CHAPTER

1

POLYMERS

1.0. INTRODUCTION

A polymer is a large molecule composed of many smaller repeating structural units (the monomers) bonded together by covalent bonds. The word polymer is derived from the Greek word polymerose (poly-many, meros-part). In this context, a large molecule is commonly arbitrarily regarded as one having a molecular weight of at least *one thousand* or as one containing hundred structural units or more.

The term **macromolecule** simply means a large molecule and is often used synonymously with polymer. In fact, the terms polymer and macromolecule are not equivalent since macromolecules, in principle, need not be composed of repeating structural units. Thus, vitamin B_{12} is a macromolecule but not a polymer whereas protein is a macromolecule as well as a polymer.

Polymers are so common in our everyday lives that we rarely take notice of their presence. They are used to make commercial products as diverse as clothing and compact disks, calculators and styrofoam cups, packing for food, and insulation. Plastic play such an important role in the industrialised world that we may have moved from the age of **metals** into the **Age of plastics**. Chemists have learned to manufacture polymers in the laboratory, but nature mastered the technique long ago. All living cells produce a complex array of different types of macromolecules. Wood for example, contains macromolecules, and so does cotton. The human body contains a rich variety of **biochemical** macromolecules.

Polymeric materials may be inorganic, organic, natural or synthetic. Organic polymeric materials are commonly classified as adhesives, paints, fibres, plastics and rubbers. The physical properties of an individual polymeric materials are largely determined by molecular weight, strength of intermolecular forces, regularity of polymer structure and flexibility of the polymer molecule.

Basic Concepts and Definitions

Polymer : Polymer means "many part" and designates a macromolecule made up of smaller repeating units. According to composition polymers may be classed as organic, inorganic or organo-element. The most thoroughly studied are organic polymers. The simplest organic polymer is polyethylene, the polymerisation product of ethylene. Ethylene is an unsaturated hydrocarbon which enters readily into addition reactions. Two ethylene molecules combine to form a molecule of butene.

$$CH_2=CH_2+CH_2=CH_2$$
$$\downarrow$$
$$CH_3-CH_2-CH=CH_2$$

The initial substance, ethylene, is called a **monomer** and the resulting butene is a dimer. If three ethylene molecules combine, the result is a *trimer*, four molecules form a *tetramer*, etc. If a *n* molecules of a monomer unite, they form a *polymer*.

$$\underset{\text{monomer}}{nCH_2=CH_2} \longrightarrow \underset{\text{polymer}}{\left[CH_2-CH_2 \right]_n}$$

1.01. Monomer

A monomer is a molecule that combines with other molecules of the same or different type to form a polymer. For example vinyl chloride $CH_2=CH-Cl$, is the monomer for polyvinyl chloride

$$n\,CH_2{=}CH{-}Cl \longrightarrow {-}\!\!\left[CH_2{-}\underset{}{\overset{Cl}{\overset{|}{C}}}H \right]\!\!{-}_n$$

polyvinyl chloride

Adipic acid and hexamethylene diamine are the monomers of Nylon 66.

$$n\,HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}OH + n\,NH_2{-}(CH_2)_6{-}NH_2$$

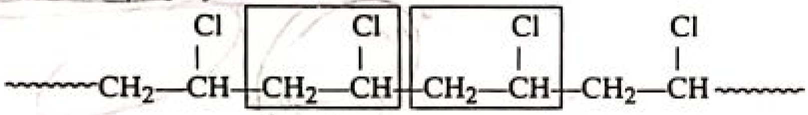
$$\downarrow$$

$$HO{-}\!\left[\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}NH{-}(CH_2)_6-NH \right]\!{-}_n$$

1.02. Repeating Unit

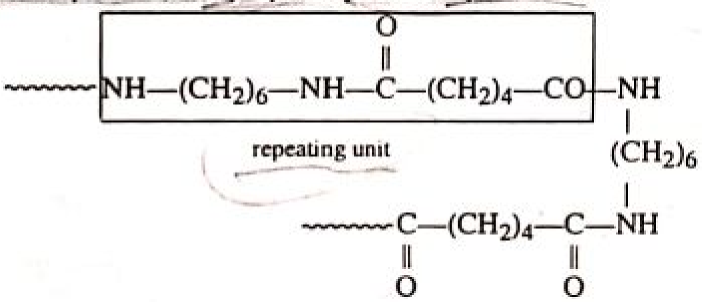
The repeating unit of a linear polymer (say) is a portion of the polymer such that the complete polymer (except for the ends) might be produced by linking a sufficiently large number of these units through covalent bonds.

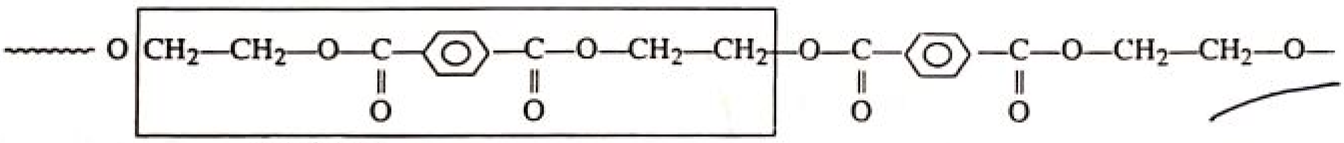
The repeating unit may comprise a single identifiable precursor as in polyvinyl chloride, polyvinylcyanide and polystyrene :



repeating unit repeating unit

A repeating unit may also be composed of the residue of several smaller molecules as in poly-(hexamethylene adipamide), or poly-(ethylene terephthalate) :

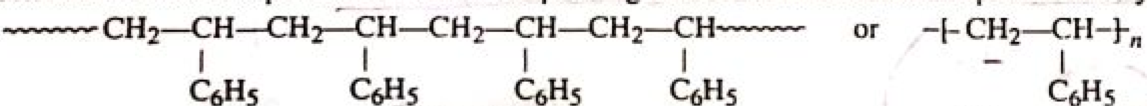




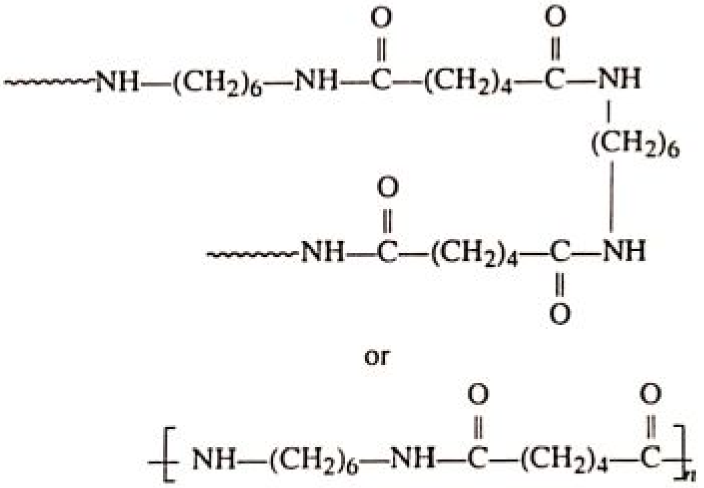
repeating unit

1.03. Representation of Polymer Structures

Polymer structures are normally drawn as follows by showing only one repeating unit. Each representation below is equivalent to the corresponding structure that has been depicted side by side.



Polystyrene Polystyrene

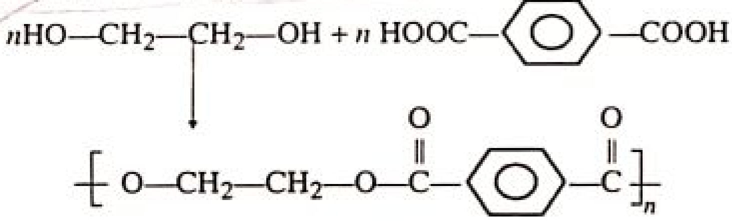


Nylon-66

The subscript n represents the number of repeating units in the polymer molecule.

1.04. End groups

The terminal or end groups of the polymer are known as end groups. The exact nature of the end groups is frequently not known and the polymer structure is therefore written only in terms of the repeating unit, as in the given structural representation :



End groups usually have negligible effect on polymer properties of major interest. For example. commercial styrene have molecular mass of about 100,000. An average polymer molecule will contain 1000 or more styrene residue, compared to two end-units.

1.05. Degree of polymerisation

The number of repeating units in the polymer molecule is called the degree of polymerisation, denoted by the letter n or P or DP. The product of the degree of polymerisation and the molecular mass (M_0) of a monomeric unit equals the molecular mass (M) of the polymer.

$$M = M_0 (DP)$$

The degree of polymerisation may vary over a wide range, from a few units to 5000 — 10,000, and more. Polymers with high degree of polymerisation are called **high polymers**, while those with a low degree of polymerisation are known as **oligomers**. High polymers have very large molecular masses, of the order from 10^4 to 10^6, and hence, are high molecular-mass compounds.

If the molecular mass of a polymer is high, the terminal or end groups of its chain need to be taken into account; and the polymer molecule can be written without them, showing only a few or even only one monomeric unit.

1.06. Polymerisation and Functionality

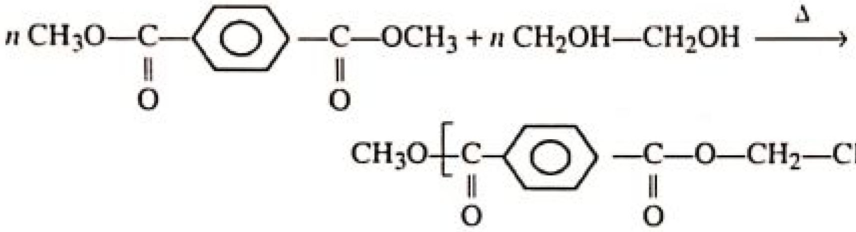
Polymerisation is a chemical reaction in which the product molecules are able to grow indefinitely in size as long as reactants are supplied. Polymerisation can occur if the monomers involved in the reaction have the proper functionalities.

The functionality of a molecule is the number of sites available for bonding to other molecules under the specific conditions of the polymerisation reaction.

A trifunctional monomer can be linked to two other molecules under appropriate conditions. Examples are :

$$n\,H_2N{-}(CH_2)_6{-}NH_2 + n\,HO{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{O}{\|}}{C}{-}OH \xrightarrow{\Delta} H{\left[NH{-}(CH_2)_6{-}NH{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{O}{\|}}{C} \right]_n} OH \quad \text{... (1)}$$

Nylon 6.6



Poly (ethylene terephthalate) ... (2)

$$n\,CH_2{=}CH_2 \xrightarrow[\text{Al}(C_2H_5)_4/TiCl_4]{\text{heptane, }60^\circ C} {+}CH_2{-}CH_2{+}_n \quad \text{... (3)}$$

Polyethylene

A polyfunctional molecule can react with more than two other molecules to form the corresponding number of new bonds during the polymerisation reaction.

If an a-functional monomer reacts with a b-functional monomer in a nonchain reaction, the functionality of the product molecule is $a + b - 2$. This is because every new linkage consumes two bonding sites. Production of a polymer in such reactions can occur only if a and b are both greater than one.

The following points about functionality should be noted :

(i) Use of the term functionality here is not the same as in organic chemistry where a carbon-carbon double bond, for eample, is classified as a single functional group. Double band is treated as bifunctional group in polymerisation.

(ii) Functionality refers in general to the overall reaction of monomers to yield products. It is not used in connection with the individual steps in a reaction sequence. For example, the free radical polymerisation of styrene is a chain reaction in which a single step involves attack of a radical with ostensible functionality of one on a monomer with functionality two.

(iii) Functionality is defined only for a given reaction. A glycol has a functionality of two in esterification, but its functionality is zero in amide forming reactions. Similarly the functionality of 1, 3-butadiene may be two or four depending on the particular double-bond addition reaction.

(iv) The condition that monomer be bifunctional or polyfunctional is a necessary, but not sufficient, condition for polymerisation to occur in practice. Not all reactions between polyfunctional monomers actually yield polymers. The reaction must also proceed clearly with good yield to give high molecular-weight products. For example, propene has a functionality of two in reactions involving the double bonds but free radical reactions do not produce macromolecules whereas polymersiation in heptane at 70°C with an $(C_2H_5)_3Al \mid TiCl_3$ catalyst does yield high polymers.

(v) Functionality is a very useful concept in polymer science.

Carother's Equation

According to the Carothers average functionality (f_{av}) can be calculated by the equation (1).