

## Chapter

# 2 *CONDENSATION POLYMERS AND BIOMASS*



### Introduction

Polymers are molecules that occur commonly in nature. Natural polymers are called biopolymers. Cellulose, starch, proteins and DNA are all examples of biopolymers. Biopolymers are formed from their monomers by a process called condensation. The resulting polymers are called condensation polymers. In this section we shall focus on cellulose as an important condensation polymer in nature. We shall also examine some of the research into the production of synthetic biopolymers.

### In this chapter

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**Figure 2.1**

Toothbrush bristles are produced from the condensation polymer called nylon.

## 2.1 CONDENSATION POLYMERS

### Remember

Before beginning this section, you should be able to:

- identify that carbon can form single, double or triple covalent bonds with other carbon atoms
- explain the relationship between carbon's combining power and ability to form a variety of bonds, and the existence of a large number of carbon compounds
- summarise and collate information from a range of resources.

### Key content

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

- explain what is meant by a condensation polymer
- describe the reaction involved when a condensation polymer is formed.

**condensation polymerisation:** step-growth polymerisation in which two monomers combine with the elimination of a smaller molecule

**condensation reaction:** a reaction in which two molecules combine together with the elimination of a smaller molecule.

**ester:** an organic molecule containing the  $\text{—COO—}$  functional group

**amine:** an organic molecule containing the  $\text{—NH}_2$  functional group.

**carboxylic acid:** an organic molecule containing the  $\text{—COOH}$  functional group



**CONDENSATION  
OF AN AMINE  
WITH A  
CARBOXYLIC ACID**

### Condensation polymerisation

**Condensation polymerisation** is sometimes called 'step-growth' polymerisation. The important aspects of this type of polymerisation are:

- monomers combine via a chemical process called *condensation*.
- a small molecular weight molecule (e.g. water) is eliminated at each condensation step.

Let us examine two types of simple **condensation reactions**, the formation of esters and amides and their polymerisation.

#### Formation of an ester

When an alcohol molecule reacts with a carboxylic acid they combine to form a larger molecule called an **ester**. Water molecules are eliminated in the process. Thus if methanol ( $\text{CH}_3\text{OH}$ ) reacts with ethanoic acid ( $\text{CH}_3\text{COOH}$ ) in the presence of a catalyst, methyl ethanoate ester and water are formed.



#### Formation of amide

When an **amine** molecule reacts with a **carboxylic acid** they combine to form a larger molecule called an amide. Water molecules are eliminated. Thus, if aminoethane ( $\text{CH}_3\text{CH}_2\text{NH}_2$ ) reacts with propanoic acid ( $\text{CH}_3\text{CH}_2\text{COOH}$ ), ethyl propanamide and water are formed.



These simple condensation reactions, however, are insufficient to produce long-chain polymers. In order to produce a polymer, each reactant must possess at least two functional groups so that the step-growth process can continue.

#### Formation of a polyester

To produce a polyester, one monomer must be a dicarboxylic acid (i.e. a hydrocarbon with two  $\text{COOH}$  groups) and the other monomer must be a diol (i.e. a hydrocarbon with two  $\text{OH}$  groups). Dimers are formed in the first step. Dimers can continue to add more monomers so that the chain grows in steps.



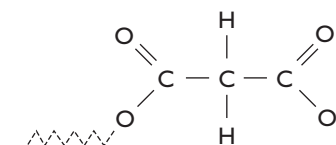
Figure 2.2 illustrates the step-growth process that leads to the formation of a polyester.

#### Formation of a polyamide

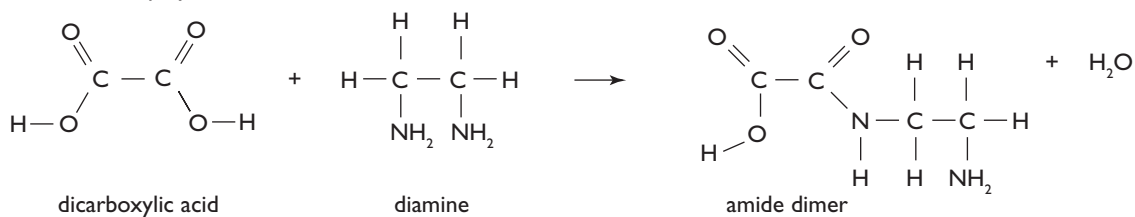
To produce a polyamide, one monomer must be a dicarboxylic acid and the other must be a diamine (i.e. a hydrocarbon with two amino groups). The chain grows by condensing with more monomers until a polymer is formed.



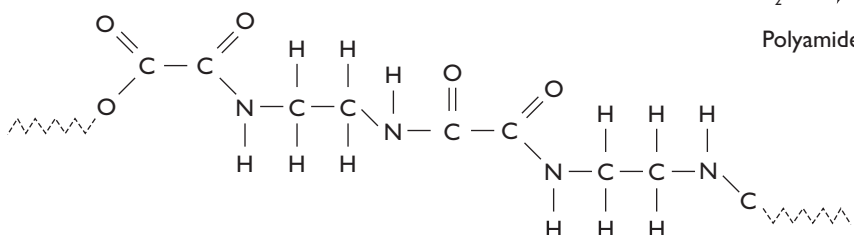
Figure 2.4 illustrates the step-growth process that leads to the formation of a polyamide.



Polyesters are formed when dicarboxylic acids condense with diols.

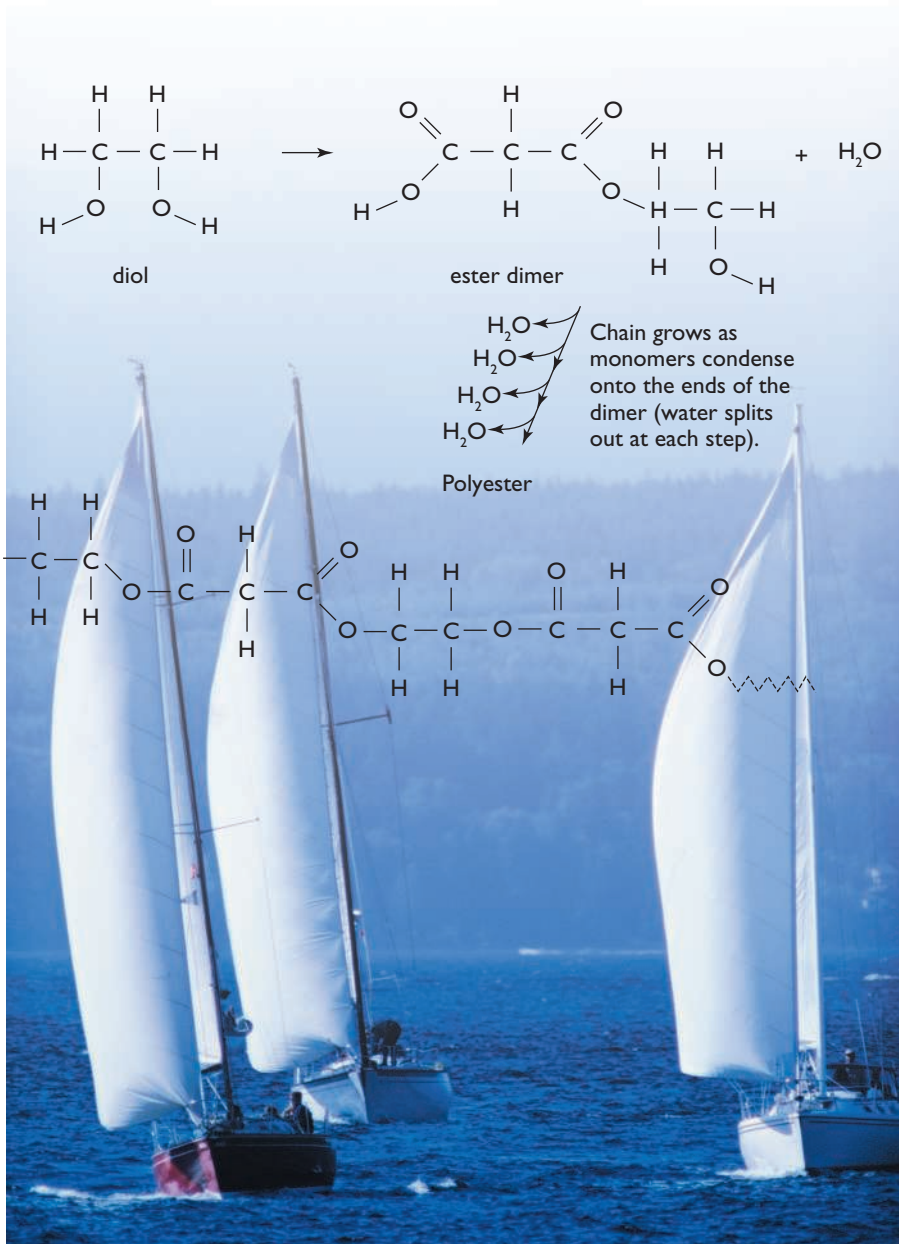


Polyamides are formed when dicarboxylic acids condense with diamines.



## Polyamide

Chain grows as monomers condense onto the ends of the dimer (water splits out at each step).



Most sails today are made of polyester.





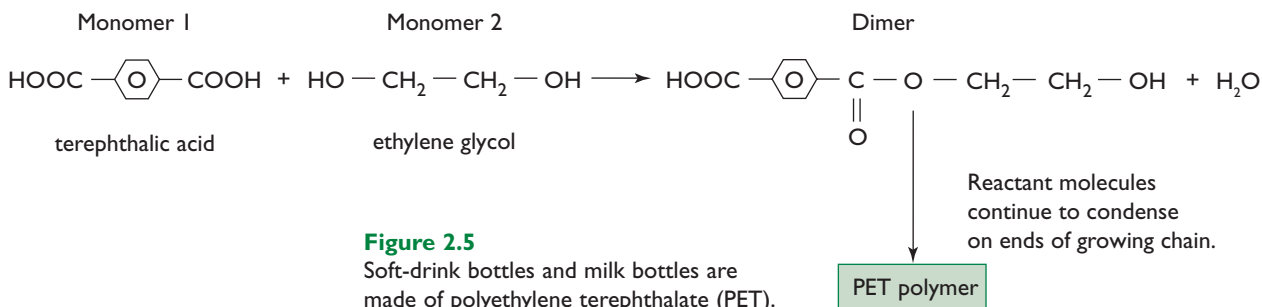
## CONDENSATION POLYMERISATION

### Useful condensation polymers

In modern society we use many condensation polymers. Let us examine a few common examples.

#### Polyethylene terephthalate (PET)

Many plastic soft-drink and milk bottles are made from the PET polymer. PET is an example of polyester. Figure 2.5 shows the structural equation for the formation of the ester dimer when terephthalic acid and ethylene glycol condense. You will remember from Chapter 1 that ethylene glycol can be manufactured from ethylene.



**Figure 2.5**

Soft-drink bottles and milk bottles are made of polyethylene terephthalate (PET).

Velcro was invented in 1957 by a Swiss engineer called George de Maestral. He observed how plant burrs stick to clothing and animal fur using their tiny hooks. He used nylon to develop a plastic product that would behave the same way as plant burrs.

Nylon was commercially marketed in the USA in 1938. It was first used to make women's stockings. Initially, production could not keep up with demand.

This polymer is also used as a fibre in the manufacture of fabrics for clothing. Many clothes are made from *terylene* or *dacron* which are composed of PET fibres. Polyesters are quick-drying fibres that form fabrics that do not readily crease. This makes them ideal for items like drip-dry shirts.



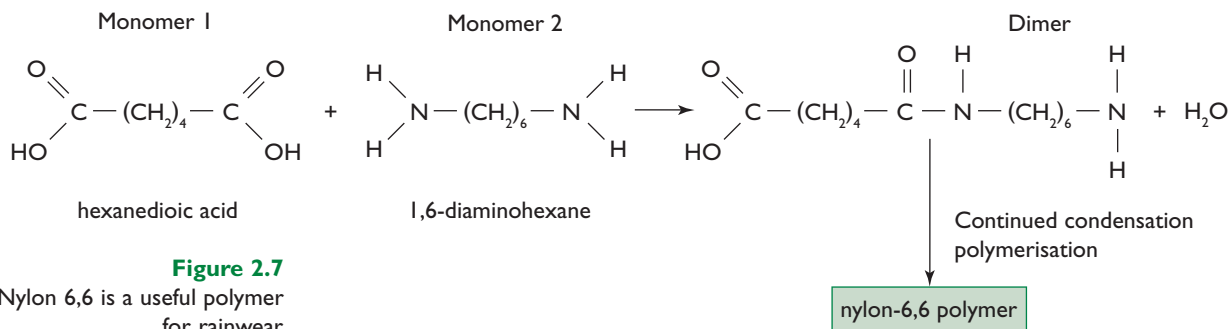
**Figure 2.6**

Velcro is a plastic product developed from nylon. Velcro is now widely used in clothing, footwear, luggage and for sporting equipment.

#### Nylon

Nylon is a strong, hardwearing fibre that does not absorb water very well. This hydrophobic nature allows it to be used in rainwear.

Nylon is a polyamide. There are several different types of nylon. Figure 2.7 shows the structural equation for the formation of the amide dimer when hexanedioic acid and 1,6-diaminohexane condense. As the chain grows, a nylon polymer is formed. This particular nylon is called nylon-6,6.



**Figure 2.7**

Nylon 6,6 is a useful polymer for rainwear.

## 2.1 Questions

1. Polymerisation can occur in two different ways. Distinguish between addition polymerisation and condensation polymerisation.
2. Figure 2.8 shows the structural formulae of several monomers. Use this information to write structural equations for the formation of the dimer in each of the following condensation polymerisations.
  - (a) propanedioic acid + butan-1,4-diol (or, 1,4-butanediol)
  - (b) butanedioic acid + 1,3-diaminopropane

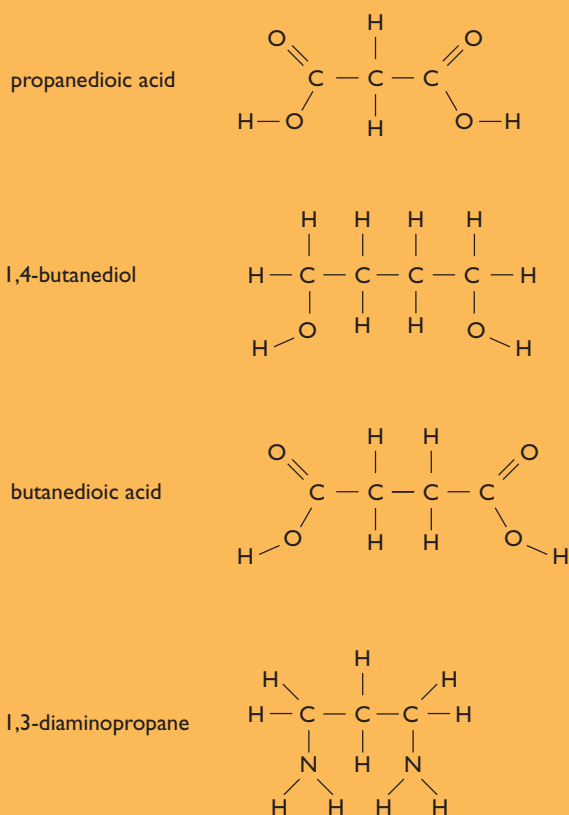


Figure 2.8

3. Figure 2.9 shows a short section of a polyester chain. Use this information to draw the structures of the two monomers that make up this chain.

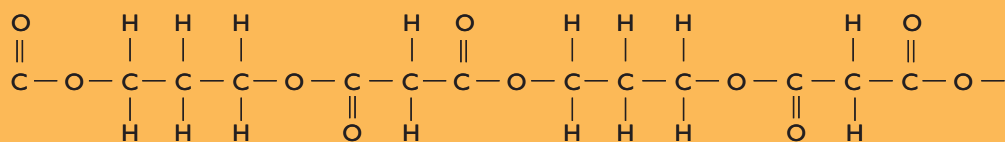


Figure 2.9

4. Nylon-6 is a synthetic condensation polymer formed from the 6-aminohexanoic acid monomer. Figure 2.10 shows the structure of the monomer.

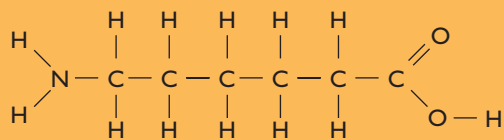


Figure 2.10

- (a) Name the two functional groups involved in the condensation reaction.
  - (b) Draw a short section of the polymer chain that forms from this monomer.
  - (c) Name the molecule that is eliminated at each step of the polymerisation process.
5. Proteins are examples of polyamides. They are condensation polymers formed from the condensation polymerisation of monomers called *amino acids*. Chemists can also manufacture chains of amino acids called *polypeptides*. Figure 2.11 shows the structure of the amino acid called *alanine*. Draw a short section of the polyalanine condensation polymer.

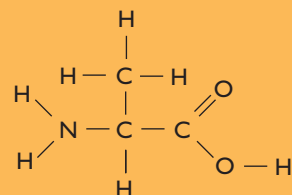


Figure 2.11 Alanine is an amino acid found in proteins. It can be polymerised to form polyalanine.

## 2.2 BIOMASS

### Remember

Before beginning this section, you should be able to:

- explain what is meant by a condensation polymer
- describe the reaction involved when a condensation polymer is formed.

### Key content

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

- describe the structure of cellulose and identify it as an example of a condensation polymer found as a major component of biomass
- identify that cellulose contains the basic carbon-chain structures needed to build petrochemicals and discuss its potential as a raw material
- discuss the need for alternative sources of the compounds presently obtained from the petrochemical industry
- use available evidence to gather and present data from secondary sources and analyse progress in the recent development and use of a named biopolymer. This analysis should (a) name the specific enzyme(s) used or organism used to synthesise the material and (b) provide an evaluation of the use or potential use of the polymer produced, related to its properties.

### Cellulose

Cellulose is a biopolymer formed by the condensation polymerisation of glucose monomers. Cellulose fibres are produced by plants to give their cell walls strength and shape. Humans have used cellulose for thousands of years to make paper and linen. Cotton fibre is another natural product composed of cellulose molecules. Cellulose can also be modified to produce filaments of rayon (or 'artificial silk'). This is done by digesting the cellulose fibre in sodium hydroxide solution followed by extrusion into acid. Modern rayon has fire retardants added, and is known as *viscose rayon*.



Figure 2.12 Rayon or artificial silk is a polymer derived from cellulose.

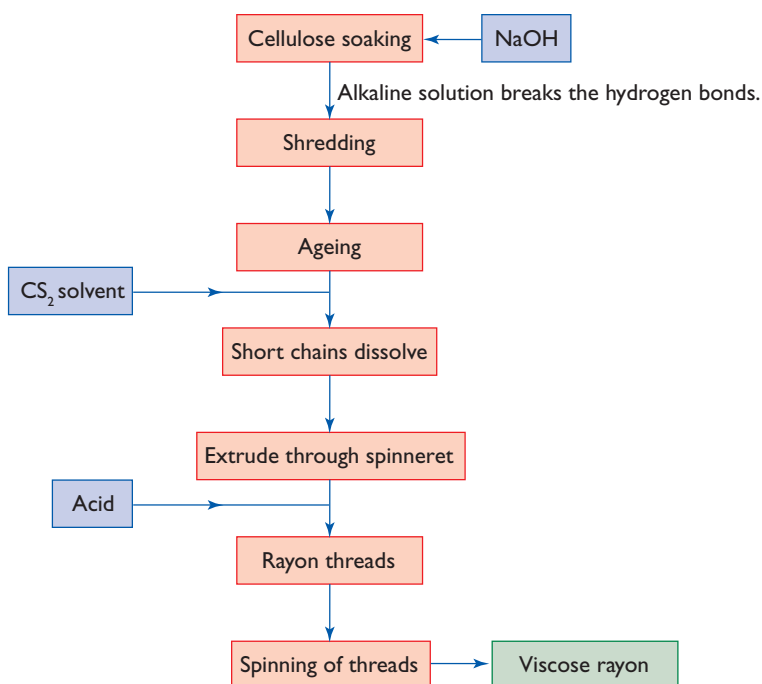
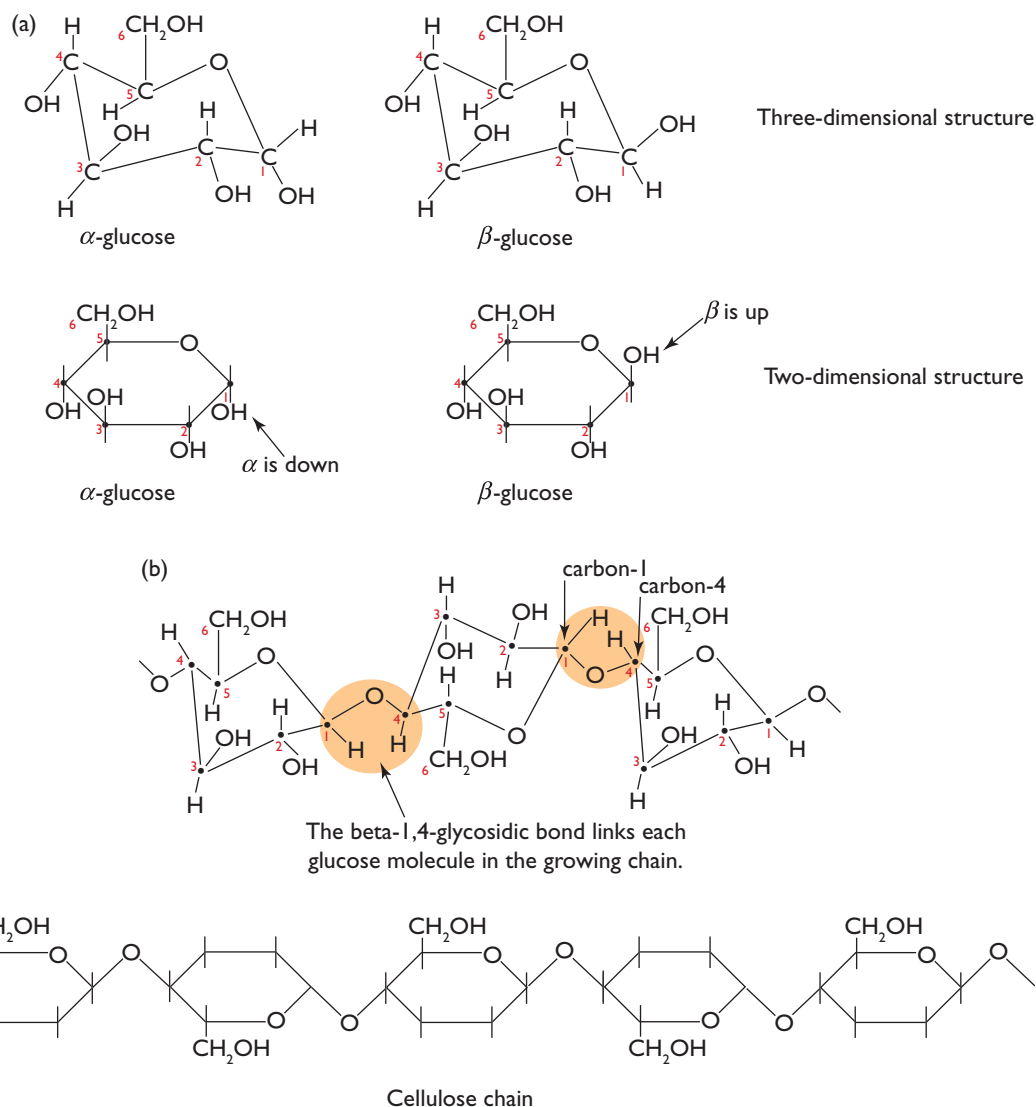
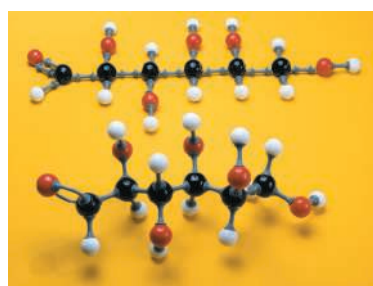


Figure 2.13 Cellulose is digested in alkali and then extruded into acid to form rayon threads.

## The formation of cellulose

Figure 2.14a shows the structure of glucose. There are numerous OH groups in the glucose molecule. There are two structural forms of glucose called alpha-glucose and beta-glucose. It is the beta form that leads to cellulose formation. During condensation polymerisation, beta-glucose monomers link together by a beta 1,4-glycosidic bond to form a beta-maltose dimer. Maltose dimers then continue to condense and the polymer chain increases in length. Ultimately up to 10 000 glucose units will form the long, unbranched cellulose chain. Figure 2.14c shows this condensation polymerisation process and the structure of a section of the cellulose polymer. This diagram shows that the CH<sub>2</sub>OH groups on the C-5 position alternate on opposite sides of the chain. This alternating arrangement maintains a linear structure in the polymer. Cellulose is insoluble in water because its structure exposes few OH groups to the water molecules in the environment.



**Figure 2.14**

- (a) The glucose model helps us visualise the bond angles in the molecule.  
(b) Ring numbering and conformation of CH<sub>2</sub>OH groups along the chain.  
(c) Polymerisation of glucose to form cellulose.



Cellulose is a polysaccharide produced by green plants. A bacterium called *Xanthomonas campestris* forms polysaccharide chains called *xanthan*. Xanthan is employed as a thickener in the food industry. Thickeners are used in ice creams, sauces, syrups and desserts.

**biomass:** carbon-based matter, mainly from plants, that stores chemical energy produced by photosynthesis. Biomass represents a massive quantity of a carbon-based renewable resource.

## Cellulose as a raw material

Fossil fuels such as natural gas, coal and petroleum are non-renewable resources. Consumption of these resources has accelerated in the last 200 years and we face a future in which these fossil fuels will eventually run out. Alternative sources of carbon compounds must be developed to allow the economies of nations to grow. Cellulose represents one major source of carbon compounds. Cellulose contains the basic carbon chain structures that are needed to build compounds that are presently obtained from petrochemicals. Cellulose is a major component of **biomass**.

Biomass is a renewable resource. Biomass is formed when green plants use carbon dioxide, water and solar energy for photosynthesis. In the past, human beings have utilised biomass for food or as wood for building materials. Humans have also exploited fossilised biomass in the form of coal.

The great bulk of biomass is composed of carbohydrate (cellulose, hemicellulose, starch and sugars); the remainder is lignin. Lignin consists of non-sugar-type molecules linked together in large sheet-like structures. Lignin can be removed from the biomass, and the cellulose fibres that are recovered can be used to make paper and textiles.

Biomass represents a very large energy resource. Only 7% of this resource is currently utilised.

### Problems in utilising biomass

Two main problems with utilising biomass are:

- cost — fossil fuels are currently much cheaper to produce than biomass fuels. Considerable energy is needed to plant, fertilise, harvest and process energy crops.
- suitable land — fertile land is required to grow energy crops. In many places the small amount of fertile land is exclusively devoted to the growth of food crops. Farming also alters the local water table and the demand for soil nutrients.



**Figure 2.15**

Sugarcane is grown to produce sugar. The waste stalks and leaves can be used as a fuel or they can be converted to ethylene and eventually into petrochemicals.

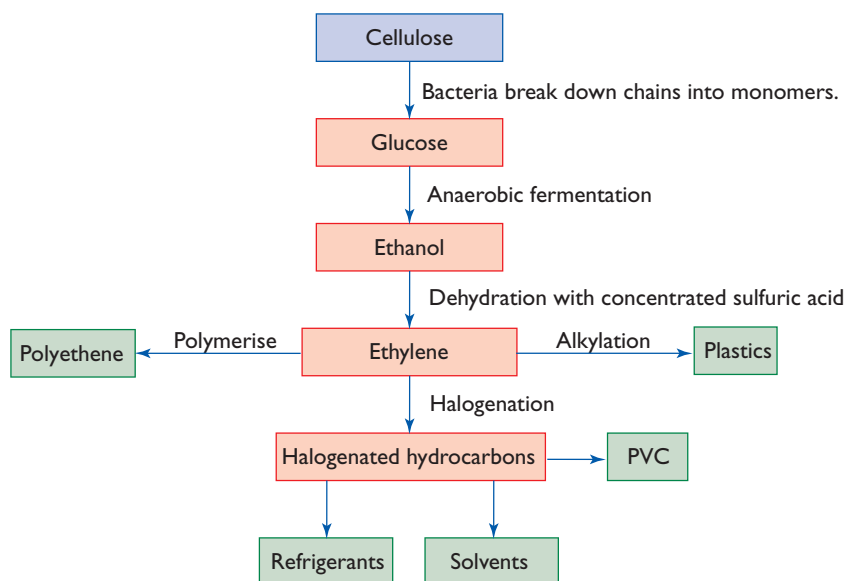


## Research into utilising biomass

Two important fields of research are the production of petrochemicals and the production of fuel gases.

### Production of petrochemicals

Cellulose is a potential source of petrochemicals because of its long carbon chain structure. Figure 2.16 shows a proposed possible method of producing petrochemicals from cellulose, using ethylene as an intermediate.



**Figure 2.16**

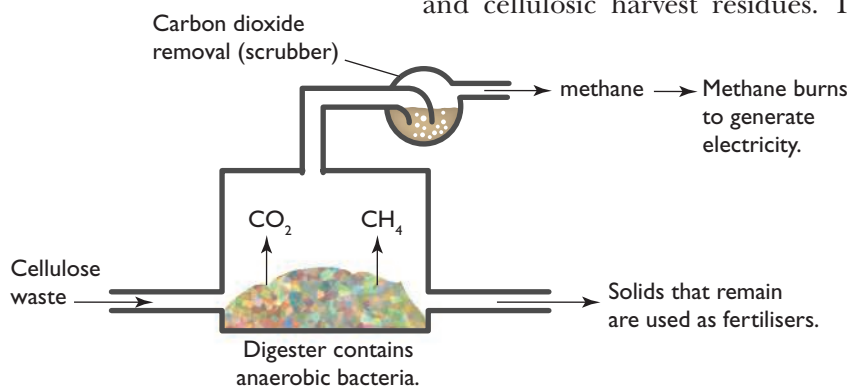
The carbon chains of cellulose are able to be converted into a variety of petrochemicals.

Human beings can digest starch but not cellulose. Some of the cellulose is fermented by the microflora of the large intestine to produce short-chain fatty acids. These fatty acids are absorbed and act as an energy source.

Bacteria that live in the intestines of termites and ruminants produce enzymes that break down cellulose into glucose monomers. Enzymic breakdown of cellulose is the first step in the production of petrochemicals. Alternatively, the cellulose can be broken down chemically via acid hydrolysis. The glucose produced can be fermented by yeast to form ethanol that can be readily dehydrated to yield ethylene. From ethylene a wide variety of petrochemicals (e.g. halogenated hydrocarbons and polymers) are currently manufactured. This method of generating ethylene from cellulose via ethanol is much more expensive than the current methods of obtaining ethylene. Research continues to find more-efficient and low-cost methods of utilising the carbon chains in cellulose.

### Production of fuel gases

Methane is an important fuel gas that can be generated by anaerobic fermentation of agricultural waste. Such waste includes animal manure and cellulosic harvest residues. The anaerobic bacteria initially digest the biomass into organic acids, sugars and alcohols. In later stages, methane and carbon dioxide are produced. The methane produced can be used directly as a fuel on the farm; any residues make excellent fertiliser.



**Figure 2.17**

Methane can be produced by the anaerobic respiration of biomass.

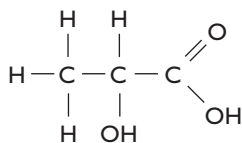
## Synthetic biopolymers

Non-biodegradable plastics are a major problem for our environment. When they are dumped in landfills they remain there without significant decay for hundreds of years. As a response to growing concern, biodegradable plastics are being developed.

### PLA — Polylactic acid

Polylactic acid is a biodegradable polymer that exhibits both strength and flexibility. The raw material is lactic acid, which is derived from starch waste obtained from potatoes or sorghum. The use of such waste would lead to huge savings in the use of petroleum and petrol. The first step in the production of PLA involves the conversion of starch waste to simple sugars that are fermented by bacteria to produce lactic acid. Water splits out as the lactide dimer forms. The dimer undergoes further chain growth to form the PLA polymer.

(a) Lactic acid



(b) Polymerisation of lactic acid

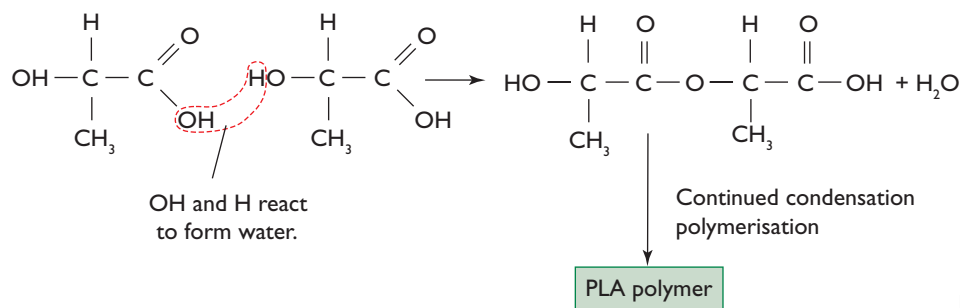


Figure 2.18

Polylactic acid is a synthetic biopolymer.

## 2.1 DATA ANALYSIS

Development of polylactic acid (PLA)

PLA polymers are similar to polystyrene in that they have a high gloss and clarity. They also have high tensile stress. Like PET, PLA polymers resist greases and are readily heat-sealed.

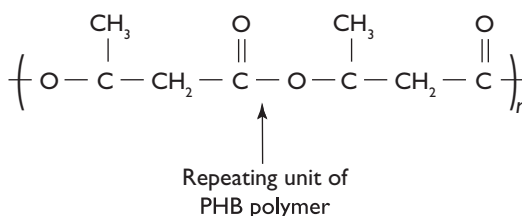
There is ongoing research into starch-based polymers such as PLA because of their potential to replace petrochemical plastics. In the future, these plastics could be used to make plastic bags, food packaging and disposable tableware.

### PHB — polyhydroxybutyrate

Bacteria such as *Clostridium*, *Pseudomonas* and *Syntrophomonas* can be used to synthesise polyester polymers called PHA's or polyhydroxyalkanoates. One of these is called PHB or poly-3-hydroxybutyrate. PHB is a stiff, brittle polymer that is rapidly degraded by bacteria to form carbon dioxide. This property is essential for future plastics as they would rapidly degrade in landfills. PHA plastics (or 'bacterial plastics' as they are also called) have low impact strength, which is a disadvantage in many applications.

The bacterium *Ralstonia eutrophus* (formerly *Alcaligenes eutrophus*) is used to produce a copolymer with PHB called PHBV (poly-3-hydroxybutyrate-poly-3-hydroxyvalerate). The *R. eutrophus* bacteria are grown in a high glucose or high valeric acid environment. The bacteria manufacture the PHBV copolymer, which is stored in their cell walls as granules. The polymer (commercially called Biopol) can be extracted and processed into plastic products like containers for shampoo.

The cost of these 'bacterial plastics' is very much higher than that of petrochemical plastics. Research is being carried out to genetically modify bacteria to control the plastic that they form. In addition, gene splicing is being investigated as a means of transferring the PHA production capability of *R. eutrophus* to other bacteria such as the common *Escherichia coli*.



**Figure 2.19**

PHB is a polyester. It is an example of a 'bacterial plastic'.

## SYLLABUS FOCUS

### 7. USING INSTRUCTION TERMS CORRECTLY

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

#### 'Account'

This verb requires you to state reasons for an observation or statement.

#### Example:

Account for the increase in research funding on biomass over the last 25 years.

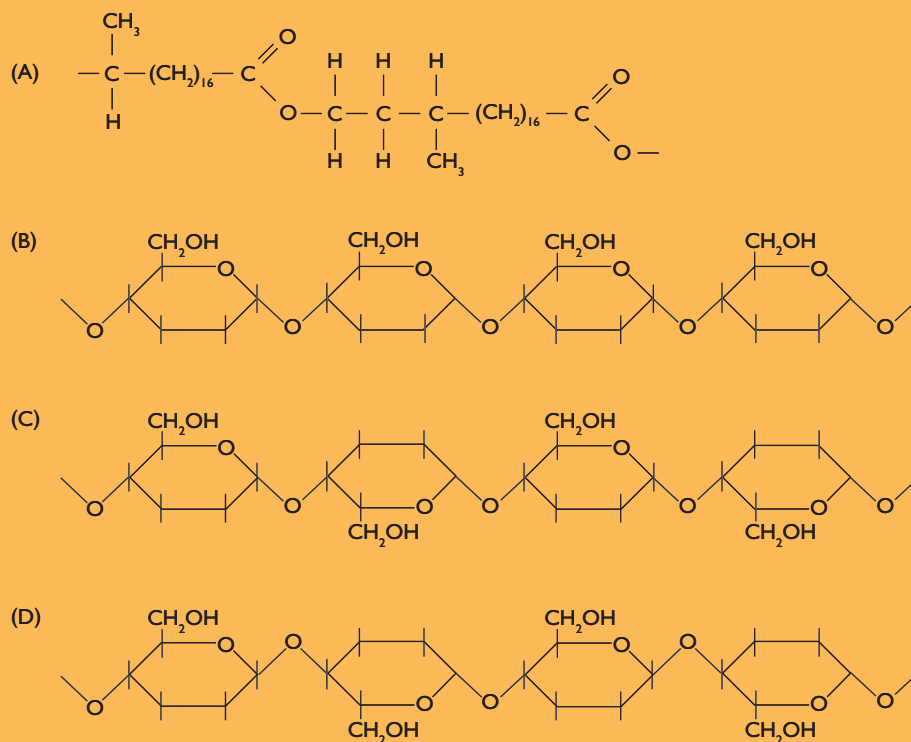
#### Answer:

Biomass consists mainly of long-chain polymers such as cellulose. These long-chain molecules are potential replacements for the carbon chains obtained by fractional distillation of crude oil. Biomass is a renewable resource whereas crude oil is not. Crude oil has a finite lifetime and as a consequence, research needs to be funded to find replacements. Biomass is plentiful and research needs to be conducted to find ways of manufacturing new products that will replace petrochemicals in the future.

## 2.2 Questions

- Claudine read in her chemistry text book that cellulose and starch are classified as biopolymers.
  - Define the term biopolymer.
  - Claudine's research identified the monomer that plants use to construct cellulose. Name the monomer which polymerises to form cellulose.
  - The two monomer units combine to form the dimer. Name the linkage that joins these two monomers.
  - Classify the formation of glucose from its monomer as an example of addition or condensation polymerisation.
  - Name one synthetic polymer made by treating cellulose fibre.
- Define the term biomass.
  - Identify the major chemical component of biomass.
- Account for the following statement:  
'Despite biomass representing a vast energy source, only about 7% of this available energy is currently being used.'
- Current research involves the development of 'bacterial plastics'.
  - Explain what is meant by this term.
  - Name an example of such a plastic and briefly describe how it is manufactured.
  - Identify some of the technological problems that need to be solved to allow these polymers to be widely used.
- Outline a possible reaction pathway to convert biomass into plastics such as polyethylene.
- PHB, or polyhydroxybutyrate, is a synthetic biopolymer that has been developed in recent years.
  - Identify bacteria that have been used to produce this polymer.
  - Name the monomer that is used to produce PHB.
  - Identify a reason that large chemical companies are carrying out such research.
- Assess current developments in the use of a biopolymer such as Biopol.
- Polylactic acid (PLA) is a commercial synthetic biopolymer made from lactic acid. One major criticism of PLA is that it releases carbon dioxide and methane when it degrades during composting. Another criticism is that fossil fuels are still needed in its production. Discuss whether these criticisms are justified.

9. Figure 2.20 shows a portion of the polymer chain for four different biopolymers. Identify the diagram that represents cellulose.



**Figure 2.20** Use the structures of the biopolymers to answer question 9.



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## SUMMARY

- Step-growth polymerisation is also called *condensation* polymerisation.
- In condensation polymerisation a small molecule such as water is eliminated at each step of the condensation process.
- Polyesters are condensation polymers. They are formed when dicarboxylic acids condense with diols.
- Polyamides are condensation polymers. They are formed when dicarboxylic acids condense with diamines. Nylon is an example of this type of polymer.
- PET (or polyethylene terephthalate) is a very useful condensation polymer. It is used in plastic milk bottles and soft drink bottles.
- Cellulose is a condensation polymer of glucose.
- Cellulose is a useful raw material. It can be used as a fuel or it can be converted to other polymers or petrochemicals.
- Like cellulose, many other biopolymers such as starch and proteins are condensation polymers.
- Cellulose is a major component of biomass. Cellulose is a polysaccharide composed of glucose monomers.
- Current research involves utilising biomass for the production of biodegradable plastics and alternative fuels such as ethanol.
- Polylactic acid and polyhydroxy butyrate are biodegradable biopolymers. Biodegradable polymers may eventually replace polymers derived from petroleum.



# DATA ANALYSIS

## 2.1 DATA ANALYSIS

### DEVELOPMENT OF POLYLACTIC ACID (PLA)

Read the following information and then answer the questions on the next page.

#### History of PLA

The first low molecular weight polymer of lactic acid was made in 1932 at the DuPont laboratories. The process was patented in 1954 but because of the high cost of obtaining the monomer, little further research and development was conducted until the 1980s. During the period 1987–92, Cargill Inc. (USA) developed a pilot plant for PLA production; then in 1997, Cargill–Dow undertook the commercialisation of the polymer. By 2002 the Nebraska and Iowa facilities were producing large commercial quantities of PLA from corn starch.

#### Production of PLA

The corn is milled to extract the starch. Dextrose (a sugar) is extracted from the starch and this is anaerobically fermented with microorganisms such as *Lactobacillus* bacteria or certain fungi such as *Rhizopus oryzae* to produce lactic acid. In the polymerisation process, two lactic acid molecules are condensed to form a cyclic lactide dimer which is purified by vacuum distillation. A solvent-free melt polymerisation process opens the dimer ring, and chains of the lactic acid polymer with molecular weights greater than 100 000 amu are formed.

#### Properties of PLA

PLA's properties compare favourably to those of other commercial polymers. The essential difference between this polymer and other polymers such as HDPE, polypropylene (PP) and PET is that it is biodegradable and thus will not cause long-term disposal problems, as they can be composted.

Table 2.1

Polymer	PLA	HDPE	PP
Melting point (°C)	176	135	160
Density (g/cm <sup>3</sup> )	1.26	1.35	1.6
Tensile strength (MPa)	43	60	28
Elongation (%)	29	300	500

#### Comparing PLA and PET

Both PLA and PET are condensation polymers. PLA is more hydrophilic than PET. Thus fabrics woven from PLA fibres are more 'wetable' and allow greater moisture transfer and 'breathability' than PET fabrics. This occurs because of the grooves that run along the length of the PLA fibres. PLA has a lower refractive index than PETs and thus PLA fabrics can be dyed to deeper and brighter colours than PET fabrics. In terms of flame properties, both PLA and PET do burn, but PLA produces less smoke and a lower flame temperature. Flames tend to spread less rapidly than with PET materials. PLA is also highly resistant to UV degradation. PLA, however, has poor abrasion resistance and this limits its usefulness in applications where abrasion resistance is important.

#### Uses of PLA

PLA can be produced as fibres, coatings, films, cast sheets, foams and in injected moulded forms. Its applications are therefore diverse and include:

- fabrics
- dinnerware
- food-wraps
- rigid containers, dairy containers and food trays
- garbage bags.

# DATA ANALYSIS

## Questions

1. Explain why little research and development of PLA occurred until the 1980s.
2. Classify PLA as an addition polymer or condensation polymer.
3. Identify:
  - (a) a microorganism use that will produce lactic acid monomers.
  - (b) the biochemical process used to convert sugars to lactic acid.
4. State an important benefit to the environment in the use of PLA polymers over other commercial polymers.
5. Describe two characteristics of PLA that make it superior to PET.
6. Identify some uses of polylactic acid.
7. Explain why PLA fabrics are suitable for sports wear.