

Study Notes on Polymer Chemistry





A polymer is made up of a large number of monomeric structural units which are repeated over and over again to form a giant molecule called a macromolecule.

CLASSIFICATION OF POLYMERS

Based on origin:

- Natural polymers: Starch, cellulose, silk, wool
- Semi-Synthetic polymers: Neoprene, Silicone rubber
- Synthetic polymers: Polythene, PVC

Based on structure of polymers:

• **Linear polymers:** made up of long and straight chains. *e.g.*, high-density polyethene, polyvinyl chloride, etc.



 Branched-chain polymers: consist of linear chains having branches, e.g., low-density polythene.



• Cross-linked or Network polymers: consists of strong covalent bonds between various linear polymer chains, *e.g.*, bakelite, melamine.



Based on mode of polymerisation:

 Addition polymers: These are formed by the repetitive addition of monomer molecules such as alkenes or alkynes, *e.g.*, homopolymer -polythene and copolymer- Buna-S, Buna-N

$$n CH_2 = CH - CH = CH_2 + n C_6H_5CH = CH_2$$
 — \rightarrow — $(CH_2 - CH = CH - CH_2 - CH_2 - CH_2)$ — Butadiene - Styrene copolymer (Buna - S)



 Condensation polymers: These are formed by the combination of monomers with the elimination of simple molecules such as water or alcohol. e.g., Terylene or dacron and polyamides- Nylon-6,6

n H₂N (CH₂)₆NH₂ + n HOOC (CH₂)₄ COOH

$$\longrightarrow \frac{1}{1} \text{NH (CH2)}_{6} \text{NHCO(CH2)}_{4} \text{CO} + n \text{ H}_{2}\text{O}$$
Nylon 6, 6

Based on molecular forces:

• **Elastomer**: weak intermolecular forces of attraction and possesses elastic character. *e.g.*, Vulcanized rubber.

$$\left(\begin{array}{c} CH_2-C=CH-CH_2 \\ I \\ Cl \\ Neoprene \end{array}\right)_n$$

• **Fibers**:. strong intermolecular forces like hydrogen bonding and possess high tensile strength *e.g.*, polyamides (nylon 6, 6), polyesters (terylene), etc.

$$\begin{array}{cccc} H & H & O & O \\ \downarrow & & \parallel & \parallel \\ N-(CH_2)_6-N-C(CH_2)_4-C & \uparrow_n \\ & \text{Nylon 6,6} \end{array}$$

 Thermoplastics: softens on heating and becomes hard on cooling. e.g., polyethylene, polystyrene,PVC

$$Cl$$
 CH_2-CH
 DVC

• Thermosetting Polymers or Resin: becomes hard on heating. e.g., bakelite, urea formaldehyde polymer.



Molar Masses of Polymer: The molar mass of polymer can be defined as a statistical average rather than a specific number since polymerization occurs in such a way to produce different chain lengths.

Weight average molecular weight (M_W)

$$M_W = \sum_{i=1}^N w_i \mathrm{MW}_i$$

where, w_i is the weight fraction of polymer chains having a molecular weight of MW_i

Number average molecular weight (M_N)

$$M_N = \sum_{i=1}^N X_i MW_i$$
.

where, MW_i is the molecular weight of each individual polymer chain and X_i refers to the mole fraction of each chain length.

The ratio M_w / M_n is called the *polydispersity index (P.D.I)*. The broadness of a molecular weight distribution of a polymer is measured by P.D.I, i.e. if the polydispersity index is larger, the broader will be the molecular weight distribution.

For all real polymers, M_n<M_w

TACTICITY OF POLYMER:

The difference in the configuration of a polymer molecule when the positioning of the monomeric units in a polymer takes place in an orderly or random manner is known as tacticity.

On the basis of tacticity, the structure of the polymer may be divided into the following categories (i) Isotactic (ii) Syndiotactic (iii) Atactic

If all chiral centers have the same configuration, the arrangement of the side groups is called *isotactic*



If every other chiral center has the same arrangement, it is called *syndiotactic*

A random arrangement of the side groups is called *atactic* or *heterotactic*.



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