Lesson 35

Modern Chemistry

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OXFORD
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Founded 1894

Lesson 35

SET WORK

SUBJECT: Macromolecules.

READING: Mathews, Chapters 29 and 30

NOTES

MACROMOLECULES

A macromolecule is a giant molecule, usually based on a very long chain of carbon atoms. It may have a relative molecular mass of the order of a million. Macromolecules may be man-made or occur naturally.

MAN-MADE (SYNTHETIC) MACROMOLECULES

Man-made, synthetic, or artificial macromolecules are often referred to as **polymers**. They are usually derived from crude oil and are hence by-products of the oil industry. The most familiar forms of man-made polymers are in substances like plastics and man-made fibres. They may be sub-divided into two categories, addition polymers and condensation polymers.

ADDITION POLYMERS

An addition polymer is formed from a small unit, a monomer, which contains a carbon-carbon double bond (i.e. an alkene). Under the right conditions, the double bond splits open and a link-up with other monomers occurs to form a long carbon chain. The most common addition polymer is polyethene (polyethylene), formed by heating ethene at 200 $^{\circ}$ under 1000 atmospheres pressure in the presence of oxygen catalyst. The equation shows quite clearly the reaction mechanism:

$$\ldots\ldots\ CH_2{=}CH_2 \ + \ CH_2{=}CH_2 \ + \ CH_2{=}CH_2 \ldots\ldots$$

$$\searrow$$

$$\ldots\ldots\ CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\ \ldots\ldots$$

The equation is more usually abbreviated, and shown as:

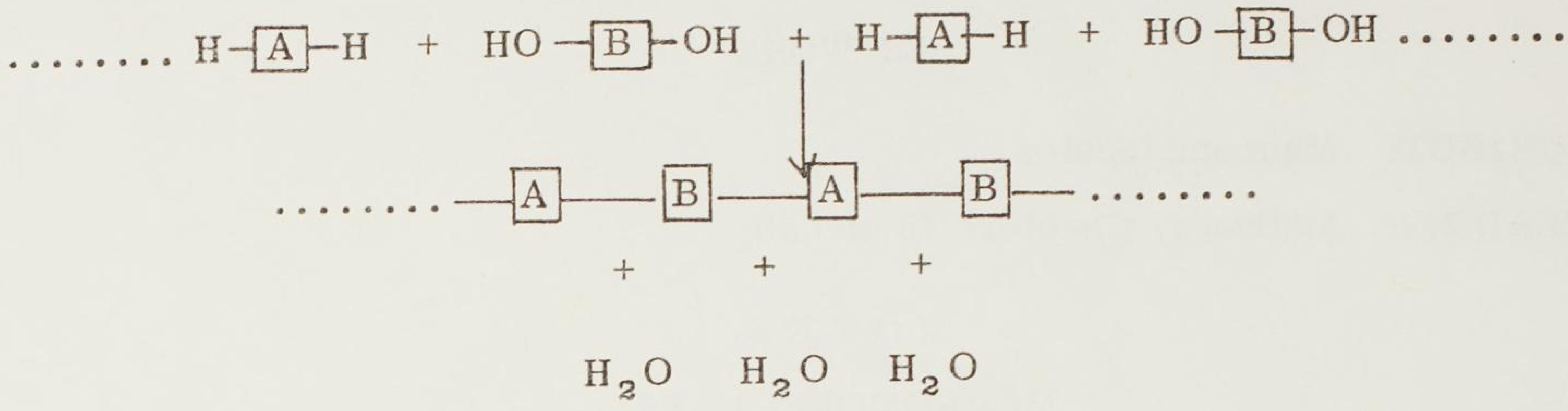
$$n(CH_2{=}CH_2) \longrightarrow (\!\!-CH_2-CH_2-\!\!)_n$$

ethene   polyethene

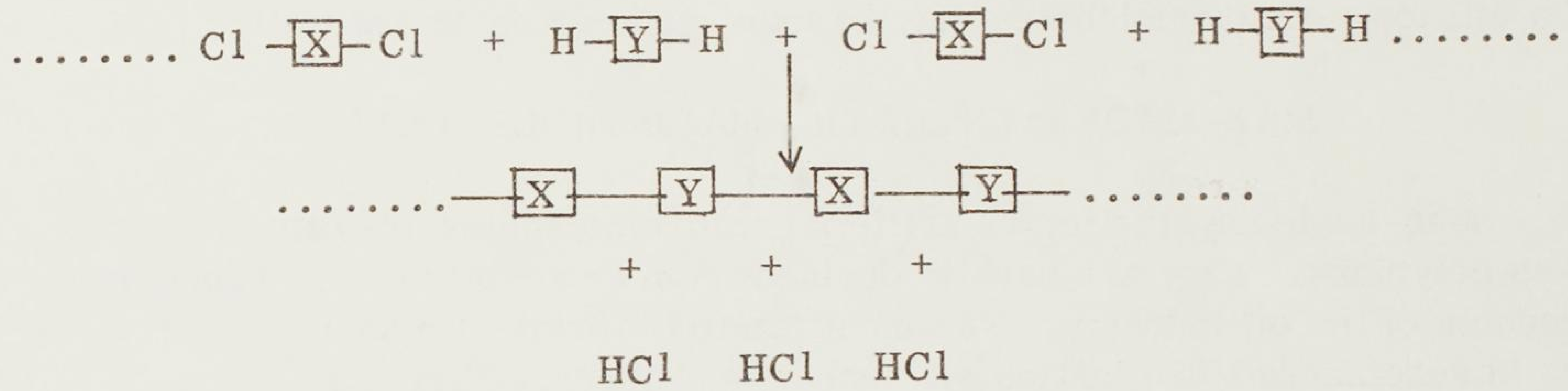
In an addition polymerisation reaction, the monomer gives the polymer with no other by-product.

CONDENSATION POLYMERS

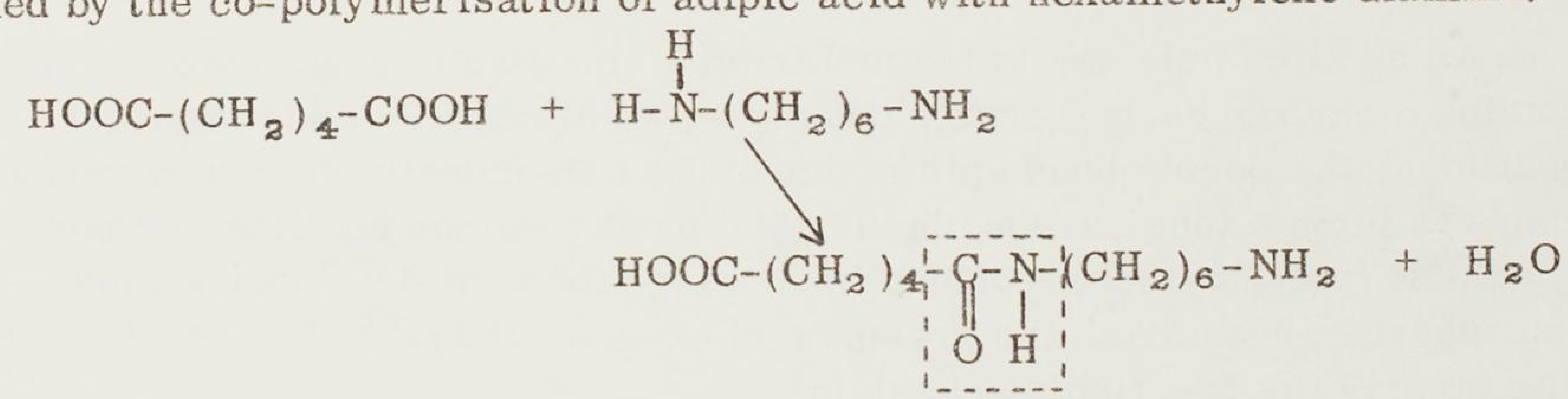
A condensation polymer is formed by the joining up of two different, small molecules to form an alternating chain by releasing a small simple molecule such as hydrogen chloride or water. For example:



or



The most usual example of a condensation polymer is that of nylon, formed by the co-polymerisation of adipic acid with hexamethylene diamine:



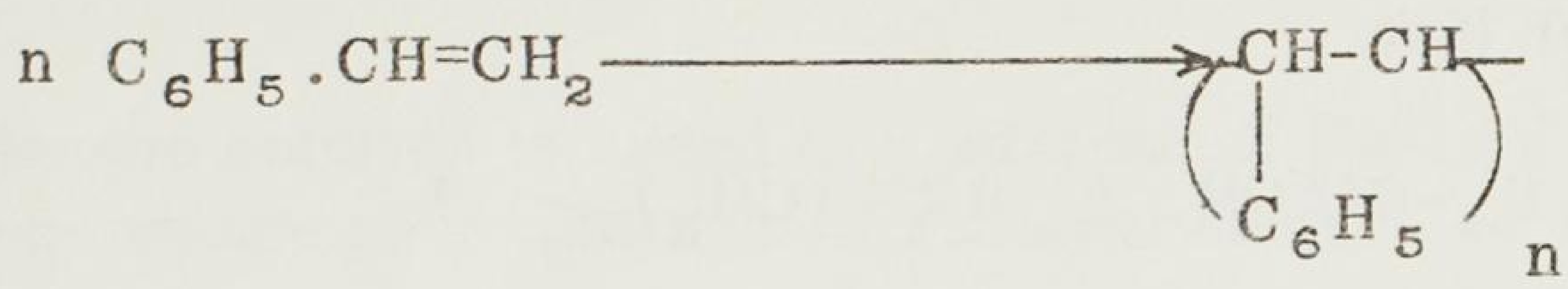
The two units form an alternating chain, each joined by the linkage shown in the dotted box, called a peptide link.

A simple strand of nylon can be easily prepared in the laboratory. Adipic acid dissolved in carbon tetrachloride is placed in a beaker, and hexamethylene diamine dissolved in water is added carefully. The two solvents are immiscible and water floats on the carbon tetrachloride, ensuring that the two reactants only meet at the interface of the two solvents. This interface can be removed and, as it is removed, a new interface immediately forms. The result is a continual removal of the interface which results in a nylon thread.

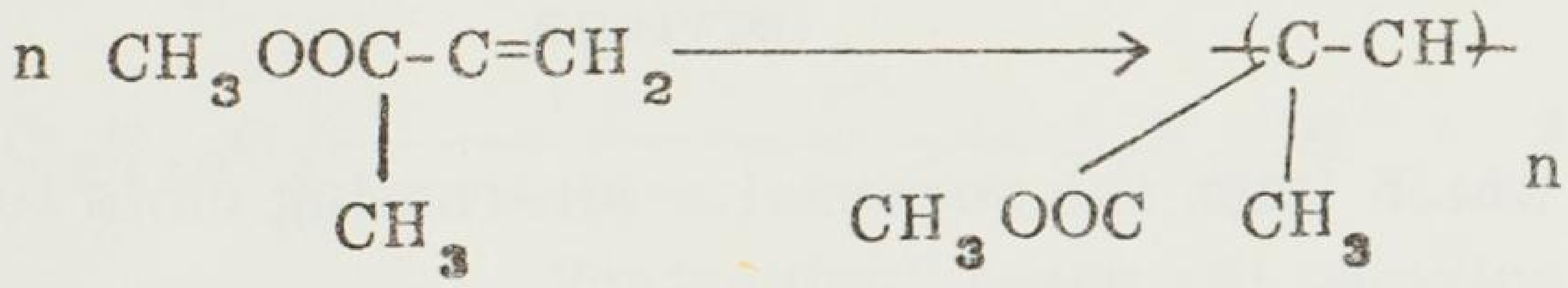
OTHER EXAMPLES OF MAN-MADE POLYMERS

1. **Addition polymers**

Two very common addition polymers are polystyrene and polymethyl methacrylate (perspex). In both cases a double bond present in the monomer splits open and a resulting polmeric chain forms.



styrene polystyrene

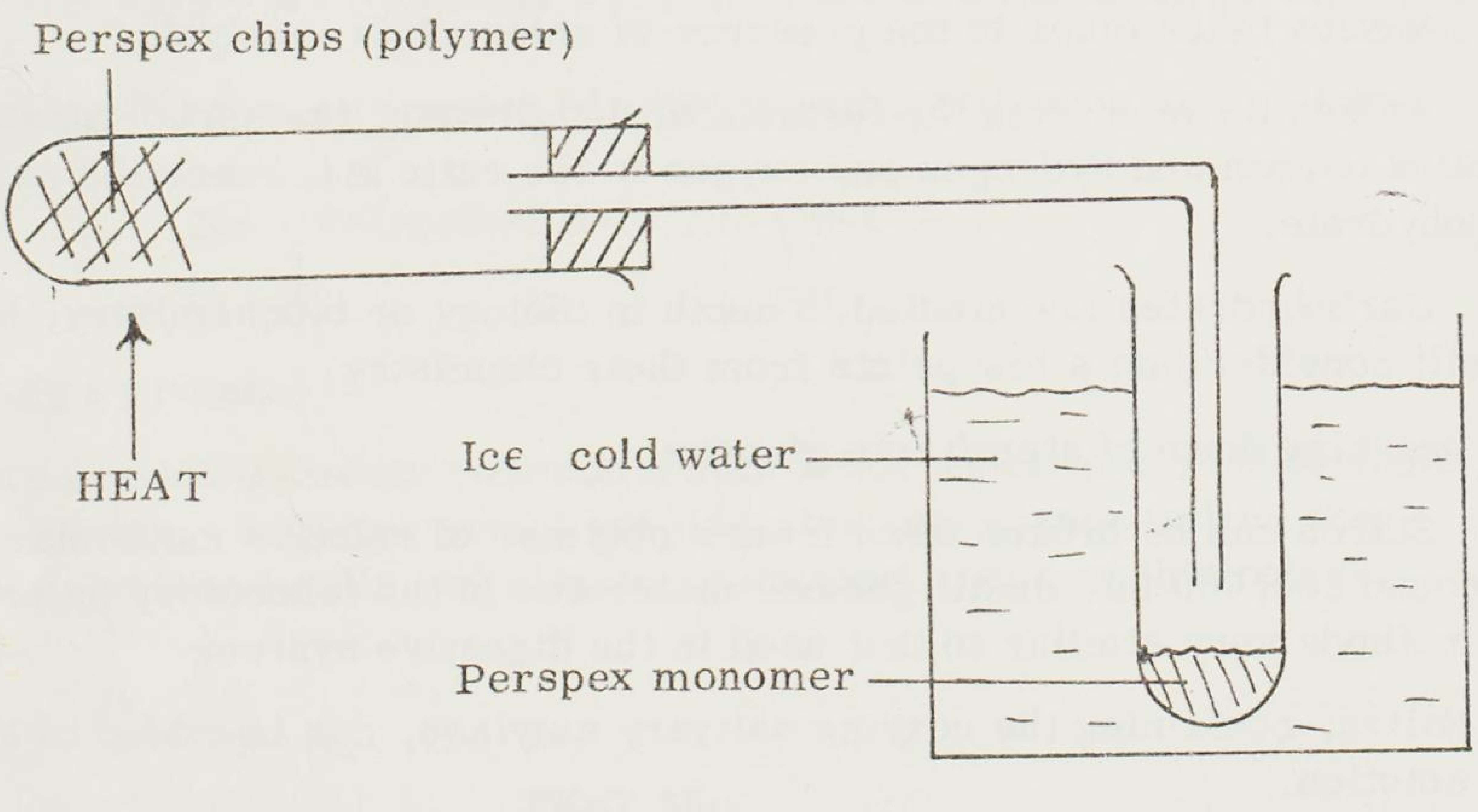


perspex monomer methyl methacrylate

perspex polymer polymethyl methacrylate

The similarity with polyethene should be clear; a double bond has split open giving a repeating unit. The only great difference is that one of the carbon atoms in the repeating unit has larger groups attached to it.

Perspex may be depolymerised and then polymerised again in a simple laboratory reaction. The depolymerisation is brought about simply by heating the solid in the following apparatus which condenses the monomer vapour as a foul smelling, poisonous liquid:



The reverse polymerisation is simply achieved by adding a catalyst such as lauroyl peroxide to the monomer. This is a reaction very similar to that which takes place in many commercial glues and filling compounds where a little "hardener" is added to a paste to form a solid compound.

2. **Condensation polymers**

Another common condensation polymer is terylene, formed by the co-polymerisation of terephthalic acid and glycol. This polymer is joined by an ester link:

$$\underset{\text{terephthalic acid}}{HOOC\text{-}C_6H_4\text{-}CO\text{-}OH} + \underset{\text{glycol}}{H\text{-}O\text{-}(CH_2)_2\text{-}OH}$$

$$\longrightarrow \underset{\text{terylene}}{HOOC\text{-}C_6H_4\text{-}CO\text{-}O\text{-}(CH_2)_2\text{-}OH} + H_2O$$

The ester linkage which joins the successive alternating units together gives this sort of polymer the name "polyester"

NATURALLY OCCURRING MACROMOLECULES

CARBOHYDRATES

Carbohydrates occur in vast quantities in animals and plants. They occur as a result of natural biological reactions such as that where carbon dioxide and water combine, using light energy in a plant to give a sugar, glucose:

$$6CO_2 + 6H_2O + \xrightarrow[\text{energy}]{\text{light}} C_6H_{12}O_6 + 6O_2$$

The reaction takes place in the presence of chlorophyll catalyst.

As can be seen from the formula of the glucose, the carbohydrate contains carbon and hydrogen and oxygen in the ratio 2:1; hence the name carbohydrate.

Carbohydrates are studied in depth in biology or biochemistry, here we will consider just a few points from their chemistry.

The breaking down of starch into glucose

Starch can be broken down from a polymer of relative molecular mass of around 500,000 into small glucose molecules in the laboratory by using two methods very similar to that used in the digestive system:

1. Saliva, containing the enzyme salivary amylase, can be added to starch solution.

2. Starch solution can be hydrolysed by warming it with dilute hydrochloric acid.

The equation for the reaction is:

$$\underset{\text{starch}}{(C_{12}H_{22}O_{11})_n} + nH_2O \longrightarrow \underset{\text{glucose}}{2nC_6H_{12}O_6}$$

The progress of the reaction can be checked at any stage by testing the reaction mixture for starch or glucose as follows:

1. When iodine solution is added to starch solution, a deep blue colour results.

2. When glucose solution is added to a mixture of Fehling's solutions 1 and 2, a deep orange precipitate occurs on warming.

The breaking down of glucose into ethanol

This reaction is that on which the brewing industry is based, and is usually called fermentation. Yeast contains the enzyme zymase which brings about the following reaction:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH \; + \; 2CO_2$$

The reaction usually never goes to completion because a solution in excess of 11% alcohol kills the yeast. Any further concentration of alcohol has to be brought about by fractional distillation.

This reaction, like any other biochemical reaction involving enzymes, progresses best at about 37^oC.

PROTEINS

Proteins are naturally occurring polymers based on a group of compounds called amino-acids of general formula:

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R-CH2-COOH
   |
  NH2
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where R represents a group of atoms such as CH_3, C_2H_5 etc.

They group together in a sequence of units joined together by amide links:

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.... -NH-CH-CONH-CH-CONH-CH-CO- ....
         |       |       |
         R       R'      R''
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thus forming a protein.

There are about twenty common amino-acids which give rise to many different proteins. Proteins are of considerable importance to life; they control the function of cells and also make up most enzymes (biological catalysts).

TEST 35

1. You are given a 10% solution of adipic acid dissolved in carbon tetrachloride, and a 10% solution of hexamethylene diamine dissolved in water. Adipic acid is $HOOC-(CH_2)_4-COOH$ and hexamethylene diamine is $H_2N-(CH_2)_6-NH_2$. Taking 50 cm^3 of each explain:

   (i) Two tests by which the two solutions could be distinguished.

   (ii) How they could be used in the laboratory to make a nylon thread.

(iii) Which reagent is present in excess. (C=12, H=1, O=16, N=14).

2. Explain how a carbohydrate polymer such as starch could be broken down in stages to a simple monomer such as ethene.

3. Explain, giving two examples of each, the difference between addition and condensation polymerisation.

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Specimen Answers to Test 34

1. The Haber process involves the production of ammonia from the gases hydrogen and nitrogen. The equation for the process is:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad H = -46\ kJ$$

The importance of temperature on the reaction hinges around the equilibrium and the fact that it is an exothermic reaction. The equilibrium will be moved to the right by a low temperature since it is exothermic, but the time taken for this reaction to take place is very long. If a higher temperature is used, the equilibrium will shift to the left, but this lower yield of ammonia will be reached more quickly.

The temperature used is a compromise temperature of 500 °C. This establishes the equilibrium quickly, giving around a 10% conversion. It is really a case of ammonia being obtained little and often, and this exceeding a large yield occasionally.

From the equation it can be seen that four molecules of gas combine to give two molecules of gas. This also means that four volumes of gas yield two volumes of gas. This is, of course, a contraction in volume which is helped by a high pressure. The pressure used, 200 atmospheres, is the maximum that can be used without too much hydrogen diffusing out of the plant; this is again a compromise since for the equilibrium, the higher the pressure the better the yield of ammonia.

2. Soap and detergent can both be made in the laboratory from castor oil. Soap is made by heating castor oil with very concentrated sodium hydroxide solution. On adding salt and allowing the solution to cool, a crust of soap separates out on the surface.

Detergent is prepared by adding sulphuric acid to castor oil in the proportions one part concentrated sulphuric acid to two parts castor oil. The mixture is stirred and the products of the strongly exothermic reaction are poured into a lot of cold water when detergent separates out as a slimy solid.

Soap and detergent both work in a similar way; they are long chain organic molecules which interfere with the surface tension effect of water. This allows water to wet and hence clean more efficiently.

Soap and detergent differ considerably in their chemical properties, the most important difference being that the magnesium and calcium salts of detergent are soluble in water. This means that with detergent, no scum forms on the surface of hard water. Detergent also more effectively dissolves grease than does soap.

3. In the Ostwald process, catalytic oxidation is used to oxidise ammonia to nitrogen monoxide. Ammonia and air are passed through a heated platinum grid at 1000^{o} where catalytic oxidation, due to the platinum, takes place. The equation for the reaction is:

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

In the contact process for manufacture of sulphuric acid, catalytic oxidation is again used. Sulphur dioxide and oxygen are cooled and cleaned and passed over platinum or vanadium pentoxide catalyst at $450^{o}C$. In a strongly exothermic reaction the yield of sulphur trioxide approaches 98%. For this reaction the equation is:

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

In both manufacturing processes, the solubility of gases in water is the important final stage of the reaction. In the Ostwald process, nitrogen dioxide and oxygen pass up a tower to meet a descending stream of water in which they dissolve:

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

In the contact process, the final stage is to dissolve sulphur trioxide in concentrated sulphuric acid, and then dilute the oleum formed. This is not strictly speaking a straight dissolving of the gas in water, because this reaction is so exothermic that the resulting acid boils and showers the plant with acid. The reaction can be described, however, by the equation:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

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