

UNIT 4: Polymer & Polymerization

1. Introduction to Polymers

- **Polymers** are large molecules formed by **repeating small units (monomers)** through polymerization.
 - Example: Plastics, rubbers, resins, and fibers are all polymers.
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2. Types of Polymerization

A. Addition Polymerization (Chain Growth Polymerization)

- Involves monomers with **double or triple bonds** that form polymers **without any byproduct formation**.
- Example: PVC, Teflon, PMMA.

Mechanism of Free Radical Polymerization (Addition Polymerization):

1. **Initiation:** Formation of free radicals using initiators like **Benzoyl Peroxide**.
 - $\text{R-O-O-R} \xrightarrow{\text{heat/light}} 2 \text{R}\cdot$ (Free Radicals)
 2. **Propagation:** Free radical attacks a monomer, continuing the chain reaction.
 - $\text{R}\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{R-CH}_2\text{-CH}_2\cdot$
 3. **Termination:** Two free radicals combine, stopping the reaction.
 - $\text{R-CH}_2\text{-CH}_2\cdot + \text{R}\cdot \rightarrow \text{R-CH}_2\text{-CH}_2\text{-R}$
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B. Condensation Polymerization (Step Growth Polymerization)

- **Two different monomers react**, forming a polymer and **eliminating a small molecule** like H_2O , NH_3 , or HCl .
 - Example: Nylon-6,6, Polyester, Phenol-Formaldehyde.
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3. Classification of Polymers

A. Based on Source:

1. **Natural Polymers** – Found in nature (e.g., Rubber, Starch, Proteins).
2. **Synthetic Polymers** – Man-made (e.g., PVC, Nylon, Teflon).
3. **Semi-Synthetic Polymers** – Modified natural polymers (e.g., Rayon).

B. Based on Structure:

1. **Linear Polymers** – Straight-chain molecules (e.g., PVC, Nylon).
2. **Branched Polymers** – Side branches (e.g., Low-Density Polyethylene).
3. **Cross-linked Polymers** – 3D network (e.g., Bakelite, Vulcanized

Rubber). **C. Based on Molecular Forces:**

1. **Elastomers** – Stretchable (e.g., Rubber).
2. **Fibers** – High strength (e.g., Nylon, Polyester).
3. **Thermoplastics** – Softens on heating (e.g., PVC, Teflon).
4. **Thermosetting Polymers** – Hardens permanently (e.g., Bakelite).

4. Thermoplastic vs Thermosetting Polymers

Property	Thermoplastics	Thermosetting Polymers
Softening on Heat	Softens & reshaped multiple times	Hardens permanently
Structure	Linear/Branched	Cross-linked
Examples	PVC, Teflon, Nylon	Bakelite, Urea-Formaldehyde
Recyclability	Recyclable	Non-Recyclable

5. Biodegradable Polymers

- **Polymers that decompose naturally** by microbial action.
- Example: **Polylactic Acid (PLA)**, **Polyhydroxybutyrate (PHB)**.

6. Important Polymers: Preparation, Properties & Uses

1. PVC (Polyvinyl Chloride)

- **Preparation:** Polymerization of **Vinyl Chloride ($\text{CH}_2=\text{CHCl}$)**.
- **Properties:** Hard, brittle, water-resistant.
- **Uses:** Pipes, cables, synthetic leather.

2. PMMA (Polymethyl Methacrylate) - Acrylic

- **Preparation:** Polymerization of **Methyl Methacrylate ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$)**.
- **Properties:** Transparent, shatter-resistant.
- **Uses:** Lenses, acrylic glass.

3. Teflon (Polytetrafluoroethylene - PTFE)

- **Preparation:** Polymerization of **Tetrafluoroethylene** ($\text{CF}_2=\text{CF}_2$).
- **Properties:** Non-stick, heat-resistant, chemically inert.
- **Uses:** Non-stick cookware, insulation.

4. Nylon 6 & Nylon 6:6

- **Nylon 6 Preparation:** From **Caprolactam** by **ring-opening polymerization**.
- **Nylon 6:6 Preparation:** From **Hexamethylenediamine** + **Adipic Acid**.
- **Properties:** Strong, wear-resistant.
- **Uses:** Fibers, ropes, gears.

5. Polyester

- **Preparation:** From **Terephthalic Acid** + **Ethylene Glycol**.
- **Properties:** Wrinkle-resistant.
- **Uses:** PET bottles, clothing.

6. Phenol-Formaldehyde (Bakelite)

- **Preparation:** Polymerization of **Phenol** + **Formaldehyde**.
- **Properties:** Hard, electrical insulator.
- **Uses:** Electrical switches, handles.

7. Urea-Formaldehyde

- **Preparation:** Polymerization of **Urea** + **Formaldehyde**.
- **Properties:** Rigid, non-conductive.
- **Uses:** Adhesives, particle boards.

8. Buna-N (Nitrile Rubber)

- **Preparation:** Copolymerization of **Butadiene** + **Acrylonitrile**.
- **Properties:** Oil-resistant.
- **Uses:** Fuel hoses, gloves.

9. Buna-S (Styrene Butadiene Rubber - SBR)

- **Preparation:** Copolymerization of **Butadiene** + **Styrene**.
- **Properties:** Tough, abrasion-resistant.
- **Uses:** Tires, footwear.

7. Vulcanization of Rubber

- **Process:** Heating **natural rubber with sulfur** to **increase elasticity & strength**.
 - **Reaction:** Rubber + Sulfur (S₈) → Cross-linked Rubber • **Uses:** Tires, conveyor belts.
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8. Summary of Important Polymers

Polymer	Type	Monomer(s)	Uses
PVC	Addition	Vinyl Chloride	Pipes, insulation
Teflon	Addition	Tetrafluoroethylene	Non-stick cookware
Nylon 6:6	Condensation	Hexamethylenediamine + Adipic Acid	Ropes, fabrics
Bakelite	Condensation	Phenol + Formaldehyde	Electrical switches
Buna-N	Copolymer	Butadiene + Acrylonitrile	Fuel hoses