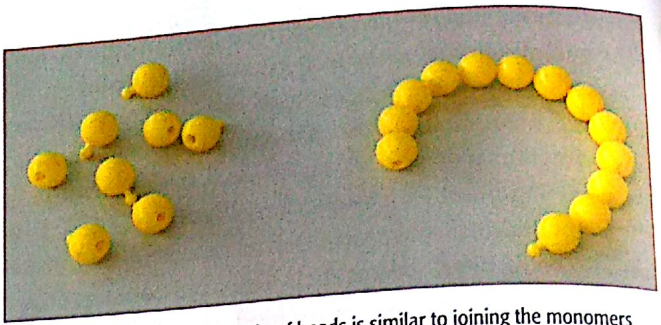
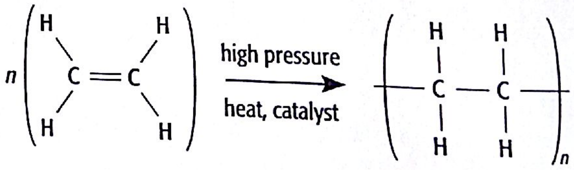


Figure 11.14 Making a chain of beads is similar to joining the monomers together to make a polymer.

The alkene fragments from the catalytic cracking of petroleum fractions produced the starting monomers for the first plastics. Alkenes such as ethene contain a C=C double bond. These molecules can take part in **addition reactions** (see page 258) where the double bond is broken and other atoms attach to the carbons. The double bond in ethene enables many molecules of ethene to join to each other to form a large molecule, poly(ethene) (Figure 11.15). This is an **addition polymer**. When first made by ICI, it was a revolutionary new material called 'Alkathene'. It is now commonly called by the trade name 'polythene'.

Various conditions can be used to produce different types of poly(ethene). Generally a high pressure, a temperature at or above room temperature and a catalyst are needed. The reaction can be summarised by the equation:

$$\text{ethene} \xrightarrow[\text{heat, catalyst}]{\text{high pressure}} \text{poly(ethene)}$$



where *n* is a very large number.

Study tip

When drawing the structure of poly(ethene) and other polymers, do not forget to put the *n* outside the bracket.

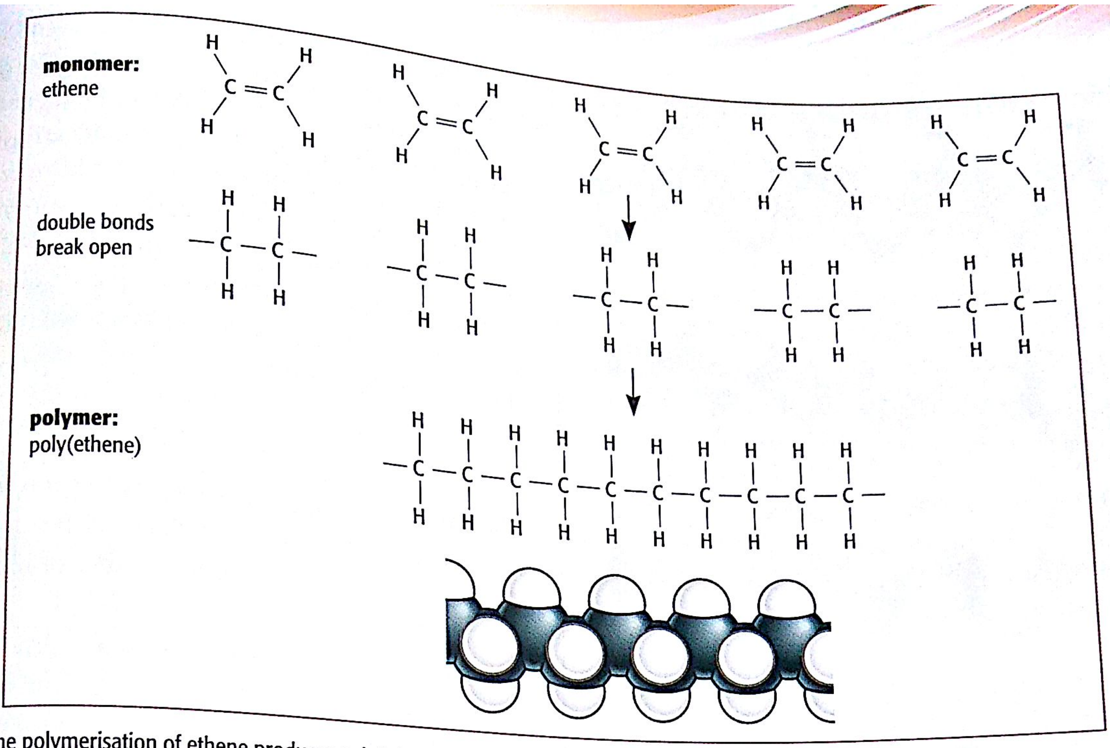
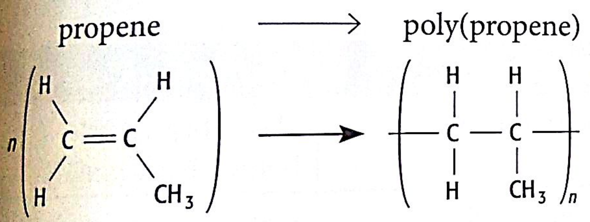


Figure 11.15 The polymerisation of ethene produces poly(ethene), whose structure is shown.

Poly(ethene) was found to be a chemically resistant material that was very tough and durable, and a very good electrical insulator.

Other alkene molecules can also produce addition polymers. Propene will polymerise to produce poly(propene):

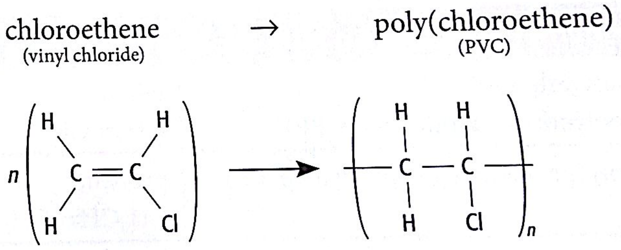


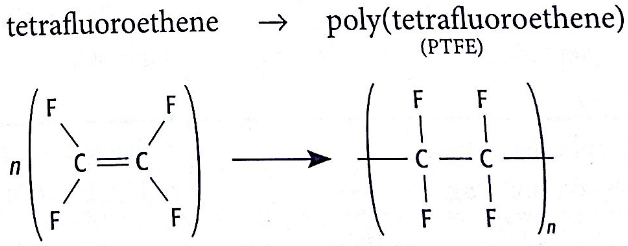
This long-chain molecule is similar in structure to poly(ethene) but with a methyl (—CH_3) group attached to every other carbon atom in the chain (Figure 11.16a). It is commonly referred to by its trade name 'polypropylene'.

Study tip

The diagram of the structure of poly(propene) is quite easy to get wrong. It is important to realise that the —CH_3 group is a side-group here – it does not become part of the chain. The chain is formed by the carbon atoms that are joined by the C=C bond in the monomer.

Chemists also experimented with other substituted alkenes to produce plastics with particular properties in mind. Poly(chloroethene) (known by the trade name of polyvinyl chloride or PVC) and poly(tetrafluoroethene) (known by the trade name of polytetrafluoroethylene, 'Teflon' or PTFE) are two such polymers:





Their structures are shown in Figures 11.16b and c.

Poly(chloroethene) (PVC) was found to be stronger and harder than poly(ethene) and therefore good for making pipes for plumbing. PTFE proved to have some unusual properties: it was very stable at high temperatures and formed a very slippery surface. The properties of some addition polymers are given in Table 11.2. Such synthetic polymers have proved to be very versatile. Many, for example poly(propene), are easy to shape by melting and moulding. Poly(propene) is therefore used to make sturdy plastic objects such as crates. However, it can also be drawn out into long fibres for making ropes.

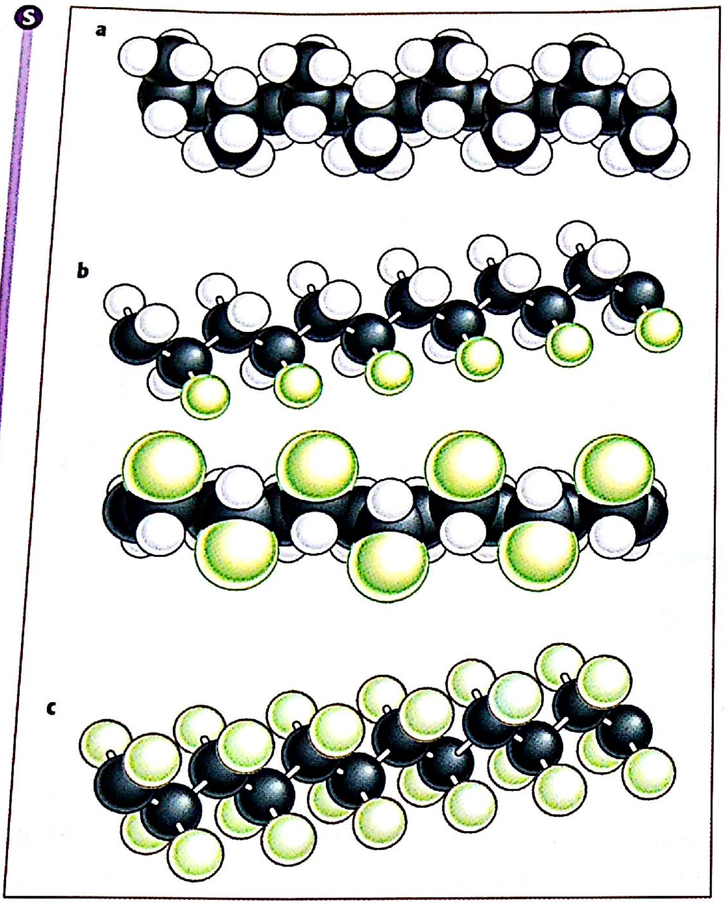


Figure 11.16 The structures of **a** poly(propene), PP, **b** poly(chloroethene), PVC, and **c** poly(tetrafluoroethene), PTFE.

Some of the properties of **addition polymers**:

- All polymers are long-chain molecules made by joining together a large number of monomer molecules.
- Addition polymerisation involves monomer molecules that contain a C=C double bond.
- Addition polymers are homopolymers, made from a single monomer.
- During addition, the double bonds open up and the molecules join to themselves to make a molecule with a very long chain.

Polymer (and trade name(s))	Monomer	Properties	Examples of use
poly(ethene) (polyethylene, polythene, PE)	ethene $CH_2{=}CH_2$	tough, durable	plastic bags, bowls, bottles, packaging
poly(propene) (polypropylene, PP)	propene $CH_3CH{=}CH_2$	tough, durable	crates and boxes, plastic rope
poly(chloroethene) (polyvinyl chloride, PVC)	chloroethene $CH_2{=}CHCl$	strong, hard (not as flexible as polythene)	insulation, pipes and guttering
poly(tetrafluoroethene) (polytetrafluoroethylene, Teflon, PTFE)	tetrafluoroethene $CF_2{=}CF_2$	non-stick surface, withstands high temperatures	non-stick frying pans, non-stick taps and joints
poly(phenylethene) (polystyrene, PS)	phenylethene (styrene) $C_6H_5CH{=}CH_2$	light, poor conductor of heat	insulation, packaging (foam)

Table 11.2 Examples of some widely used addition polymers.

Activity 11.4
Comparing different plastics

Skills

A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate)

A03.3 Make and record observations, measurements and estimates

A03.4 Interpret and evaluate experimental observations and data

ICT skills

Different plastics have been devised for different purposes. This activity explores both the physical property of density and the chemical properties of acid/alkali and solvent resistance of a range of different materials. The results of the investigation can be linked with the uses to which the plastics are put and to a PowerPoint or poster presentation on the impact of plastics on the environment.

A worksheet, with a self-assessment checklist, is included on the CD-ROM.

Questions

11.5 Give the molecular and structural formulae of ethene.

11.6 State what is meant by addition polymerisation and give an equation for the formation of poly(ethene) from ethene.

11.7 Draw the structure of the repeating unit in the following polymers:
  a poly(propene) **b** poly(chloroethene) (PVC).

11.8 What is the monomer used for making Teflon?

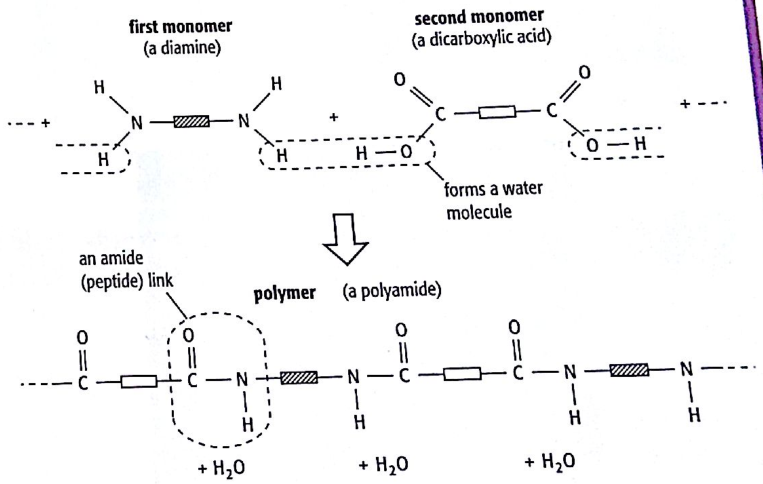
11.9 Give a use for the following polymers:
  a poly(propene) **b** poly(vinyl chloride)
  c poly(tetrafluoroethene).

11.4 Condensation polymerisation

Nylon

In the early 1930s, DuPont were conducting research into artificial fibres. Knowledge of silk and wool gave clues as to how protein molecules are built. Wallace Carothers imitated the linkage in proteins and produced the first **synthetic fibre**, 'nylon'. **Nylon** is a solid when first formed, but it can then be melted and forced through small holes. The long filaments cool, and the fibres produced are stretched to align the polymer molecules and then dried. The fibres can be woven into fabric to make shirts, ties, sheets, etc., or turned into ropes or racquet strings. However, nylon is not just made into fibres. It has proved to be a very versatile material and can be moulded into strong plastic items such as gearwheels.

Nylon is a copolymer of two different monomers, a diamine and a dicarboxylic acid. Each monomer consists of a chain of carbon atoms (which are shown in the following diagrams simplified as blocks). At both ends of the monomers are functional groups. An amine group (—NH_2) on the first monomer reacts with a carboxylic acid group (—COOH) on the second monomer to make a link between the two molecules. Each time a link is made, a water molecule is lost:



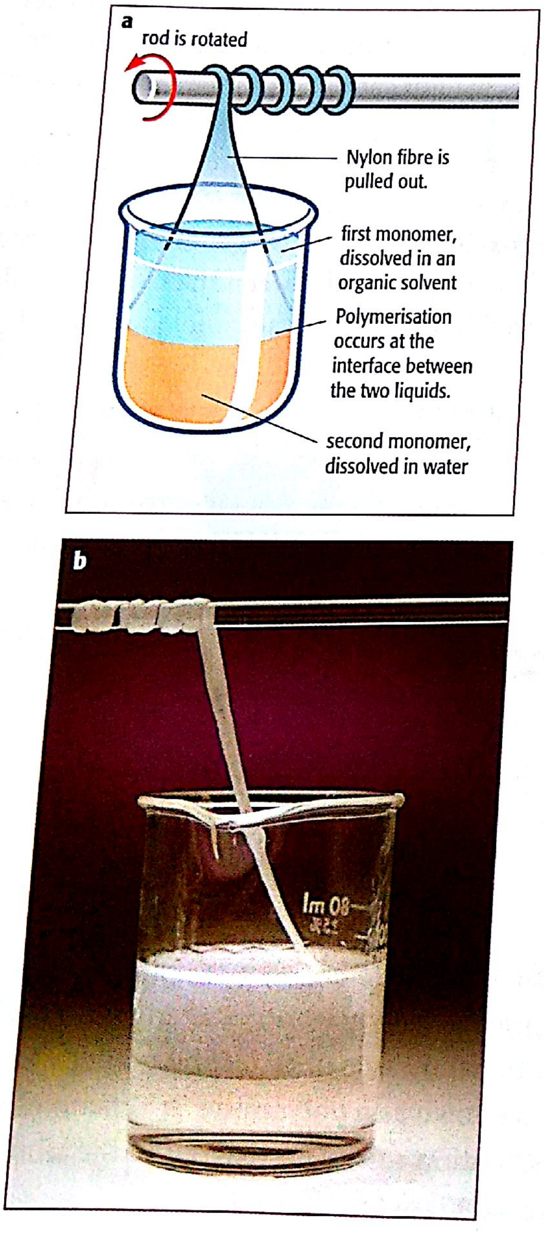
As a result, this type of polymer is known as a **condensation polymer**. Because an **amide link** (or peptide link) is formed during polymerisation, nylon is known as a **polyamide**. A version of nylon polymerisation can be carried out in the laboratory (Figure 11.17, overleaf).

Study tip

Questions on the structure of nylon, and other condensation polymers, are difficult. You will not be asked the detailed structure of the monomers. You can represent the central structure of each monomer as a block, as shown in the diagrams here.

You should know the structure (and name) of the links between the monomers in the chain, though – in this case the peptide link.

It is worth practising these diagrams to make sure you are very familiar with them and can recall them readily.



e 11.17 Nylon is a polyamide and can be made in the laboratory.

Activity 11.5
The nylon rope trick

Skills

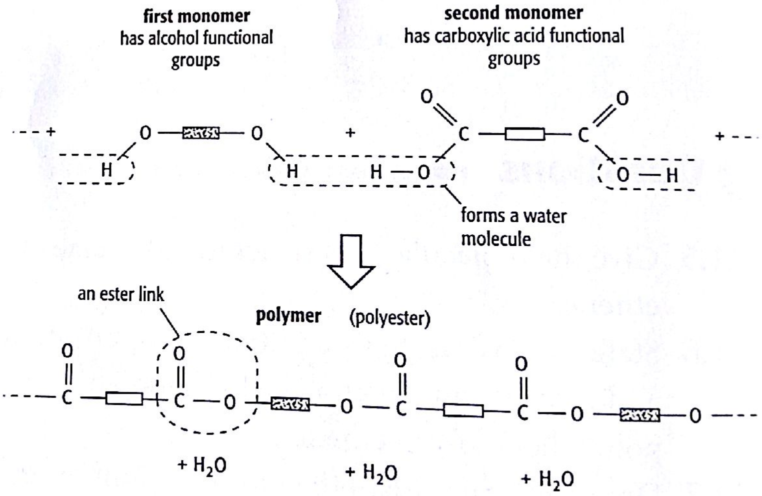
A03.3 Make and record observations, measurements and estimates

This demonstration shows the production of nylon at the interface between two reactant layers. A solution of decanedioyl dichloride in cyclohexane is carefully floated on an aqueous solution of 1,6-diaminohexane. Nylon forms at the interface and can be pulled out as fast as it is produced, forming a long thread – the 'nylon rope' (see Figure 11.17).

A worksheet is included on the CD-ROM.

Polyesters

Condensation polymerisation can also be used to make other polymers with properties different from those of nylon. **Polyesters** are condensation copolymers made from two monomers. One monomer has an alcohol group (—OH) at each end. The other monomer has a carboxylic acid group —COOH) at each end. When the monomers react, an **ester link** is formed, with water being lost each time:



One such polyester has the trade name 'Terylene'. Like nylon, Terylene can be turned into fibres and woven into clothing. Terylene clothing is generally softer than that made from nylon (Figure 11.18).

The ester linkage that joins the monomer units in the man-made fibre Terylene can be broken down by acid or alkaline **hydrolysis**. So it is not good news if spots of alkali fall on your shirts or sweaters!

Figure 11.18 Shirts are often made out of a fabric made of Terylene and cotton.

Comparing synthetic addition and condensation polymers

Some immensely useful synthetic polymers have been made by the two types of polymerisation. Both methods take small molecules and make long repeating chains from them. However, there are differences between the two methods. These are summarised in Table 11.3.

The re-use, recycling and disposal of plastic waste

Plastic rubbish is a common but unwelcome sight around the world. Over the past 30 years, plastics have taken over as replacement materials in many applications. This is not surprising because they are light, cheap and corrosion-resistant, and they can be easily moulded and dyed bright colours. The problem arises because most plastics are not **biodegradable** – there are no natural microorganisms that can break them down.

Some modern plastics are suitable for re-use. Soft-drinks bottles can be made from a plastic with the trade name 'polyethylene terephthalate' (PET) (Figure 11.19). These bottles are sturdy and have

Figure 11.19 Soft-drinks bottles are often made from polyethylene terephthalate, PET.

	Addition polymerisatiom	Condensation polymerisation
monomers used	usually many molecules of a single monomer	molecules of two monomers usually used
	monomer is unsaturated, usually contains a C=C bond	monomers contain reactive functional groups at ends of molecule
reaction taking place	an addition reaction – monomers join together by opening the C=C double bond	condensation reaction with loss of a small molecule (usually water) each time a monomer joins the chain
nature of product	only a single product – the polymer	two products – the polymer plus water (or some other small molecule)
	non-biodegradable	biodegradable
	resistant to acids	hydrolysed by acids

Table 11.3 A comparison of the processes of making synthetic polymers.

several advantages for this particular use.

In some countries, schemes for the re-use of these bottles are operated. However, such a re-use policy is not suitable for most plastics. So what do we do with our waste plastic? We must either recycle it or dispose of it. Recycling is more economical and satisfactory than the alternative, of depositing plastic waste in landfill sites. But there are problems with recycling because most plastic waste is a mixture of different types.

Identification numbers and symbols (Figure 11.20) are in use to identify different plastics for recycling. Methods of sorting plastic waste by optical scanners, or manually, are being introduced. Once sorted, alternative treatments are available for recycling the different types of plastic waste.

Incineration can be used to burn plastic waste, though care must be taken not to release toxic fumes into the air. Incineration of PVC, for instance, can release acidic fumes of hydrogen chloride. **Pyrolysis** – the burning of the plastic waste at around 600 °C in the absence of air – is an alternative to incineration. Most of the products from pyrolysis can be used as fuels or separated by fractional distillation. They can then be made into monomers for making more plastics. Research is also being carried out to produce plastics that are biodegradable or **photodegradable** (can be broken down by the action of light). A poly(ethenol) plastic has been developed that is soluble in hot water.

Biological polymers

All living organisms rely on polymers for their existence. These polymers range from the very complex DNA that makes life itself possible to the more straightforward proteins and carbohydrates that keep living things 'running'.

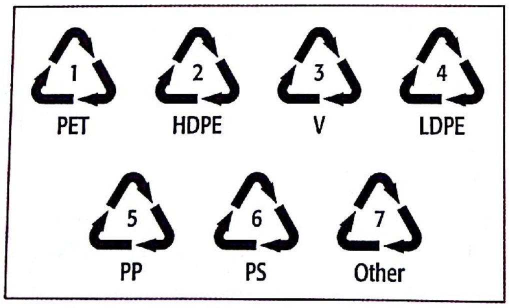
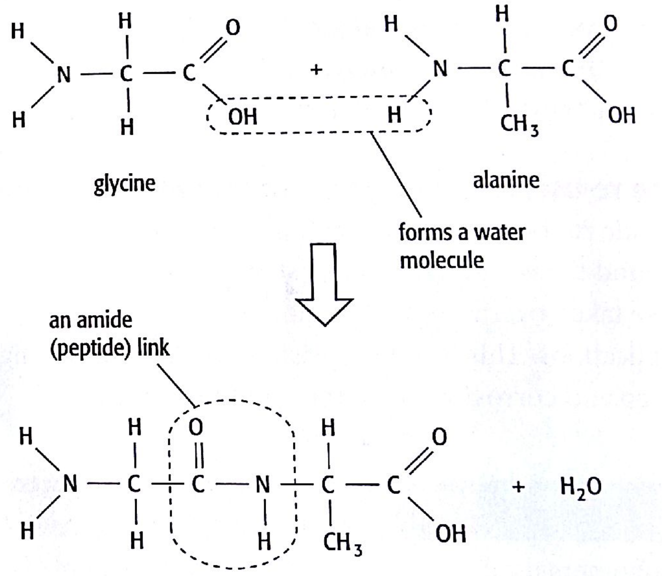


Figure 11.20 Different identification symbols help with the sorting of plastics for recycling. The symbols stand for the following plastics: 1 = polyethylene terephthalate (PET); 2 = high-density poly(ethene); 3 = vinyl polymers such as PVC; 4 = low-density poly(ethene); 5 = poly(propene); 6 = poly(styrene); 7 = others, such as multi-layer plastics.

Proteins

Proteins are what cells are made of. All the tissues and organs of our bodies are made up of protein. In addition, enzymes, which are responsible for controlling the body's chemical reactions, are proteins. DNA makes life possible and allows living things to reproduce, but without proteins there would be no structure or chemistry to keep the living things going.

Proteins are built from **amino acid** monomers. There are 20 different amino acids used, and they each contain two functional groups —NH_2 and —COOH. Glycine and alanine are two of the simplest amino acids. When they react together, an amide linkage (or peptide linkage) is formed to produce a **dipeptide** (two amino acids joined together):



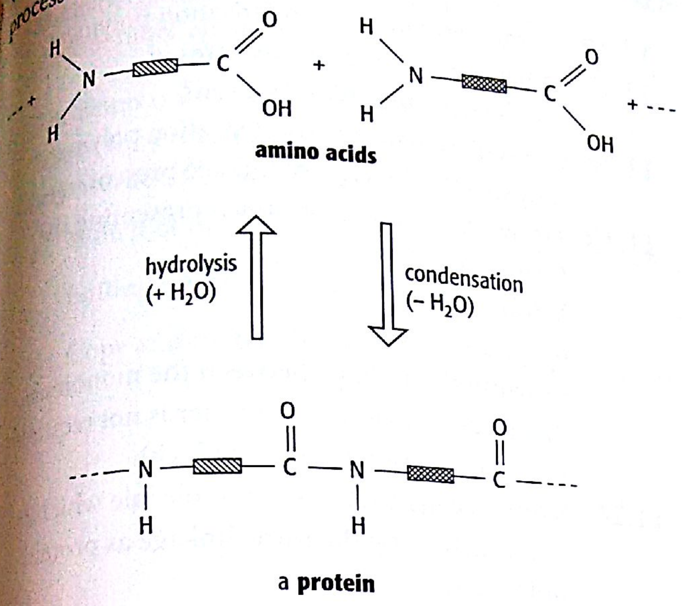
a **dipeptide**

When this is repeated many times using the different amino acids, a polymer is formed. Short polymers (up to 15 amino acids) are known as **peptides**. Chains with between 15 and 100 amino acids are known as **polypeptides**. Chains involving more than 100 amino acids are called **proteins**.

Protein analysis

Proteins can be hydrolysed (broken down) to amino acids by heating in concentrated hydrochloric acid.

(6 mol/dm³). This is the reverse of the condensation process that formed them:



The mixture of amino acids can then be separated by chromatography (see page 31). Amino acids are colourless substances, so a locating agent is used. The locating agent reacts with the amino acids to produce coloured spots.

Activity 11.6
Chromatography of amino acids

Skills

A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate)
A03.2 Plan experiments and investigations
A03.3 Make and record observations, measurements and estimates
A03.4 Interpret and evaluate experimental observations and data
A03.5 Evaluate methods and suggest possible improvements

The artificial sweetener aspartame contains two amino acids: aspartic acid and phenylalanine. In this activity, aspartame is hydrolysed by heating with hydrochloric acid and the hydrolysed product is then analysed by paper chromatography using amino acid standards to demonstrate their identity. The amino acids are located using a UV lamp or ninhydrin spray.

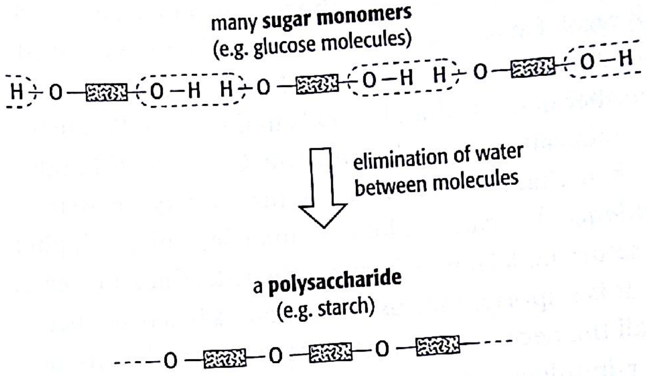
A worksheet, with a self-assessment checklist, is included on the CD-ROM.

Carbohydrates

The sugar we use to sweeten our tea or coffee is sucrose ($C_{12}H_{22}O_{11}$). This is just one example of a carbohydrate; glucose ($C_6H_{12}O_6$) is another.

Carbohydrates are an important source of energy in our bodies, and in all living organisms. A carbohydrate is a compound containing carbon, hydrogen and oxygen only. The ratio of hydrogen to oxygen is always 2 : 1 (as in water).

All long-chain carbohydrates (**polysaccharides**) are long-chain condensation polymers of sugar molecules (monosaccharides). **Starch**, for example, is a polysaccharide found in plants. Condensation polymerisation of sugar monomers produces such long-chain carbohydrates.



Starch and glycogen are two different polysaccharides of glucose, a monosaccharide. They store the glucose in an insoluble form in plants and animals, respectively. When energy is needed, cells break down the starch or glycogen back to glucose. The glucose is then oxidised by respiration. Cellulose is a third polymer of glucose. It forms the fibrous structure of plant cell walls. These three polymers differ in the way in which the glucose monomer units are linked together.

Polysaccharides can be broken down in the laboratory by warming with hydrochloric acid (acid **hydrolysis**). The sugars present in the hydrolysis mixture can then be analysed by chromatography (see page 31). A locating agent must be used to detect the spots, because sugars are colourless. An interesting comparison is to analyse the products of the acid and enzyme digestions of starch. Acid hydrolysis breaks down starch to give glucose. However, the enzyme amylase present in human saliva only breaks starch down to give maltose. This is a molecule made of two glucose units joined together. The difference can be seen on chromatography of the products.

S The presence of starch can be detected by testing with iodine solution: the solution turns a deep blue colour.

Food

Proteins and carbohydrates are two of the main constituents of food. They, together with fats, are all digested by cells and organisms and are converted back to their monomers. These monomers are then used as the building blocks for new molecular structures or as sources of energy. Our bodies can make a whole range of molecules necessary for our cells to function properly. However, some of these building blocks must come from our diet. For instance, there are some amino acids that we must obtain from our food. These are known as the **essential amino acids**.

Fats and oils are mixtures of large molecules that are the esters of long-chain carboxylic acid molecules and glycerol. Fats that contain unsaturated acids are called unsaturated or polyunsaturated fats, depending on the number of C=C double bonds in the chain. Fats that contain saturated acids, with only C—C single bonds in their chains, are known as saturated fats. There is evidence that eating a lot of animal fat, which is higher in saturated fats, may increase the risk of heart disease.

It is important for us to maintain a balanced diet of all the necessary components of our food, without over-indulgence in any aspect.

Questions

11.10 Name two natural condensation polymers.

11.11 What are the essential features of condensation polymerisation?

11.12 Name two artificial condensation polymers, and specify the type of linkage present in each.

11.13 Draw schematic diagrams representing the formation of:

a Terylene

b starch

showing the linkage between the monomers (the structure of the monomer is not required and can be represented as a block).

11.14 Nylon is a synthetic macromolecule which is held together by the same linkage as protein molecules.

a What is the name of this linkage?

b Draw a diagram of the structure of nylon (again, the structure of the monomer is not required and can be represented as a block).

c Give a major difference between the structure of nylon and of a protein.

d How can proteins be chemically broken back down to amino acids?

Summary

You should know:

- that the three major fossil fuels are coal, petroleum (crude oil) and natural gas
- how these resources provide energy and also a wide variety of chemicals
- that fractional distillation of petroleum provides a series of different hydrocarbon fractions, each with its own uses
- how these hydrocarbon fractions can be further changed by processes such as catalytic cracking, producing shorter-chain alkane molecules and alkenes from the original longer chains
- how alkene and other unsaturated molecules can be polymerised to form a range of useful addition polymers
- S that plastics made by addition polymerisation are generally non-biodegradable and pose problems for waste disposal
- S that condensation polymerisation is another means by which monomers can join together to make polymeric molecules
- S how there are both significant natural (e.g. proteins and carbohydrates) and synthetic (e.g. nylon and polyesters) condensation polymers
- S that condensation polymers can be hydrolysed both by enzymes and by concentrated acid
- S that proteins and carbohydrates are two of the main constituents of our food.

End-of-chapter questions

1 Methane, gasoline (petrol) and ethanol are all commonly used as fuels. Why are both methane and ethanol more environmentally friendly than gasoline?

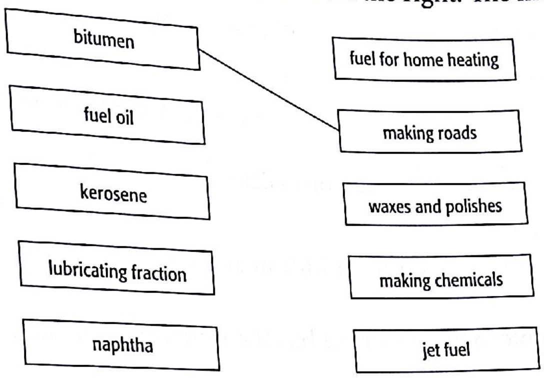
2 Petroleum is a mixture of hydrocarbons.

Two of the processes carried out in an oil refinery are fractional distillation of petroleum and cracking of hydrocarbon fractions.

a Which of the following properties of hydrocarbons is used to separate petroleum into fractions?

boiling point **chemical reactivity** **electrical conductivity** **melting point** [1]

b Copy and match the fractions on the left with their uses on the right. The first one has been done for you.



[4]

c Cracking is used to break down long-chained alkanes into shorter-chained alkanes and alkenes.

i State two conditions needed for cracking. [2]

ii The hydrocarbon, $C_{14}H_{30}$, can be cracked to make ethene and one other hydrocarbon. Complete the equation for this reaction. [1]

$C_{14}H_{30} \rightarrow C_2H_4 +$ ....

iii Draw the full structure of ethene showing all atoms and bonds. [1]

d State the name of the polymer formed from ethene. [1]

e Ethene is used to make ethanol.

i Which substance is needed for this reaction? [1]

ammonia **hydrogen** **oxygen** **steam**

ii Phosphoric acid is a catalyst in this reaction. What do you understand by the term *catalyst*? [1]

[Cambridge IGCSE® Chemistry 0620/21, Question 7, June 2010]

3 Ethene, C_2H_4, is manufactured by cracking petroleum fractions.

a i What do you understand by the term *petroleum fraction*? [1]

ii Complete the equation for the manufacture of ethene from dodecane, $C_{12}H_{26}$. [1]

$C_{12}H_{26} \rightarrow C_2H_4 +$ ....

b Two fractions obtained from the distillation of petroleum are refinery gas and gasoline. State **one** use of each of these fractions. [2]

c Ethene is an unsaturated hydrocarbon.
What do you understand by the terms **unsaturated** and **hydrocarbon?** [2]

d Ethene is used to make ethanol.

i Which of these reactions is used to make ethanol from ethene?

catalytic addition of steam **fermentation**
oxidation using oxygen **reduction using hydrogen** [1]

ii Draw the structure of ethanol showing all atoms and bonds. [2]

e Ethene is used to make poly(ethene).
Copy and complete the following sentences about this reaction. Use words from the list below.

additions **carbohydrates** **catalysts** **monomers** **polymers**

The ethene molecules which join to form poly(ethene) are the ....
The poly(ethene) molecules formed are .... [2]

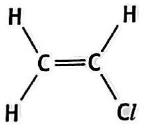
[Cambridge IGCSE® Chemistry 0620/21, Question 7, November 2010]

4 Monomers polymerise to form polymers or macromolecules.

a **i** Explain the term *polymerise.* [1]

ii There are two types of polymerisation – addition and condensation. What is the difference between them? [2]

b An important monomer is chloroethene which has the structural formula shown below.



It is made by the following method.

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \text{ dichloroethane}$$

This is then heated to make chloroethene.

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$

i Ethene is made by cracking alkanes. Complete the equation for cracking dodecane.

$$C_{12}H_{26} \rightarrow \text{....................} + 2C_2H_4$$ [1]

Another method of making dichloroethane is from ethane.

$$C_2H_6 + 2Cl_2 \rightarrow C_2H_4Cl_2 + 2HCl$$

ii Suggest a reason why the method using ethene is preferred. [1

iii Describe an industrial method of making chlorine. [2

iv Draw the structural formula of poly(chloroethene). Include three monomer units. [2

[Cambridge IGCSE® Chemistry 0620/31, Question 5, November 2010]

5 Structural formulae are an essential part of organic chemistry.

a Draw the structural formula of each of the following. Show all the bonds in the structure.

i Ethanoic acid [1

ii Ethanol [1

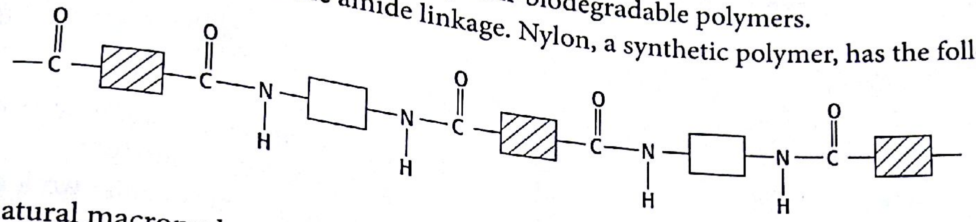
b **i** Ethanoic acid and ethanol react to form an ester. What is the name of this ester? [1]

ii The same linkage is found in polyesters. Draw the structure of the polyester which can be formed from the monomers shown below.

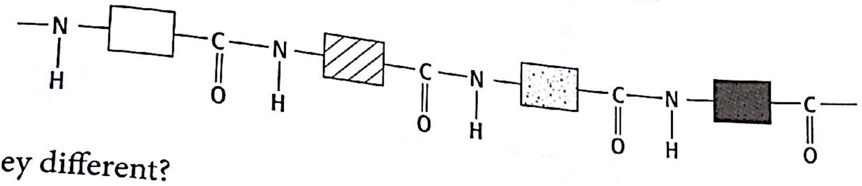
$HOOC—C_6H_4—COOH$ and $HO—CH_2—CH_2—OH$ [3]

iii Describe the pollution problems caused by non-biodegradable polymers. [2]

c Two macromolecules have the same amide linkage. Nylon, a synthetic polymer, has the following structure.



Protein, a natural macromolecule, has the following structure.



How are they different?

[2]

[Cambridge IGCSE® Chemistry 0620/31, Question 6, November 2011]