

Chapter 1

Ethylene and addition polymers

Chapter 2

Condensation polymers and biomass

Chapter 3

Ethanol and biofuels

Chapter 4

Electrochemistry and batteries

Chapter 5

Nuclear chemistry and radioisotopes

PRODUCTION OF MATERIALS



HSC MODULE 1



Chapter

1

ETHYLENE AND ADDITION POLYMERS

Introduction

Do you travel to school each day by bus or car? If so, then your journeys have been made possible by the work of many chemists, physicists, engineers and technicians. Buses and other motor vehicles are constructed from metals and metal alloys, as well as a range of plastics and other organic materials that have been developed and modified by the work of scientists. The fuel to power these vehicles has been processed and modified by chemists and chemical engineers. Research chemists in universities and industry play an important role in developing new materials from carbon-based compounds found in nature.

Petroleum is a raw material used to manufacture a vast array of important products in our society. Fossil fuels such as petroleum and coal are non-renewable resources. As fossil organic reserves dwindle, new sources of organic chemicals have to be developed. In this chapter we examine the importance of polymers produced by the petrochemical industry.

In this chapter

- I.1 Alkenes and ethylene
- I.2 Addition polymerisation

page 3

page 17

Figure 1.1

Chemists take the raw materials of nature and make them into the useful materials that we use in our society. The fuel needed for journeys to school and many other products that you use every day are made from the raw material petroleum.

1.1 ALKENES AND ETHYLENE

Remember

Before beginning this section, you should be able to:

- identify and use the IUPAC nomenclature for describing straight-chained alkanes and alkenes from C1 to C8
- compare and contrast the properties of alkanes and alkenes C1 to C8 and use the term ‘homologous series’ to describe a series with the same functional group
- describe the use of fractional distillation to separate the components of petroleum and identify the uses of each fraction obtained.

Key content

By the end of this section, you should be able to:

- construct word and balanced-formula equations of chemical reactions as they are encountered
- identify the industrial source of ethylene from the cracking of some of the fractions from the refining of petroleum
- identify that ethylene, because of the high reactivity of its double bond, is readily transformed into many useful products
- gather and present information from first-hand or secondary sources to write equations to represent all chemical reactions encountered in the HSC course
- identify data, plan and perform a first-hand investigation to compare the reactivities of appropriate alkenes with the corresponding alkanes in bromine water.

Sunflower oil can be used to replace petroleum diesel in diesel engines.

paraffins: common name for alkanes

saturated hydrocarbon: a hydrocarbon that contains only single C—C bonds and the maximum number of hydrogen atoms per carbon. Alkanes are saturated hydrocarbons.

The naming of naphthenes and aromatic molecules is not required in this course.

Revisiting petroleum refining

Many of the important materials in our society start their ‘lives’ at an oil refinery. Australia is not self-sufficient in petroleum, and supplies are imported from various locations overseas. The process of fractional distillation of petroleum was studied in the *Preliminary Course*. Let us briefly recall the major ideas.

- Petroleum is a mixture of crude oil and natural gas.
- Crude oil is separated into *fractions* using the process of fractional distillation. Each fraction contains a mixture of molecules that have a specified range of boiling points.
- The composition and boiling ranges of these fractions vary somewhat from one refinery to another (see Table 1.1).

Table 1.1 Typical crude oil fractions and uses

Boiling range (°C)	Carbon atoms/chain	Name of fraction	Common uses
<30	1–4	refinery gas	natural gas, bottled gas
30–125	5–8	gasoline (petrol fraction)	car fuel, petrochemical feedstock, solvents
90–220	7–13	gasoline (naphtha fraction)	cracking into smaller molecules to make more petrol and alkenes
175–275	11–16	kerosene	home heating, aviation fuel, conversion to petrol ('cracking')
260–340	15–18	diesel oil	furnace fuel, diesel engines, conversion to petrol ('cracking')
>350	16–40	lubricating and fuel oils, paraffin waxes	lubricants, clear waxes and polishes
>400	>40	residue	asphalt (bitumen road surfaces)

- Light fractions with lower boiling points rise higher in the fractionating column. Heavier fractions with higher boiling points are collected from lower in the column.
- Each fraction is composed of **paraffins**, naphthenes and/or aromatics. The proportions of these components vary considerably from one oilfield to another across the world.
- Paraffins are hydrocarbon molecules with single covalent bonds between neighbouring carbon atoms. They are examples of **saturated hydrocarbons**. They are also called *alkanes*. The alkanes are predominantly straight chained with a smaller number of branched-chain molecules.
- Naphthenes are ring-shaped, saturated molecules that are also called *cycloalkanes* or *cycloparaffins*. Their boiling points are higher than those of the equivalent paraffin molecules.
- Aromatics are ring molecules based on benzene (C_6H_6).



Figure I.2

A typical fractionating tower in an oil refinery. Temperatures range from about 350°C at its base to a mere 20°C at the top.

Paraffins	Naphthenes	Aromatics
<pre> H H H H H H C---C---C---C---C---H H H H H H </pre> <p style="text-align: center;">hexane</p>	<pre> H H H---C---C---H H C---C---H H H H---C---C---H H H H </pre> <p style="text-align: center;">cyclohexane</p>	<pre> H H---C---C=---C---H H---C---C=---C---H H H </pre> <p style="text-align: center;">benzene</p>
<pre> H H---C---H H H---C---C---H H---C---H H H---C---C---H H H </pre> <p style="text-align: center;">2,2,4-trimethylpentane</p>	<pre> H H---C---H H---C---C---H H---C---H H---C---H H H </pre> <p style="text-align: center;">1,4-dimethylcyclohexane</p>	<pre> H H---C---C=---C---H H---C---C=---C---H H H H---C---H H H </pre> <p style="text-align: center;">toluene</p>

Figure I.3

Paraffins, naphthenes and aromatics are components of petroleum fractions.

SYLLABUS FOCUS

1. NAMING HYDROCARBONS AND THEIR ISOMERS

The rules for chemical nomenclature are laid down by the International Union of Pure and Applied Chemistry (IUPAC). Although we covered the rules for naming alkanes and alkenes in the preliminary course, let us review the major ideas here.

Straight-chain alkanes (C_nH_{2n+2})

In IUPAC nomenclature, the name of each alkane is a combination of a *stem* and a common *suffix*. The suffix used for all alkanes is ‘-ane’. The names for each stem are summarised in the table below:

Stems for naming hydrocarbons. (n = number of carbon atoms per molecule.)

n	1	2	3	4	5	6	7	8
Stem	meth	eth	prop	but	pent	hex	hept	oct

Example: If $n = 4$, the straight-chain alkane is called *butane*.

The molecular formulae, condensed structural formulae and structural formulae for pentane and heptane, both straight-chain alkanes, are shown in Figure 1.4.

Example 1: pentane

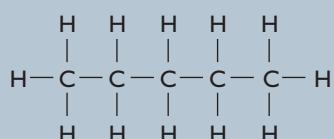
Molecular formula



Condensed structural formula



Structural formula



Example 2: heptane

Molecular formula



Condensed structural formula



Structural formula

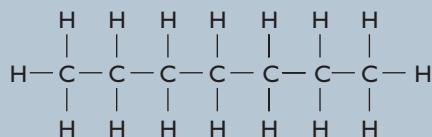


Figure 1.4

Nomenclature, molecular formulae, condensed structural formulae and structural formulae for several straight-chain alkanes.

Branched-chain alkanes (C_nH_{2n+2})

Many alkanes consist of branched chains. The molecules can be considered as a straight-chain alkane with small hydrocarbon chains branching off the main (or parent) chain. The smaller hydrocarbon chains often contain one or two carbon atoms. They are named after their parent alkanes and are collectively called *alkyl groups*. Methyl groups ($—CH_3$) and ethyl groups ($—C_2H_5$) are common.

The rules for naming branched-chain alkanes are described below.

Naming branched-chain alkanes

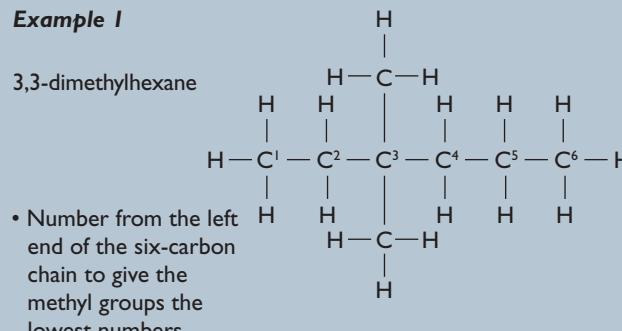
- Select the longest unbranched chain. This is the main chain. Identify the number of carbons in the main chain and select the appropriate naming stem.
- Locate and identify the alkyl groups branching from the main chain.
- Number the chain from an end so that the alkyl **functional groups** have the lowest set of location numbers. These positions are called *locants*.
- Name the alkyl functional groups using prefixes before the name of the main parent chain. Use locants to identify their positions where required to avoid ambiguity.
- When more than one alkyl functional group is present, name them in alphabetical order.

Names of alkyl functional groups

—CH_3	$\text{—C}_2\text{H}_5$	$\text{—C}_3\text{H}_7$	$\text{—C}_4\text{H}_9$	$\text{—C}_5\text{H}_{11}$
methyl	ethyl	propyl	butyl	pentyl

Figure 1.5 provides examples of the use of this system of nomenclature.

Example 1



Example 2

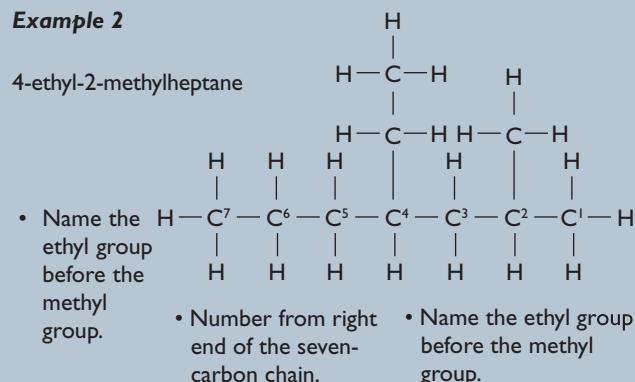


Figure 1.5

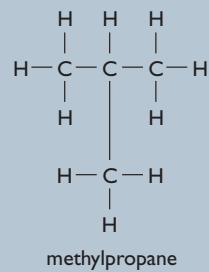
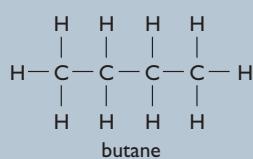
Use the IUPAC nomenclature rules to name the branched-chain alkanes.

Branched-chain alkanes are **isomers** of straight-chain alkanes.

Example: An alkane with the molecular formula C_4H_{10} could be either a straight-chain alkane (butane) or a branched-chain alkane (methylpropane). Thus butane and methylpropane are isomers. Their physical and chemical properties are similar but not identical.

Figure 1.6 shows some examples of straight-chain and branched-chain isomers of alkanes.

Isomers of butane



Isomers of hexane

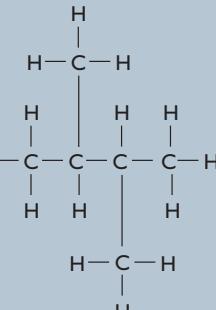
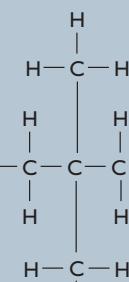
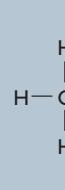
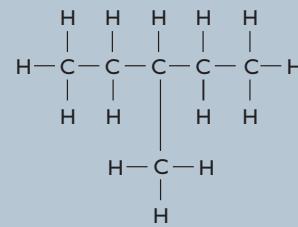
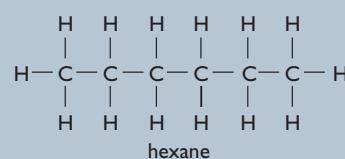


Figure 1.6

Use the IUPAC nomenclature rules to name the isomers of alkanes.

Alkenes (C_nH_{2n})

Alkenes are examples of **unsaturated hydrocarbons** as they have less than the maximum number of hydrogen atoms per molecule.

The carbon–carbon double bond in alkenes is also an example of a functional group. The presence of this double bond in the hydrocarbon chains alters the properties of the molecule. The different positions of the double bond within the hydrocarbon chain lead to the formation of different structural isomers.

The rules for naming alkenes are described below.

Naming alkenes

- Select the longest unbranched chain that contains the double bond. Identify the number of carbons in this main chain and select the appropriate stem for the name of the alkene.
- Number the main chain from the end that gives the smallest locant (or location number) to the double bond.
- According to the recently revised IUPAC nomenclature rules, name the alkene by placing the locant of the first carbon of the double bond in front of the '-ene' suffix (e.g. hept-2-ene). IUPAC also recognises alternative systematic naming rules in which the locant is placed in front of the name of the alkene (e.g. 2-heptene).
- If there are any alkyl functional groups attached to the main chain, name them alphabetically. Use locants to show their positions along the chain.

Figure 1.7 shows examples of the naming rules for branched and unbranched alkenes. Note the use of commas and dashes.

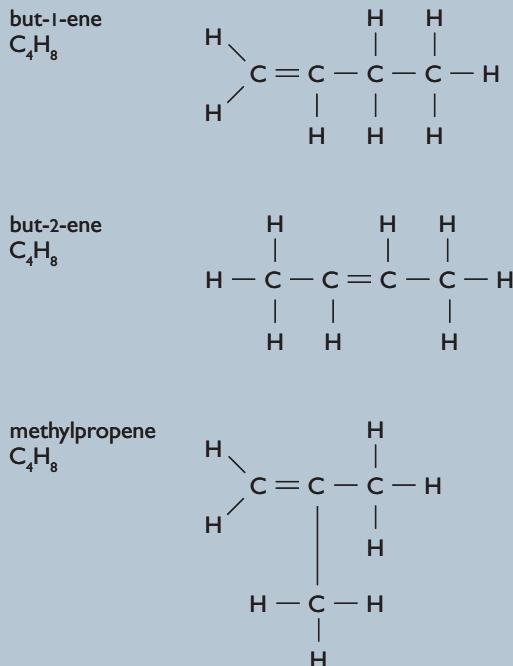


Figure 1.7

Use the IUPAC nomenclature rules to name the alkenes and their isomers.

functional group: a group of atoms attached to or part of a hydrocarbon chain, which controls the physical and chemical properties of the molecule

isomers: molecules with the same molecular formula but different structural formulae

unsaturated hydrocarbon: a hydrocarbon containing less than the maximum number of hydrogen atoms per molecule. Alkenes (containing a C=C or double bond) and alkynes (containing a C≡C or triple bond) are examples of unsaturated hydrocarbons.

catalytic cracking: decomposition of long-chain molecules into smaller chains, when heated with a catalyst.

Hydrocarbon cracking

The petrol derived from the gasoline fraction is insufficient to meet the need for this fuel in Australia and overseas. A proportion of the heavier fractions (such as naphtha, kerosene and diesel) must be broken down into smaller hydrocarbon chains to produce sufficient quantities of petrol to supply the increasing number of vehicles on our roads. Many of the smaller molecules that were formed by the cracking process are branched-chain hydrocarbons, and these types of molecules are better fuels than straight-chain molecules because they cause less engine 'knock' or 'pinging' as they combust. The octane rating system is used to measure the degree of engine knocking that various fuels produce.

Long-chain hydrocarbons can be broken down into smaller chains by a process called *cracking*. Thermal cracking and **catalytic cracking** are two procedures that are commonly used. Ethylene (ethene) is one of the important products of the cracking process.

Thermal cracking of naphtha

Thermal (or steam) cracking is commonly used at the Orica petrochemical plant in Botany, Sydney. It provides a high yield of ethylene. Long pyrolysis coils are used to heat the hydrocarbon feedstocks and steam to about 750–900°C inside the furnace. Furnaces may contain 100 such coils each up to 80 m in length. There are three main steps in the process: initiation, propagation and termination.

Initiation

Free radicals are produced when the hydrocarbon chains are split into fragments at high temperatures. These radicals are reactive, as they have an unpaired electron.

Propagation

The free radicals decompose to produce smaller free radicals and release alkenes such as ethylene.

Termination

Hydrocarbon molecules can reform when free radicals react with other free radicals. These hydrocarbons can be recycled for further cracking.

Example: Cracking of decane

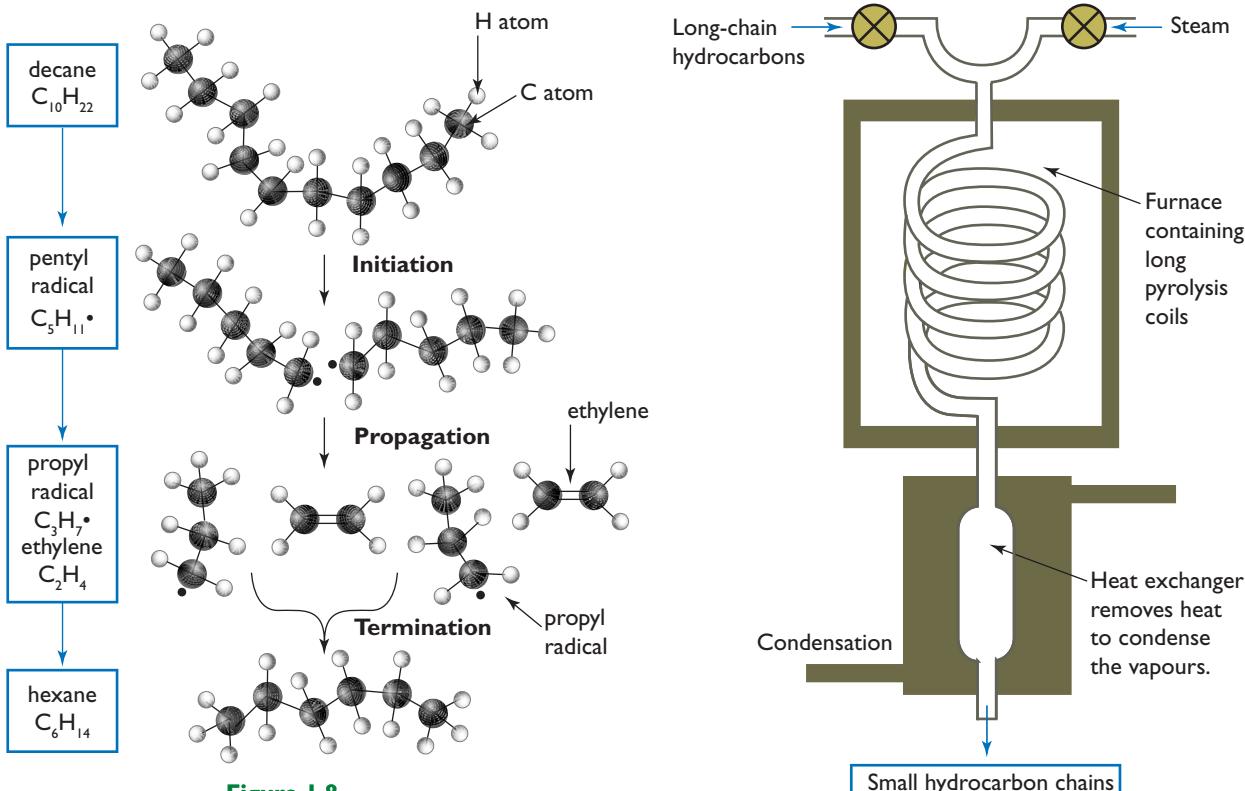
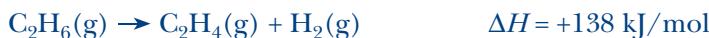


Figure 1.8

A typical thermal cracker operates at about 750–900°C.

Thermal cracking of ethane

Ethylene can also be produced by the cracking of ethane (C_2H_6). The vast oil and gas fields of the Cooper Basin in the central Australian desert supply the liquefied natural gas (LNG) from which ethane can be extracted. The natural gas from this field consists of about 9% ethane. Ethane is now used as a feedstock in the Orica's Botany plant. Ethane is cracked (at 850°C) to form ethylene and hydrogen. The mixture of products once formed is rapidly cooled to prevent reaction reversal. Steam is generated for this process using the waste heat. If the products are allowed to stay too long at the high temperatures they decompose to form carbon.



This reaction is endothermic. Higher yields of ethylene are, therefore, favoured by higher temperatures.

SYLLABUS FOCUS

2. USING INSTRUCTION TERMS CORRECTLY

When answering questions it is important to know what the instruction terms ('verbs') require you to do. Here are some examples:

'Identify'

This instruction word requires you to recognise and name a substance, process, event or person.

Example:

Identify the raw material from which kerosene is extracted.

Answer:

Petroleum or crude oil undergoes fractional distillation and kerosene is one of the fractions that is recovered from the fractionating tower.

'Describe'

This verb requires you to provide characteristics or features of a substance or process.

Example:

Describe the conditions under which naphtha can be thermally cracked.

Answer:

The naphtha and steam are heated to about 750–900°C in long pyrolysis coils inside the furnace.

SAMPLE PROBLEM I.I

SOLUTION

Identify the safety issues in the industrial process of thermal cracking.

The verb 'identify' requires you to recognise and name the safety issues in this process.

Fire is the major risk. There is the potential for leaks of flammable hydrocarbon vapours from this closed process. Steam build-up has the potential to cause explosions if the structural integrity of the equipment is not continuously monitored and maintained. Some hazardous gases (e.g. CO, H₂S) are produced and ventilation is essential to avoid poisoning if leaks occur.

Catalytic cracking

In modern society the demand for petrol is very high. This demand is not met by fractional distillation of crude oil alone. To boost the supplies of petrol, very long-chain hydrocarbons (C₂₅ to C₁₀₀) are cracked into smaller chains. The process used is called *catalytic cracking*. The heavy crude oil is heated in the presence of a catalyst composed of a zeolite (an aluminium silicate). The many cavities and channels inside the porous catalyst provide a high internal surface area for reaction. Lower temperature (about 500°C) can then be used and this produces considerable savings in energy. Hydrogen atoms are removed from the hydrocarbons onto the catalyst's surface. The positive hydrocarbon ion that forms undergoes further reactions leading to the formation of the final products.

Catalytic cracking can also yield small molecules such as ethylene or propene. These hydrocarbons can be recovered and used by the petrochemical industry. In the example below, the 2-methylheptane is a branched-chain isomer of octane. This branched-chain molecule will have a higher octane rating if used as a fuel.

Example:



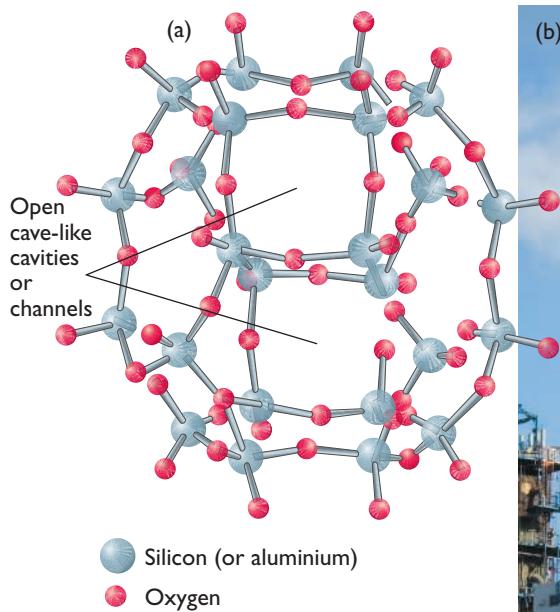


Figure 1.9

- (a) Zeolite catalyst structure;
- (b) Photo of a typical catalytic cracking unit

SYLLABUS FOCUS

3. WRITING CHEMICAL EQUATIONS

You are required in the HSC course to construct word and balanced-formula equations for all the reactions studied.

The following information summarises the steps involved in writing a balanced symbolic equation:

- Reactants are the chemicals that are allowed to react. Their formulae are written on the left-hand side of the arrow.
- Products are the chemicals produced in the reaction. Their formulae are written on the right-hand side of the arrow.
- Write the word equation for the reaction.
- Write the chemical formula for each reactant and product.
- Check each side of the equation for atom conservation.
- If the atom numbers are unbalanced, place coefficients in front of each formula until you have balanced them. Re-check that the atoms are now balanced.
- Use standard abbreviations to write the ‘state’ next to each reactant and product:
(s) = solid; (l) = liquid; (g) = gas; (aq) = aqueous or dissolved in water.

Worked example: Cracking of hexane vapour

Reactants: hexane

Products: propene; hydrogen

- Word equation:



- Write the correct formula for each substance:



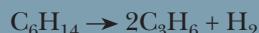
- Check for atom conservation:

Reactants: C = 6; H = 14

Products: C = 3; H = 8

Atoms do not balance.

- Insert coefficients to balance the atoms:



- Re-check atom balance:

Reactants: C = 6; H = 14

Products: C = 6; H = 14

Atom balance has been achieved. The equation is balanced.

- Insert states:



Alkanes, alkenes and their chemical properties

Alkanes and alkenes are non-polar molecules. They are insoluble in water but soluble in many other non-polar solvents such as benzene, turpentine and kerosene.

Alkanes are commonly called *paraffins* (Latin: *little affinity*) because of their relative unreactivity towards many common chemical reagents. In order to make alkanes react with reactive molecules such as chlorine, UV light is used to produce reactive free radicals.

Alkenes are often called *olefins* (Latin: *oil loving*) due to their oily nature compared with alkanes. Alkenes are more reactive molecules due to the high electron density of the double bond. Electronegative elements (such as chlorine, bromine and oxygen) are attracted to the double bond and electrons are transferred as they react.

Alkenes commonly react with molecules such as chlorine, bromine, hydrogen chloride and water by a process called **addition**. When hydrogen gas reacts with an alkene in the presence of a suitable catalyst (e.g. nickel), the process is called **hydrogenation**. Hydrogenation is an important reaction in the food industry where the proportion of double bonds to single bonds in fat molecules can be changed by reaction with hydrogen. Liquid fats can be turned into more-solid fats by this procedure.

addition: a chemical reaction in which a small molecule adds across a double or triple bond of a hydrocarbon molecule

hydrogenation: an addition reaction in which hydrogen molecules add onto an unsaturated molecule

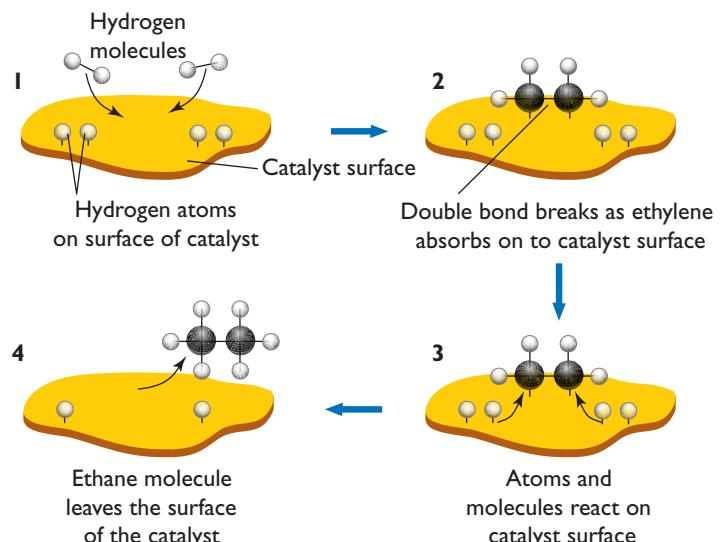


Figure 1.10

A nickel surface is a suitable catalytic site for the hydrogenation of ethylene.

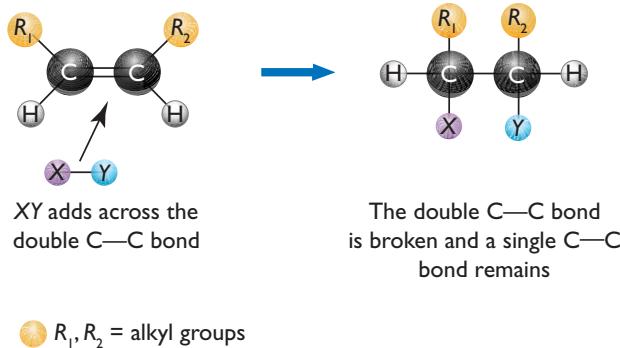


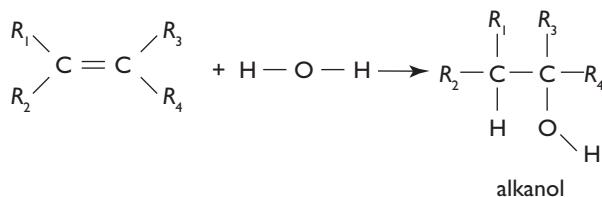
Figure 1.11

When molecules add across the double bond, a substituted alkane forms.

Let us examine some common addition reactions of alkenes.

Hydration

Alkenes will react when heated with water in the presence of a suitable acid catalyst such as phosphoric acid or sulfuric acid. The O—H bond of the water breaks, and a H atom and an OH group add across the double bond, causing it to break. The final product is an alkanol, and the double bond has been destroyed.



$R_1, R_2, R_3, R_4 = \text{alkyl groups}$

Figure 1.12

An alkanol is formed when water adds across a double bond.



BROMINATION OF ETHYLENE

1.1 PRACTICAL ACTIVITIES



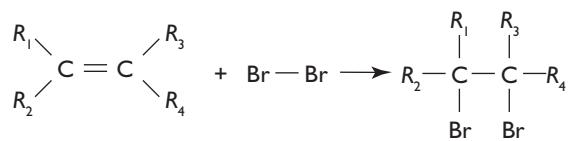
Reactivity of alkanes and alkenes

substitution reaction: a reaction in which hydrogen atoms in a hydrocarbon are replaced by other atoms

Bromination

When an alkene is mixed with a solution of bromine in an organic solvent (such as cyclohexane or chloroform), the bromine molecule reacts with the double bond and bromine atoms add across the double bond. The final product is called a *dibromoalkane*. The nomenclature of haloalkanes is discussed in HSC Module 3 (Chemical monitoring and management).

Decolourisation of the bromine solution indicates that the addition reaction has occurred. Where the decolourisation of bromine is used to test for the presence of unsaturation in hydrocarbons, it is important to exclude UV light as this will promote a **substitution reaction** with alkanes, and the bromine solution will also slowly decolourise.



A dibromoalkane

Figure 1.13

A dibromoalkane is formed when bromine adds across the double bond (in an organic solvent).

SYLLABUS FOCUS

4. FURTHER EXAMPLES OF THE REACTIONS OF ALKENES

Use this additional information to extend your knowledge of the reactivity of double bonds and the useful products that can be obtained. Ethylene is used as a representative alkene.

Addition reactions

Hydrohalogenation

In this type of addition reaction, a hydrogen halide (e.g. HF, HCl, HBr, HI) is reacted with the alkene. The addition product is a *haloalkane*.



The product in the above example is chloroethane. It can be used as a solvent, as a refrigerant or as an ethylating agent in other reactions.

Production of ethanol

Ethylene reacts with water vapour at 300°C under high pressure in the presence of a phosphoric acid catalyst to produce ethanol. This is the common method of preparing ethanol industrially, although the fermentation of sugar is also a common method.

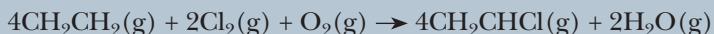


Ethanol is an important solvent. It is used in toiletries, cosmetics, detergents, disinfectants and flavourings.

Oxidation reactions

Production of vinyl chloride

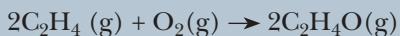
Ethylene will react with chlorine in the presence of oxygen to form vinyl chloride (chloroethene). This reaction is performed at 150°C over a copper (II) chloride catalyst. The vinyl chloride that is formed is the monomer that is used to make the plastic called *polyvinyl chloride* (PVC).



Production of ethylene oxide

Ethylene oxide is an intermediate in the production of other important petrochemicals such as 1,2-ethanediol (antifreeze) and polyesters that are used in fibres and plastic films.

Ethylene is oxidised at 250°C in the presence of silver catalyst to form ethylene oxide.



The ethylene oxide can be converted to ethan-1,2-diol (1,2-ethanediol or ethylene glycol) by reaction with acidified water.

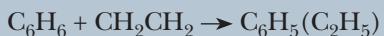


Ethylene glycol is widely used in the manufacture of condensation polymers.

Alkylation

Production of styrene

Ethylene reacts with benzene (C_6H_6) to produce ethylbenzene. The reaction requires an aluminium catalyst at high temperature and pressure (80–100°C/0.1 MPa). This product then undergoes catalytic dehydrogenation in the presence of sulfur to produce styrene. The styrene that is formed is used as the monomer for the production of polystyrene.



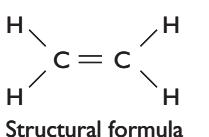
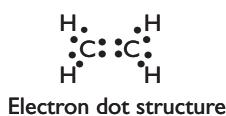
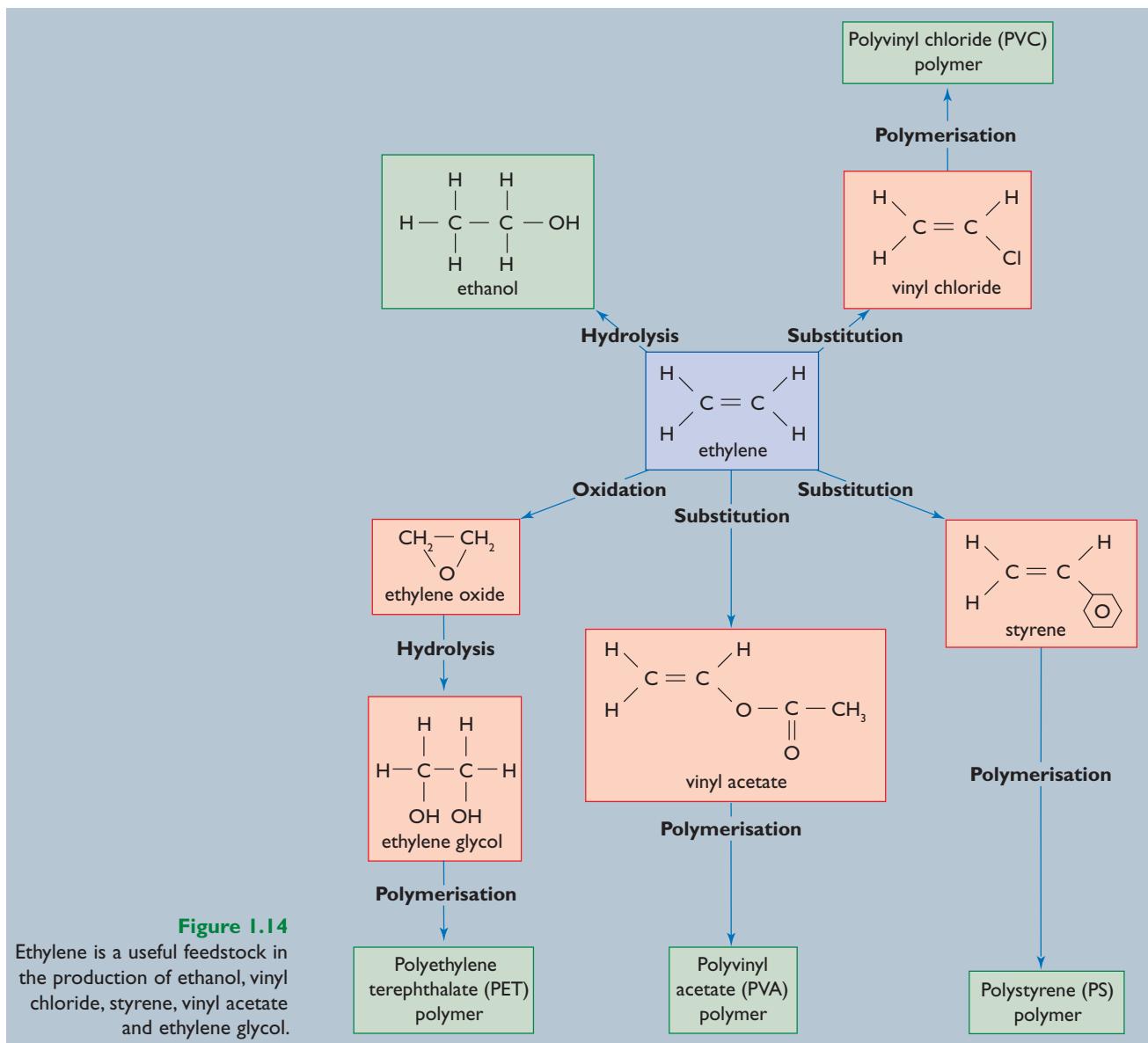


Figure 1.15
Ethylene (or ethene) is the first member of the alkene homologous series.

Ethylene and petrochemicals

Ethylene (C_2H_4) is not just a product of the petrochemical industry. It is also present in trace amounts in nature. Ethylene, a colourless and sweet smelling gas, is a plant hormone that is involved in fruit ripening and seed germination. Like other hydrocarbons, ethylene is flammable, with a low solubility in water. Its melting point is -169°C and its boiling point is -104°C .

Ethylene is manufactured from various hydrocarbon fractions produced by the fractional distillation of crude oil. The petroleum fractions (or feedstocks) that are used to produce ethylene are usually naphtha and liquefied petroleum gas (a mixture of propane (C_3H_8) and butane (C_4H_{10})) and liquefied natural gas. The natural gas from Australia's gas fields of the west coast contains 8% ethane, which is used to produce ethylene by thermal cracking. Over 50% of the world's ethylene is made from the cracking of naphtha. Ethylene and other products made from it are classified as *petrochemicals*.

Petrochemicals derived from ethylene

Today, ethylene ranks as one of the top five products produced by the chemical industry worldwide. Its industrial importance lies in its use in the production of petrochemicals including polymers, solvents, detergents and packaging. The high reactivity of the double bond in ethylene is responsible for the vast variety of products that can be made from it.

Table 1.2 illustrates some of the important products derived from ethylene.

Table 1.2 Petrochemicals derived from ethylene

Process	Products	Uses
polymerisation	polyethylene	film, sheeting, pipes
oxidation	ethylene glycol polyvinyl acetate	antifreeze, adhesives, paints
halogenation	ethyl bromide polyvinyl chloride	solvents, refrigerants, pipes, coatings, insulation
alkylation	polystyrene	packaging, insulation
hydration	ethanol	solvents, antiseptics

SYLLABUS FOCUS

5. ETHYLENE AND SOCIETY

Use this additional information to extend your knowledge of ethylene.

Early methods of ethylene production

The seventeenth century German chemist John Becher prepared impure ethylene from alcohol (ethanol) by dehydrating it with concentrated sulfuric acid. Later it was discovered that ethylene could also be produced by passing ethanol vapour over red-hot clay. Further investigations showed that heated silica (SiO_2) or heated alumina (Al_2O_3) also dehydrated ethanol to produce ethylene.



Ethylene and the sugar industry

Until 1966, the petrochemical plant at Botany used ethanol from the sugarcane industry to manufacture ethylene. The ethanol is produced by the fermentation of molasses. One method of dehydrating ethanol is to react it with concentrated sulfuric acid.

Ethylene is still produced by ethanol dehydration in some modern plants. The dehydration of the ethanol is achieved by passing the ethanol vapour over a bed of alumina and phosphoric acid in a reactor. The reaction occurs in two steps, during which an intermediate ‘ether’ is formed:



This process has a typical ethylene yield of 94%.

Ethylene and the coke ovens

When coal is heated in the absence of air ('destructive distillation') various volatile materials including ethylene are produced. Ethylene can also be produced from coke, which is the product of the carbonisation of coal. This process is carried out in coke ovens in the absence of air. About 2% of the coke oven gas is ethylene. The ethylene can be extracted from the other gases by liquefaction. This source of ethylene was important prior to World War II.

Ethylene from coal

A mixture of carbon monoxide and hydrogen gas is known as *synthesis gas*. It can be made by heating coal with steam and air. After purification, synthesis gas can be converted at optimum conditions of temperature and pressure to a mixture of hydrocarbons, including ethylene, by passing the gas over different catalysts.

Environmental issues in ethylene production

The main issues to be considered in the production of ethylene are:

- reducing the use of fossil fuels and the associated release of greenhouse gases such as carbon dioxide; this can be achieved by cracking ethane from LPG rather than cracking naphtha
- reducing water usage (used for heating or cooling) by recycling.

1.1 Questions

1. Identify the fractions produced from crude oil fractional distillation, which contain molecules with the following numbers of carbon atoms per chain or ring.
(a) 6 (b) 12 (c) 17
2. Name the following straight-chain hydrocarbons.
(a) C_4H_{10}
(b) C_8H_{18}
(c) $CH_3CHCHCH_3$
(d) $CH_3CH_2CH_2CH_2CH_3$
(e) $CH_3CH_2CH_2CH_2CH_2CHCH_3$
3. Name the structural isomers of pentane.
4. Compare the processes of thermal cracking and catalytic cracking.
5. Explain how the structure of the zeolite catalyst assists in the process of cracking.
6. Write a balanced equation for the reaction in which propene undergoes vapour phase bromination in the presence of bromine molecules.
7. Hex-2-ene (2-hexene) is converted by a chemical reaction into hexane. Name the process that has occurred, and name the other reactant.
8. Ethylene is an important industrial compound.
 - In which physical state does it exit at $25^\circ C$ and 100 kPa?
 - Write the molecular formula of ethylene.
 - Write the empirical formula of ethylene.
9. Describe the chemical nature of the raw materials used to produce ethylene today.
10. Ethylene can be prepared by passing ethanol (C_2H_5OH) vapour over red-hot clay. Water vapour is also formed. Write a balanced equation for this reaction.

11. Ethylene has the following physical properties: melting point = $-169^\circ C$; boiling point = $-104^\circ C$.
 - A sample of ethylene is cooled to $-150^\circ C$ at 100 kPa. Identify whether the ethylene will be a solid, liquid or gas at this temperature?
 - The temperature of the sample is now raised to $0^\circ C$. Identify the change of state that has occurred. Classify this change in state as either an endothermic or exothermic process.
12. (a) Free radical initiation is the first step in thermal or steam cracking. A sample of octane (C_8H_{18}) is to be cracked. Assuming that the octane molecules are split symmetrically to form free radicals, write a balanced equation for this process and name the free radicals produced.
(b) The free radicals produced in (a) decompose to form ethylene and another free radical. Write a balanced equation for this reaction, and name the new free radical.
(c) If the free radicals formed in (b) combine with one another then a termination step results. Write an equation for a termination step.
13. Pentadecane is an alkane with 15 carbon atoms per molecule.
 - Write the molecular formula of pentadecane.
 - Pentadecane can be catalytically cracked to produce decane and pentene. Write a balanced equation for this reaction.
 - The pentene that forms undergoes further cracking to form ethylene and propene. Write a balanced equation for this reaction.

14. Catalytic cracking is carried out at 500°C in the absence of air. At this temperature, larger hydrocarbon molecules can be cracked into smaller molecules on the surface of a zeolite catalyst.
- Suggest a reason for the reaction being carried out at an elevated temperature.
 - Suggest a reason for excluding air.
 - Explain why ethylene and propene would be considered by-products of the catalytic process.
15. The following data was collected to show the distribution of cracking products from two different hydrocarbon feedstocks.

Products	Feedstocks (% by mass of products)	
	Ethane	Naphtha
ethylene	53	34
ethane	35	4
propene	0.9	14
others	11.1	48

- Identify the feedstock that produces the greater proportion by mass of ethylene.
- What percentage of the ethane feedstock is converted to products?
- Suggest why over 50% of the world's ethylene is derived from naphtha rather than ethane.

1.2 ADDITION POLYMERISATION

Remember

Before beginning this section, you should be able to:

- identify that ethylene, because of the high reactivity of its double bond, is readily transformed into many useful products.

Key content

By the end of this section, you should be able to:

- identify that ethylene serves as a monomer from which polymers are made
- identify polyethylene as an addition polymer and explain the meaning of this term
- outline the steps in the production of polyethylene as an example of a commercially and industrially important polymer
- identify the commercially significant monomers vinyl chloride and styrene by both their systematic and common names
- describe the uses of the polymers made from the above monomers in terms of their properties
- analyse information from secondary sources such as computer simulations, molecular model kits or multimedia resources to model the polymerisation process.

Addition polymers

In the last fifty years there has been a rapid increase in the production and use of ethylene. This increase has been largely due to the production of polymers such as polyethylene (polyethene). About 60% of our ethylene production is directed towards the production of polymers.

Polymers are long-chain molecules composed of repeating sub-units called **monomers**. Polymers are sometimes called *macromolecules* as they can have very large molar weights (e.g. high-density polyethylene, HDPE, can have a molar weight of 3 million g/mol). The term *polymer* is derived from the Greek prefix *poli* (many) and root '*mer*' (unit). The 'unit' is, of course, the monomer molecule. Ethylene and propylene (propene) are common monomers. Figure 1.17 shows a section of a polymer chain of polyethylene derived from the ethylene monomer. During the reaction the double bond of the monomer is broken in order to form the polymeric chain.

Addition polymerisation

Polyethylene is one member of a class of polymers known as *addition polymers*. The production of these polymers involves alkene monomers reacting together via an addition reaction. Polyethylene kitchen bowls

first appeared in retail shops in 1948. Since then many other types of addition polymers have been produced.



Figure 1.16

Polyethylene can be transformed into many useful products including food wraps that help to keep food fresh.

polymer: a long-chain macromolecule composed of repeating sub-units called monomers

monomer: a sub-unit of a polymer chain

Synthetic polymers are commonly referred to as *plastics*. The word *plastic* literally means *pliable* or *able to be moulded*. This ability to be moulded is not shared by all polymers.

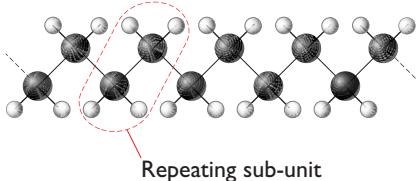


Figure 1.17

The polyethylene chain consists of repeating units of $-\text{CH}_2\text{CH}_2-$

addition polymerisation: polymerisation of monomers by an addition reaction

dimer: two monomers that have bonded together

Addition polymerisation is achieved in two ways. One method involves the use of initiator molecules; the other uses catalytic surfaces. Polyethylene is produced by both methods.

Polymerisation using an initiator

Monomers do not start to form polymers unless a molecule called an *initiator* is added. The initiator molecule is decomposed (by laser light or heat) to form reactive free radicals. The role of the free radical initiator is to combine with and break the carbon-carbon double bond to form a reactive (or activated) monomer free radical. The monomer free radicals then combine with alkene monomers via an addition reaction to form a **dimer** radical. This addition process continues and the polymer chain grows longer. To stop the reaction, an inhibitor is often added to halt the formation of radicals. This can be done at any time, so the size and molecular weights of polymer chains can be regulated to some degree. Figure 1.18 shows the distribution of molecular weight that can occur in a sample of polymer.

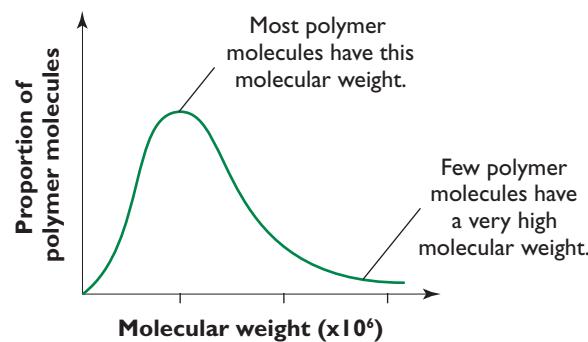


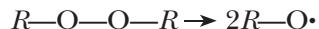
Figure 1.18

A polymer sample is made up of chains of many different lengths.

Low-density polyethylene (LDPE) is produced in this way. Figure 1.19b shows how the presence of radicals leads to the formation of the polymer chain in the production of LDPE. This process occurs at a high pressure (100–300 MPa) and a moderately high temperature (300°C).

The steps are:

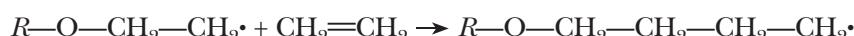
1. A peroxide initiator such as benzoyl peroxide is used. The peroxide is heated to produce peroxide free radicals ($R =$ benzoyl group or other suitable chain).



2. Activated monomers form as the peroxide free radicals combine with some monomers. This is called *activation*.

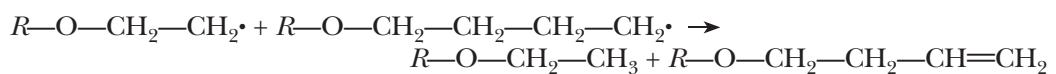
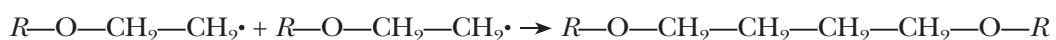


3. Activated monomers react with more ethylene monomers to increase the chain length. This is called *propagation*.

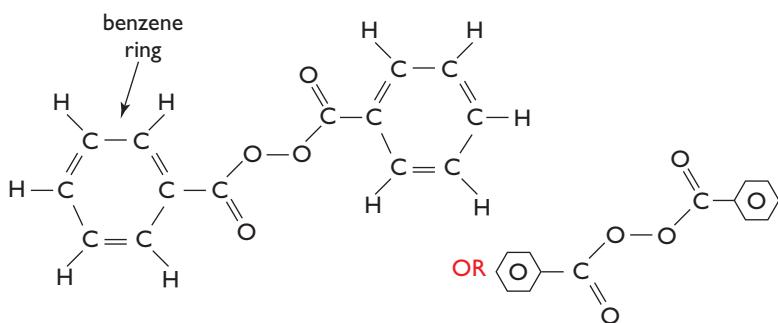


Some branching of the polymer chain occurs, as during chain growth the radical end often curls or ‘bites back’ on part of the existing chain and removes a hydrogen atom resulting in an unpaired electron within the chain, rather than at the end (see Figure 1.19c)

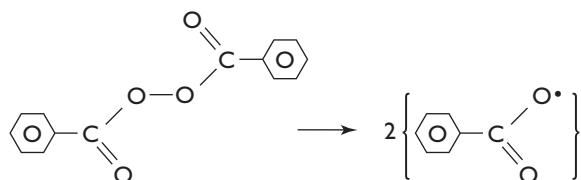
4. The process of chain growth terminates when the free radicals (of variable chain length) combine to form non-activated species.



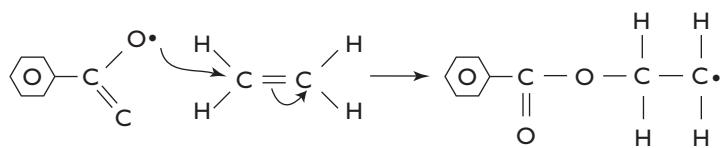
Addition of inhibitors or lowering the pressure and temperature can also stop the polymerisation.



Step 1: Production of free radicals from benzoyl peroxide



Step 2: Production of activated monomers



Step 3: Chain propagation

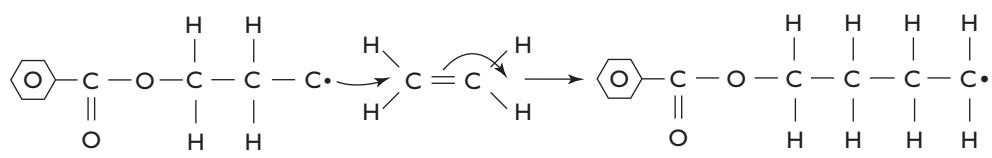
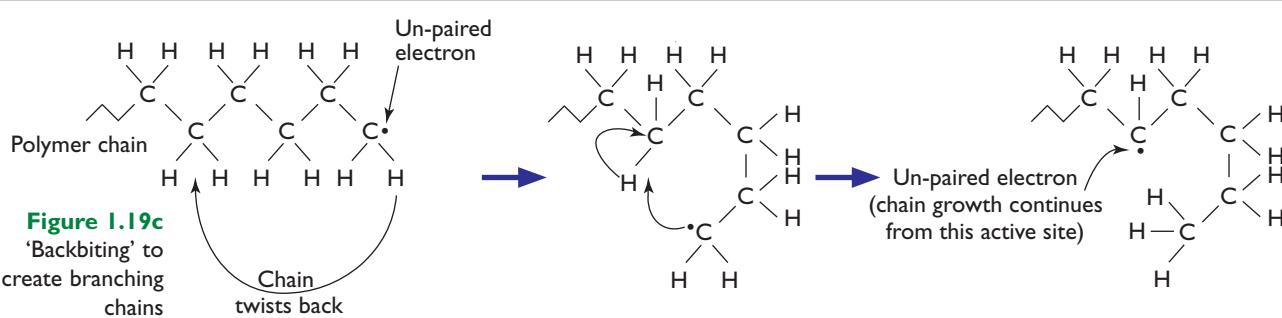


Figure 1.19b
Production of LDPE by high-pressure polymerisation with an initiator





ADDITION POLYMERISATION OF ETHYLENE

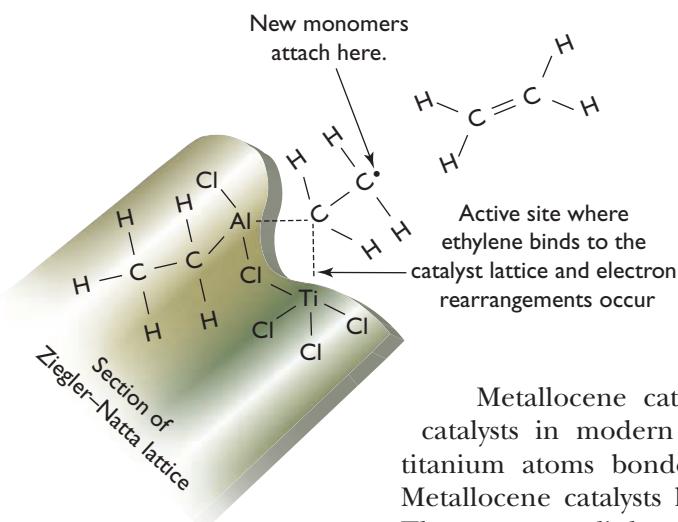


Figure 1.20
Ziegler–Natta catalyst is made of titanium chloride and triethyl aluminium chloride.

Polymerisation using a surface catalyst

Various compounds can act as surface catalysts in the production of addition polymers. Chromium oxide, for example, can be used in the production of polyethylene to create a high-density polymer (HDPE). By varying the pressure some degree of cross-linking between the polymer chains can be achieved. This gives added strength to the polymer.

A commercial low-pressure process was developed by Karl Ziegler in Germany in 1953 to produce HDPE. Ziegler discovered that high-density polyethylene could be readily manufactured by passing ethylene gas through a liquid alkane solution (at $\sim 60^\circ\text{C}$) containing tiny amounts of titanium chloride and triethyl aluminium chloride, which acted as catalysts. Further research and development led to the Ziegler–Natta method still used today. A typical HDPE molecule produced by the Ziegler–Natta method could have a molar weight of 3 million g/mol compared with molar weights of 1 million g/mol for LDPE.

Metallocene catalysts are gradually replacing the Ziegler–Natta catalysts in modern plants. These catalysts consist of zirconium or titanium atoms bonded to chlorine and two cyclopentadienyl rings. Metallocene catalysts have only one active site on the catalyst surface. The monomers link to the growing chain at this site. Consequently, linear chains of polyethylene of similar length can be formed. Greater control of the polymerisation process and improved quality of the polymer product are therefore the major reasons for the shift to metallocene catalysts.

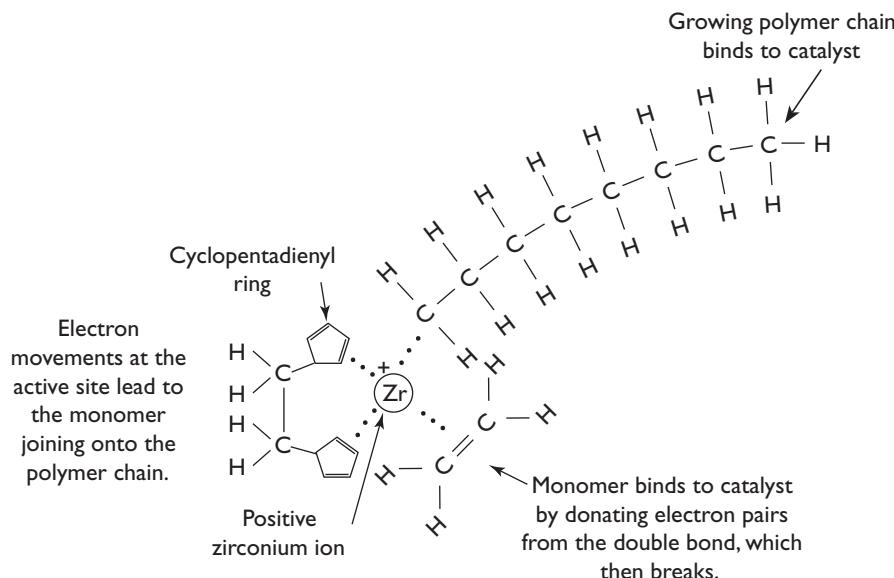


Figure 1.21
Metallocene catalysts are replacing Ziegler–Natta catalysts.

'A chemist setting out to build a giant molecule is in the same position as an architect designing a building. He has a number of building blocks of certain shapes and sizes, and his task is to put them together into a structure to serve a particular purpose.'
— Giulio Natta, winner of the 1963 Nobel Prize in Chemistry

Properties and uses of polyethylene and other addition polymers

The conditions of the polymerisation process lead to changes in the properties of the polymer. Polyethylene polymers are chemically unreactive. They are also electrical insulators. Some polymer chains are linear while others are branched or cross-linked.

Linear polymer chains

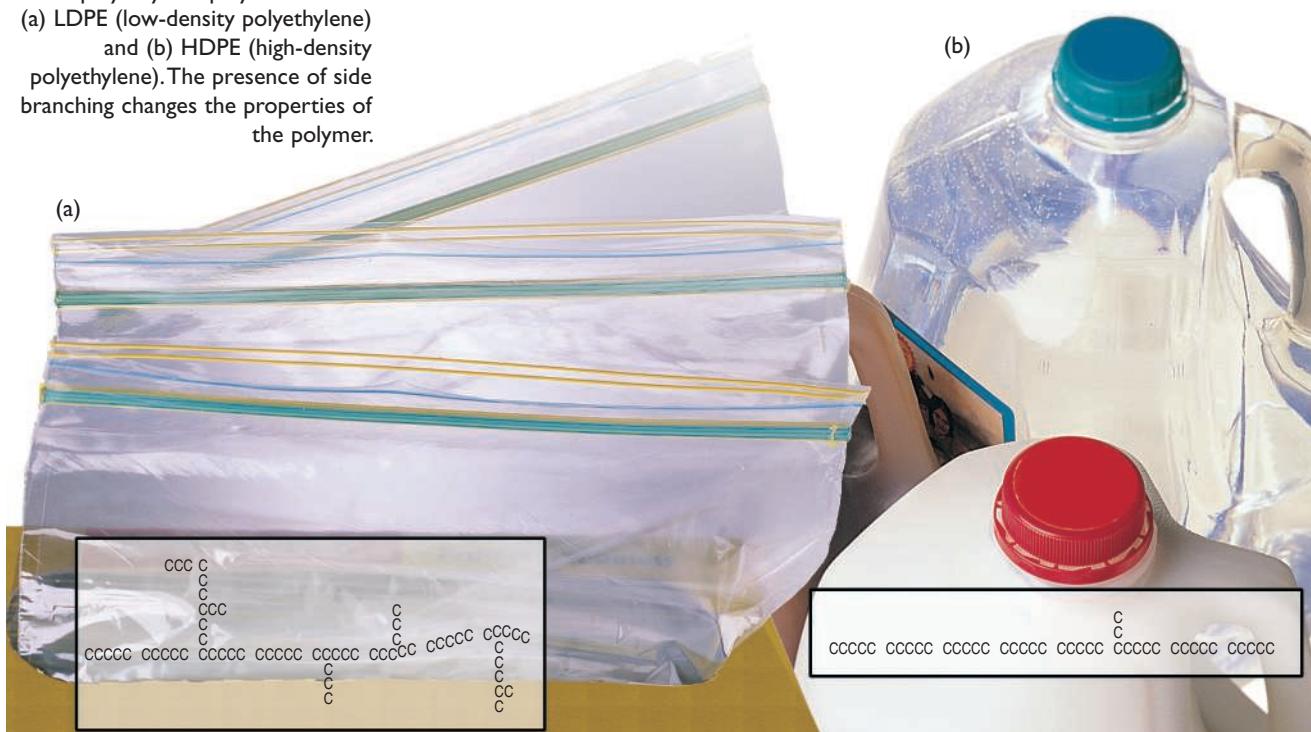
Linear polymer chains can pack closely together, and the dispersion forces between chains hold the chains tightly. This results in polymers that are quite rigid. High-density polyethylene (HDPE) is an example of a linear polymer with very little side branching. Microscopic examination of such polymers reveals the presence of crystalline regions where the molecules are uniformly arranged. The greater the proportion of crystalline regions the greater the strength of the polymer. About 80–95% of HDPE consists of crystalline regions that extensively scatter and refract light, so that these polymers appear translucent or white. The non-crystalline regions are said to be *amorphous*. HDPE has a typical melting point of 135°C. High-density polyethylene is used to make durable items like bowls, buckets, freezer bags, agricultural pipes and petrol tanks because it is tough.

Branched polymer chains

In some polymers, small chains branch off the main chain. Low-density polyethylene (LDPE) is an example of a polymer in which branching side chains are present. These branches may be short or long and their presence causes disruption in the packing of the polymer chains in the lattice. As a consequence there are fewer crystalline regions present in such polymers. About 40–55% of LDPE consists of crystalline regions. LDPE molecules are softer and more flexible than HDPE molecules owing to the weaker dispersion forces between the polymer chains. LDPE polymers are also more transparent because there is less scattering and refraction of light that passes through the solid. LDPE polymers typically have melting points that are lower than those of HDPE molecules. LDPE has a typical melting point of 80°C. Low-density polyethylene is commonly used to make plastic bags, squeeze bottles, electrical insulation and the plastic cling-wrap used for protecting food. LDPE film can also be used to waterproof cardboard food and drink containers.

Figure 1.22

The carbon backbone in a portion of a polyethylene polymer chain in (a) LDPE (low-density polyethylene) and (b) HDPE (high-density polyethylene). The presence of side branching changes the properties of the polymer.



Cross-linked polymer chains

Some polymer chains are interconnected by covalent bonds. These polymers are said to be *cross-linked*. Cross-linking significantly enhances the rigidity and strength of a polymer. The melting point rises as the extent of cross-linking increases. Polymers that are used in adhesives and laminates tend to be cross-linked. The very tough plastic used in the caps of soft-drink bottles is made from cross-linked polyethylene (CLPE).

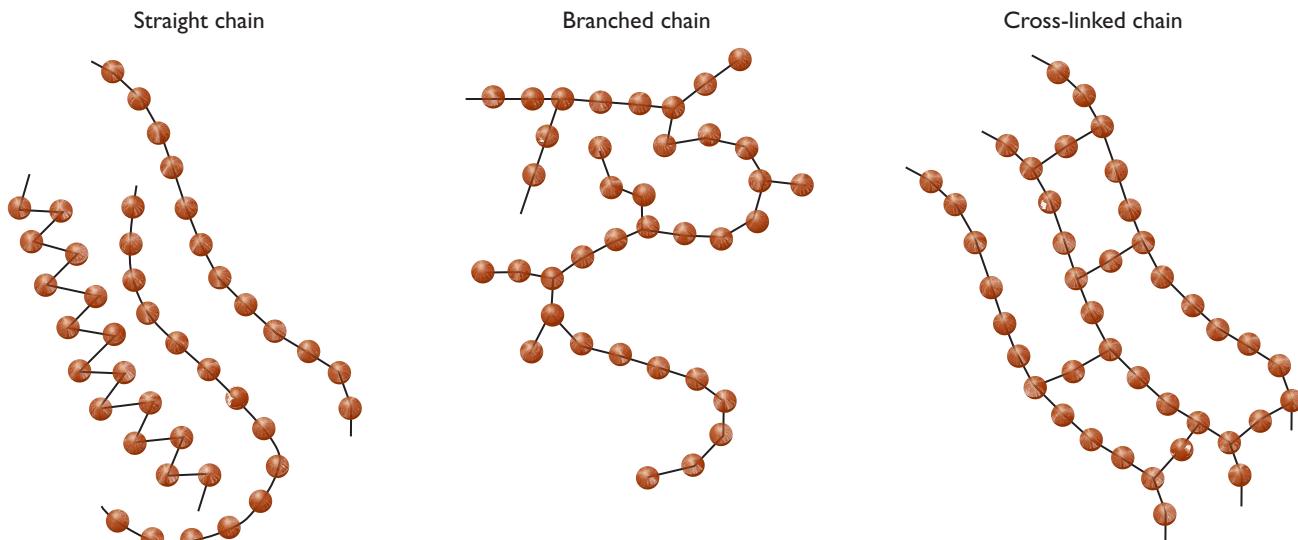


Figure 1.23
The presence of side branching and cross-linking changes the properties of a polymer.

Plastic production and development began in the middle of the nineteenth century following a competition organised by a manufacturer of billiard balls. At that time billiard balls were made of ivory, which was becoming very scarce, and governments were beginning to ban the slaughter of elephants from which ivory was obtained.

Other commercial and industrial polymers

Many commercial polymers are made by addition polymerisation. Many of these are also thermoplastics. Thermoplastics can be remoulded and set many times because they do not have cross-linking between their chains.

Thermoplastics are polymers that can be moulded when heated. As the polymer is heated the dispersion forces between the chains begin to break down and the polymer softens and forms a viscous material that is capable of being moulded. The crystalline regions of the polymer melt at a higher temperature than that of the non-crystalline (amorphous) regions.

Table 1.3 shows some commercially important monomers and their addition polymers. The monomer is known by its systematic name or by its common name as shown in brackets. Figure 1.24 shows the structure of each monomer and a section of the polymer chain. The abbreviated structural formula of each polymer is also shown.

Table 1.3 Common addition polymers

Monomer	Polymer	Uses
chloroethene or chloroethylene (vinyl chloride)	polyvinyl chloride (PVC)	soft furnishings, credit cards, guttering and pipes, floor tiles, flexible tubing
phenylethene or ethenyl benzene or vinyl benzene (styrene)	polystyrene (PS)	CD and cassette tape containers, plastic drinking glasses, fast-food containers, packaging materials, insulation

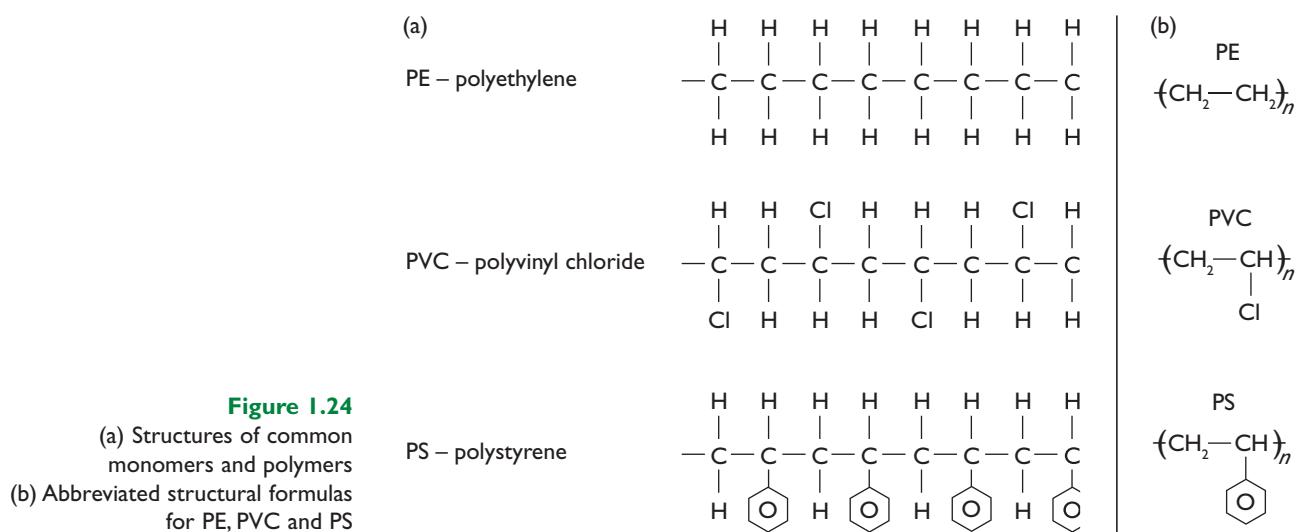


Figure 1.24

- (a) Structures of common monomers and polymers
 (b) Abbreviated structural formulas for PE, PVC and PS

Polyvinyl chloride (PVC)

Chloroethene (vinyl chloride) monomers are used to manufacture polyvinyl chloride (PVC) polymers. PVC chains vary in length from 400 to 4000 monomer units. PVC can be used to package fatty and oily foods as it is moderately resistant to chemical attack. Caustic chemicals such as sodium hydroxide, however, may attack PVC.

PVC is a hard, inflexible and brittle polymer. The presence of the large chlorine atoms along the chain increases the polymer's stiffness. The addition of various compounds can dramatically alter its properties and make PVC more useful. It is used for transparent flexible tubing, guttering, upholstery covering, surgeon's gloves, shower curtains, credit cards and electrical conduit.

Examples:

1. Softer PVC can be produced by adding a plasticiser. The plasticiser decreases the dispersion forces between the polymer chains and thus the polymer becomes more flexible.
2. Pure PVC breaks down in ultraviolet light. To use PVC products outdoors, a UV absorber must be added. Adding a UV absorber (e.g. titanium oxide) prevents UV decomposition of the plastic when it is exposed to sunlight.
3. Pure PVC decomposes when heated for long periods of time. PVC decomposes above 80°C and so is unsuitable for hot water pipes. Adding heat stabiliser compounds will improve its resistance to heat decomposition.
4. Adding flame retardant chemicals lowers the flammability of PVC.



Figure 1.25

Additives can be incorporated into PVC to change its properties for various applications.

1.2 PRACTICAL ACTIVITIES

Modelling
addition
polymerisation



Polystyrene

The monomer phenylethene (or styrene) is used to manufacture the addition polymer called polystyrene. Two major types of polystyrene are commercially manufactured: crystal polystyrene and expanded polystyrene.

Crystal polystyrene

Crystal polystyrene is a clear amorphous polymer that exhibits high stiffness and good electrical insulation properties. The stiffness results from the presence of the large benzene rings that are attached along the polymer chains. This high stiffness makes the polymer suitable for rigid items like car battery cases and handles for screwdrivers and other tools. Crystal polystyrene is brittle, but the addition of up to 10% butadiene monomer produces an opaque polymer that is more impact resistant. Polystyrene is the most widely used plastic for heat-pressed food packaging because of it is tough, rigid, cheap and stable towards most chemicals.

Crystal polystyrene has a high refractive index and this makes it suitable for containers such as drinking glasses, and packaging of CDs and audio cassettes. Because of polystyrene's low softening temperature (94°C) its use in medical care products is restricted to disposable items, as it cannot be sterilised by autoclaving.

Expanded polystyrene

Expanded polystyrene (styrofoam™) is white and has good heat and sound insulation properties. It can be produced by blowing gases through molten polystyrene and then allowing it to cool. Expanded polystyrene is used as a protective layer in packaging. Rigid polystyrene foam is an important product in protective packaging, which accounts for up to 15% of its use. Polystyrene burns incompletely in air with a hot smoky flame. Care must be taken to avoid fires as the burning polymer sticks readily to the skin. Severe burns result.

Figure 1.26

(a) Expanded polystyrene is white and has excellent insulating properties. (b) Crystal polystyrene is stiff and brittle with a high transparency.



SYLLABUS FOCUS

6. USING INSTRUCTION TERMS CORRECTLY

When answering questions, it is important to know what the instruction terms (verbs) require you to do. Here are some examples:

'Define'

This instruction word requires you to state the meaning of a term or identify the essential features of a concept.

Example:

Define the term *polymer*.

Answer:

A polymer is a long-chain macromolecule that is composed of many small, repeating molecules called monomers.

'Explain'

This instruction word requires you to provide reasons for why or how a process occurs, or to make the relationship between things evident.

Example:

Explain why benzoyl peroxide is added to ethylene during the production of low-density polyethylene.

Answer:

The ethylene monomers will not react under these conditions without an initiator. The benzoyl peroxide breaks down to form reactive free radicals and these free radicals attack some of the monomers to produce reactive monomer free radicals.

1.2 Questions

1. Define the following terms.
 - (a) Monomer
 - (b) Addition polymer
2. A monomer is represented by the following condensed structural formula:
$$\text{CH}_X\text{CH}_Y$$
where X and Y are functional groups.
This monomer undergoes addition polymerisation. There are n repeating units in the final polymer. Draw an abbreviated structural formula for the polymer that forms.
3. Figure 1.27 shows the structural formulae for two alkene monomers. These monomers undergo addition polymerisation to form polymer chains. Draw a section of the polymer chain containing three repeating units for each example.
 - (a) Propene
 - (b) Bromoethene
4. Two common forms of polyethylene are called HDPE and LDPE.
 - (a) State what these abbreviations mean.
 - (b) Describe the conditions under which

- each of these forms of polyethylene are produced.
- (c) Relate the difference in their properties to their molecular structure.
5. (a) Identify the chemical nature of Ziegler–Natta catalysts.
(b) Explain why Ziegler–Natta catalysts lead to the production of linear chains of polyethylene rather than branched chains.
6. Figure 1.28 shows the structural formula of the alkene methyl methacrylate.
 - (a) Methyl methacrylate undergoes addition polymerisation to produce a polymer chain. Draw a short section of the polymer chain.
 - (b) This transparent polymer is marketed as plexiglass™ and is used in optical equipment. Discuss the likely arrangements of the polymer chains in such a plastic that lead to its optical use.
7. Teflon™ is an addition polymer. Its chemical name is polytetrafluoroethylene (PTFE). Teflon is hard, tough and non-flammable. Draw a structural formula for the monomer that is used to make Teflon.

8. PVC is a hard, rigid, brittle polymer. It is degraded by exposure to UV light. Despite this it can be made into flexible tubing such as garden hoses as well as being used as guttering and downpipes. Explain what types of additives need to be incorporated into the PVC before it is moulded into each of the products mentioned.
9. During the manufacture of one form of polystyrene, sodium hydrogen carbonate is added to the melted polymer. The sodium hydrogen carbonate decomposes to release gases. Sodium carbonate is also formed.
- Write a balanced symbolic equation for the thermal decomposition of sodium hydrogen carbonate.
 - Name the form of polystyrene that is produced, and explain how its use is related to its structure.
10. A sample of PVC polymer is manufactured and found to be composed mainly of chains

that formed from 400 monomer units. Estimate the molecular weight of the polymer chains.

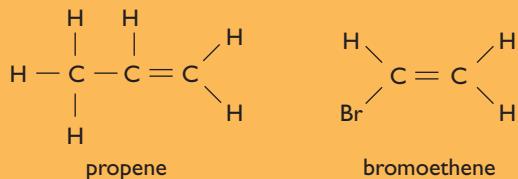


Figure 1.27

Propene and bromoethene monomers undergo addition polymerisation.

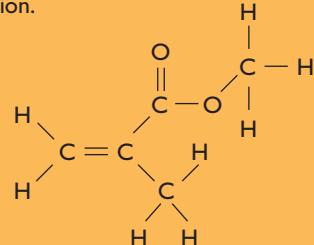


Figure 1.28

Methyl methacrylate undergoes addition polymerisation to form a plastic called plexiglass.



www.jaconline.com.au/chemnsw/chemistry2

SUMMARY

- Crude oil can be fractionally distilled to produce many useful fractions.
- Long-chain hydrocarbons can be thermally or catalytically cracked to produce small chain hydrocarbons.
- Ethylene can be produced by the thermal or catalytic cracking of fractions produced in the petroleum industry or by dehydrating ethanol.
- Ethylene is a typical unsaturated hydrocarbon. Alkenes undergo addition reactions across the reactive double bond. Bromine decolourisation is a standard test for unsaturation.
- Many petrochemicals are derived from ethylene. These include antifreeze, various solvents, refrigerants and antiseptics.
- Alkenes such as ethylene can undergo addition polymerisation to produce useful synthetic polymers such as polyethylene.
- Different forms of polyethylene can be produced. These include low-density polyethylene (PDPE), high-density polyethylene (HDPE) and cross-linked polyethylene (CLPE).
- Various catalysts have been developed to produce polymers with different structures and properties.
- Other common commercial addition polymers include polyvinyl chloride and polystyrene. Their properties are related to their bonding and structure.

PRACTICAL ACTIVITIES

1.1

PRACTICAL ACTIVITIES



REACTIVITY OF ALKANES AND ALKENES

Aim

To compare the reactivity of cyclohexane and cyclohexene using bromine water

Materials

- cyclohexane
- cyclohexene
- hexane
- hex-1-ene (1-hexene)
- bromine water in dropper bottles
- stoppered small test tubes (or semi-micro test tubes)
- test-tube rack
- droppers

Safety

- Wear safety glasses throughout this experiment.
- Organic liquids are volatile and flammable. Keep stock bottles stoppered and away from heat sources or flames at all times.
- Avoid breathing the vapours from bromine water or the organic liquids. Use a fume cupboard to perform these experiments. Use only small quantities, and all wastes should be stored in the supplied waste containers.

Method

- Place two clean and dry small test tubes in a test-tube rack.
- Add 20 drops of bromine water to each tube. Note the initial colour.
- To the first tube add 20 drops of cyclohexane. Stopper the tube with a rubber bung.
- Using a new dropper, add to the second tube 20 drops of cyclohexene. Stopper the tube.
- Gently shake each tube to mix the chemicals. Place the tubes back into the rack and allow the layers to separate. If decolourisation has not occurred fully in the second tube then you may need to add more cyclohexene.
- Extension:* Repeat this experiment with hexane and hex-1-ene (if available) and determine

whether the decolourisation of bromine occurs only with the alkene.

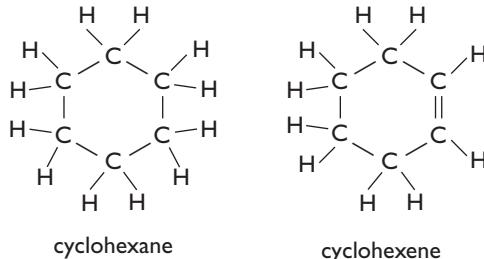


Figure 1.29

Cyclohexane is a cycloalkane. Cyclohexene is a cycloalkene.

Results and conclusion

Record your observations in tabular format. Write an appropriate conclusion

Briefly describe the outcome of your investigation.

Questions

Answer the following questions in your report on this experiment:

- Identify the functional group that reacts with the bromine water.
- Bromine water is a mixture of bromine and water molecules as well as hydrogen ions, bromide ions and hypobromous acid (HOBr), which have formed as some bromine molecules react with the water solvent. Write a balanced symbolic equation for this equilibrium reaction.
- When the bromine water decolourises as it reacts with the alkene, the reaction involves the addition of HOBr molecules across the double bond of the cyclohexene to form an alkanol. In the reaction performed in the experiment above, the product is called 2-bromocyclohexanol ($\text{C}_6\text{H}_{12}\text{BrOH}$). Write a balanced equation for the reaction of HOBr with cyclohexene.
- Use your experimental observations with bromine water and cyclohexane to explain whether bromine molecules are more soluble in water or in cyclohexane.
- Identify the variables that need to be controlled in this experiment.
- Discuss the validity of this technique in distinguishing alkanes from alkenes.

PRACTICAL ACTIVITIES

1.2

PRACTICAL ACTIVITIES



MODELLING ADDITION POLYMERISATION

Aim

To model the formation of addition polymers

Materials

- ball-and stick molecular model kits

The initiator is an organic peroxide ($R-O-O-R$). Use a different coloured ball to carbon, hydrogen and oxygen to represent the organic R group.

Method

Different student groups construct one of the polymers described below and then each polymer is displayed for class discussion.

Part A: Polyethylene (PE) (straight chain)

1. Construct one initiator molecule (see *Materials*).
2. Construct ten ethylene monomers (CH_2CH_2).
3. Decompose the initiator molecule (break the $O-O$ bond) to create two reactive free radicals ($R-O\cdot$). This is a homolytic process so you will need another connector to create the reactive end.
4. React one of the $RO\cdot$ radicals with the first monomer. The double bond is broken as the free radical initiator adds onto the molecule. A monomer radical $ROCH_2CHCl\cdot$ is formed.
5. The monomer radical then combines with a further vinyl chloride molecule and this process continues until the chain is 10 carbon atoms long.
6. Use the other $RO\cdot$ radical to repeat steps 3 to 5 with the other five monomers.
7. You should now have two identical chains. Allow these two chains to react at their free ends to make one long chain with the $RO-$ groups at either end. This is the termination step.

Part B: Polyethylene (PE) (branched chain)

1. Repeat steps 1 to 5 in Part A to produce a 10 carbon atom chain.
2. Allow ‘back-biting’ to occur at this stage. This occurs when the reactive carbon atom at the free

end of the growing chain flips over and removes a hydrogen atom from the fifth carbon atom from that end. The fifth carbon now is the free radical position and the end carbon is now part of a stable CH_3 group.

3. Use the other $RO\cdot$ radical to create a chain using the other five monomers.
4. Allow chain termination to occur by joining the chain from step 2 to the chain from step 3. A branched chain is formed.

Part C: Polyvinyl chloride (PVC)

1. Construct one initiator molecule (see *Materials*).
2. Construct ten vinyl chloride monomers (CH_2CHCl).
3. Decompose the initiator molecule (break the $O-O$ bond) to create two reactive free radicals ($R-O\cdot$). This is a homolytic process so you will need another connector to create the reactive end.
4. React one of the $RO\cdot$ radicals with the first monomer. The double bond is broken as the free radical initiator adds onto the molecule. A monomer radical $ROCH_2CHCl\cdot$ is formed.
5. The monomer radical then combines with a further vinyl chloride molecule and this process continues until the chain is 10 carbon atoms long.
6. Use the other $RO\cdot$ radical to repeat steps 3 to 5 with the other five monomers.
7. You should now have two identical chains. Allow the termination step to occur by linking these two chains at their free ends to make one long chain with the $RO-$ groups at either end.

Questions

Answer the following questions in your report on this experiment:

1. Draw diagrams of the models constructed in each part.
2. How do the polyethylene models compare to polyethylene molecules produced by chemical industry?
3. Explain the ways in which chain termination can occur.
4. For the PVC model, explain which arrangements of the chlorine atoms is likely to be most energetically stable.