

<u>Objectives</u>

After studying this Unit, you will be able to

- explain the terms monomer, polymer and polymerisation and appreciate their importance;
- distinguish between various classes of polymers and different types of polymerisation processes;
- appreciate the formation of polymers from mono- and bi-functional monomer molecules;
- describe the preparation of some important synthetic polymers and their properties;
- appreciate the importance of polymers in daily life.

15.1 Classification of Polymers



"Copolymerisation has been used by nature in polypeptides which may contain as many as 20 different amino acids. Chemists are still far behind".

Do you think that daily life would have been easier and colourful without the discovery and varied applications of polymers? The use of polymers in the manufacture of plastic buckets, cups and saucers, children's toys, packaging bags, synthetic clothing materials, automobile tyres, gears and seals, electrical insulating materials and machine parts has completely revolutionised the daily life as well as the industrial scenario. Indeed, the polymers are the backbone of four major industries viz. plastics, elastomers, fibres and paints and varnishes.

The word 'polymer' is coined from two Greek words: poly means many and mer means unit or part. The term polymer is defined as very large molecules having high molecular mass (10³-10⁷u). These are also referred to as **macromolecules**, which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. The process of formation of polymers from respective monomers is called **polymerisation**.

There are several ways of classification of polymers based on some special considerations. One of the common classifications of polymers is based on source from which polymer is derived.

Under this type of classification, there are three sub categories.

1. Natural polymers

These polymers are found in plants and animals. Examples are proteins, cellulose, starch, some resins and rubber. 2. Semi-synthetic polymers

Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category.

- 3. Synthetic polymers
 - A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna S) are examples of man-made polymers extensively used in daily life as well as in industry.

Polymers can also be classified on the basis of their structure, molecular forces or modes of polymerisation.

Intext Questions

15.1 What are polymers ?

15.2 Types of Polymerisation Reactions

15.2.1 Addition Polymerisation or Chain Growth Polymerisation

15.2.1.1

Addition

Mechanism of

Polymerisation

or chain growth polymerisation and condensation or step growth polymerisation. In this type of polymerisation, the molecules of the same monomer or diferent monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes

There are two broad types of polymerisation reactions, *i.e.*, the addition

monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes and their derivatives. This mode of polymerisation leads to an increase in chain length and chain growth can take place through the formation of either free radicals or ionic species. However, the free radical governed addition or chain growth polymerisation is the most common mode.

1. Free radical mechanism

A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. For example, the polymerisation of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzovl peroxide initiator. The process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical. This step is called chain initiating step. As this radical reacts with another molecule of ethene, another bigger sized radical is formed. The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is termed as **chain propagating** step. Ultimately, at some stage the product radical thus formed reacts with another radical to form the polymerised product. This step is called the **chain terminating step**. The sequence of steps involved in the formation of polythene are depicted as follows:

Chain initiation steps

$$\begin{array}{cccc} & & & & O & & & O \\ & & & & & O & & \\ C_{6}H_{5}-C-O-O-C-C_{6}H_{5} & & & & 2C_{6}H_{5}-C-O & & & 2\dot{C}_{6}H_{5} \\ & & & & & & \\ Benzoyl \ peroxide & & & & Phenyl \ radical \\ & & & & C_{6}H_{5}+CH_{2}=CH_{2} & & & C_{6}H_{5}-CH_{2}-\dot{C}H_{2} \end{array}$$

