Detailed Notes on Polymers

1. Types of Polymers

(a) Based on Source

- Natural Polymers: cellulose, starch, proteins, rubber.
- Synthetic Polymers: polyethylene, polystyrene, nylon.
- Semi-synthetic Polymers: rayon, cellulose acetate.

(b) Based on Structure

- Linear Polymers: polyethylene, PVC.
- Branched Polymers: low-density polyethylene.
- Cross-linked Polymers: bakelite, vulcanized rubber.

(c) Based on Polymerization Mechanism

- Addition Polymers: polyethylene, polystyrene.
- Condensation Polymers: nylon, polyester.

(d) Based on Molecular Forces

- Elastomers: weak forces, highly elastic (rubber).
- Fibres: strong H-bonds (nylon, polyester).
- Thermoplastics: soften on heating (PVC, polystyrene).
- Thermosetting plastics: harden irreversibly (bakelite).

2. Kinetics and Mechanisms of Polymerization

(a) Addition (Chain-growth) Polymerization

Occurs via free radical, ionic, or coordination mechanisms.

1. Free Radical Polymerization $\rightarrow$ Initiation, Propagation, Termination.

Rate Equation: $R_p = k_p [M][R\bullet]$

2. Ionic Polymerization $\rightarrow$ Cationic (BF_3, $AlCl_3$), Anionic (BuLi).

Living polymerization (fast propagation, rare termination).

3. Coordination (Ziegler–Natta) Polymerization $\rightarrow$ $TiCl_4$ + $AlEt_3$. Stereoregular polymers.

(b) Step-growth (Condensation) Polymerization

Reaction of multifunctional monomers.

Example: nylon-6,6 from adipic acid + hexamethylenediamine.

Rate decreases as molecular weight increases.

3. Molecular Mass of Polymers

1. Number Average Molecular Mass:

Mn = ΣNiMi / ΣNi (measured by osmometry).

2. Weight Average Molecular Mass:

Mw = $\Sigma NiMi^2$ / ΣNiMi (measured by light scattering).

3. Polydispersity Index (PDI): Mw / Mn (synthetic polymers PDI > 1).

4. Methods of Molecular Mass Determination

- Osmometry: based on osmotic pressure, $\pi = cRT/M$.
- Viscosity Method: Mark–Houwink equation $\rightarrow [\eta] = K M^a$.
- Light Scattering: scattered intensity $\propto$ Mw.