UNIT 4: POLYMERS

Introduction to Polymers

Polymer: The term "polymer" comes from the Greek words "poly," meaning many, and "meros," meaning part. Polymers are large, chain-like molecules made up of many repeating smaller units called monomers. A polymer typically consists of more than 100 monomers, and smaller chains with fewer monomers are known as oligomers. Polymers can be linear, slightly branched, or highly interconnected in a three-dimensional network. The size of a polymer molecule is defined by either its mass or the number of repeating units it contains, known as the degree of polymerization (DP). The molecular weight of a polymer is the product of the molecular weight of the repeat unit and the DP.

Monomers: Monomers are small molecules that serve as the building blocks for polymers. Each monomer has two or more functional groups, allowing it to form chemical bonds with at least two other monomer molecules. Monomers with only two functional groups (bifunctional) can only form linear polymers, while monomers with higher functionality can create cross-linked, network polymers.

Polymerization Reactions

Polymerization:
Polymerization is the chemical process by which monomer units combine to form a polymer. There are two main types of polymerization reactions: addition polymerization and condensation polymerization.

Addition Polymerization: In addition polymerization, monomers with double or triple bonds react to form a polymer without the loss of any small molecules. This reaction is also known as chain-growth polymerization. For example, ethylene (C_2H_4) can undergo addition polymerization to form polyethylene, a widely used plastic.

Steps of Addition Polymerization:

1. **Chain Initiation:** The polymerization process begins with a reactive initiator molecule (such as a free radical, cation, or anion) that reacts with a monomer, creating a reactive center.
2. **Chain Propagation:** In this step, additional monomer units continuously add to the growing polymer chain, transferring the reactive center to the chain's end.

3. **Chain Termination:** The polymerization stops when the reactive center is neutralized, preventing further chain growth. Termination can occur through various processes, such as the combination of two free radicals or chain transfer to another molecule.

Example of Free Radical Polymerization:

- **Chain Initiation:**

  Initiator ($Ra\cdot$)+Monomer ($CH_2=CH_2$)$\rightarrow Ra\text{-}CH_2\cdot$

- **Chain Propagation:**

  $Ra\text{-}CH_2\text{-}CH_2\cdot$+Monomer ($CH_2=CH_2$)$\rightarrow Ra\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\cdot$

- **Chain Termination:**

  $Ra\text{-}CH_2\text{-}CH_2\cdot + Ra\text{-}CH_2\text{-}CH_2\cdot \rightarrow$ Polymer $(CH_2\text{-}CH_2)n$

Condensation Polymerization: In condensation polymerization, monomers with two or more functional groups combine, releasing a small molecule such as water or methanol as a byproduct. This type of polymerization is also known as step-growth polymerization. Common examples include the formation of polyesters (like polyethylene terephthalate, PET) and polyamides (like Nylon 66).

Example of Condensation Polymerization:

- **Nylon 66:** This synthetic polyamide is formed by the condensation reaction between hexamethylene diamine and adipic acid, releasing water as a byproduct.

  $HOOC\text{-}(CH_2)_4\text{-}COOH + H_2N\text{-}(CH_2)_6\text{-}NH_2 \rightarrow$ Nylon 66+(2n-1) H_2O

Uses of Polymers

- **Nylon:** Used in making parachutes, ropes, clothing, stockings, hair combs, and rugs. It also reinforces automobile tires.
- **Polyethylene Terephthalate (PET):** Used in making synthetic fibers, bottles, and packaging materials. PET fabrics are durable, easily dyed, and crease-resistant.

Classification of Polymers

Polymers are large molecules made up of repeating smaller units called monomers. They can be classified in various ways based on their structure, the type of monomers they are made from, their thermal properties, and their origin. Here's a summary of the different methods of polymer classification:

1. **Based on Monomer Type:**
    - **Homopolymers:** Polymers made from a single type of monomer. For example, polyethylene is made from ethene (ethylene) monomers.
    - **Copolymers:** Polymers made from two or more different types of monomers. For example, a copolymer made from ethene and propene can have repeating units arranged either randomly or regularly along the chain.
        - **Random Copolymers:** Monomers are arranged randomly.
        - **Regular Copolymers:** Monomers alternate in a regular pattern.
2. **Based on the Polymerization Process:**
    - **Addition Polymers:** Formed by the addition of monomers with double or triple bonds, without the loss of any small molecules. Examples include polyethylene, polypropylene, and polyvinyl chloride (PVC).
    - **Condensation Polymers:** Formed by the reaction between monomers with the loss of small molecules like water. Examples include polyesters and nylon.
3. **Based on Origin:**
    - **Natural Polymers:** Occur naturally and include macromolecules like proteins (e.g., enzymes), nucleic acids (e.g., DNA), and polysaccharides (e.g., starch, cellulose).
    - **Synthetic Polymers:** Man-made polymers, often referred to as plastics. Examples include polyethylene, polypropylene, and polystyrene.
4. **Based on Thermal Properties:**
    - **Thermoplastics:** Polymers that soften when heated and harden when cooled. They can be remelted and recycled. Examples include polyethylene and polypropylene.
    - **Thermosets:** Polymers that harden permanently after being heated. They do not soften upon reheating and cannot be recycled. Examples include Bakelite and epoxy resins.

Examples of Common Polymers

- **Polyethylene:** A lightweight, non-toxic, and cheap polymer used in plastic bags, bottles, and insulation.

- **Polypropylene:** Stronger than polyethylene, used in food containers, ropes, and carpets.
- **Polyvinyl Chloride (PVC):** Used in pipes, flooring, and raincoats.
- **Polymethyl Methacrylate (PMMA or Plexiglass):** A glass substitute used in airplane windows and streetlights.
- **Teflon (PTFE):** Known for its non-stick properties, used in cookware and electrical insulation.

Thermoplastics vs. Thermosets

- **Thermoplastics** can be remelted and reshaped, making them recyclable. Examples include polyethylene and PVC.
- **Thermosets** form irreversible bonds when heated and do not melt upon reheating, making them non-recyclable. Examples include Bakelite and epoxy resins.