UNIT - IV: MACROMOLECULES

Introduction to Macromolecules:

Macromolecules are large molecules composed of repeating structural units called monomers. They play crucial roles in various biological, industrial, and material science applications. Polymers are a significant class of macromolecules, characterized by their long chains of repeating units.

Structure of Polymers:

1. **Monomers:**
    - The building blocks of polymers.
    - Small molecules that can chemically bond to form long chains or networks.
    - Examples include ethylene, propylene, styrene, vinyl chloride, etc.
2. **Polymerization:**
    - Polymerization is the process of combining monomers to form a polymer.
    - Types of polymerization:
        - Addition polymerization: Monomers add to the growing polymer chain without the formation of by-products.
        - Condensation polymerization: Monomers join together with the elimination of small molecules, such as water or alcohol.
3. **Polymer Structure:**
    - Linear polymers: Consist of long chains of monomers connected end-to-end.
    - Branched polymers: Have side chains or branches stemming from the main polymer chain.
    - Crosslinked polymers: Form a network structure due to covalent bonds between polymer chains.
    - Polymer architecture influences properties like flexibility, strength, and elasticity.
4. **Tacticity:**
    - Refers to the spatial arrangement of monomer units along the polymer chain.
    - Types of tacticity include isotactic, syndiotactic, and atactic, based on the regularity of monomer placement.

Classification of Polymers:

1. **Based on Origin:**
    - **Natural Polymers:** Derived from natural sources like plants, animals, or microorganisms. Examples include proteins, cellulose, rubber, and DNA.
    - **Synthetic Polymers:** Man-made polymers produced through chemical reactions. Examples include polyethylene, polypropylene, polystyrene, and PVC.
2. **Based on Structure:**
    - **Homopolymers:** Consist of repeating units of a single type of monomer.
    - **Copolymer:** Incorporates two or more different monomers into the polymer chain. Can be further classified into:
        - **Random Copolymer:** Monomers are randomly distributed along the chain.
        - **Block Copolymer:** Consists of blocks of different monomers along the chain.
        - **Graft Copolymer:** One type of monomer forms the main chain, with side chains of another type of monomer attached.
3. **Based on Polymerization Mechanism:**
    - **Addition Polymers:** Formed by the addition of monomers without the elimination of any by-products.
    - **Condensation Polymers:** Formed through condensation reactions, where small molecules like water or alcohol are eliminated during polymerization.
4. **Based on Molecular Forces:**
    - **Elastomers:** Polymers with low modulus of elasticity and high elongation at break. Exhibit rubber-like elasticity. Example: natural rubber.
    - **Thermoplastics:** Can be repeatedly softened by heating and hardened by cooling. Examples include polyethylene, PVC, and polystyrene.
    - **Thermosetting Polymers:** Once formed, they cannot be reshaped by heating. Crosslinked structure provides high mechanical strength and heat resistance. Example: epoxy resin

Polymerization Methods:

1. **Addition Polymerization:** This method involves the sequential addition of monomer units without the formation of by-products. It usually occurs with unsaturated monomers like ethylene or propylene. Key steps include initiation, propagation, and termination.
2. **Condensation Polymerization:** In this method, monomers with functional groups react to form a polymer chain along with the elimination of small molecules like water or alcohol. Examples include the formation of nylon and polyester.
3. **Ionic Polymerization:** It involves the initiation of polymerization through ionic species like cations or anions. This method leads to well-defined polymers with precise molecular weights.
4. **Ring-Opening Polymerization:** Monomers containing cyclic structures open up to form linear polymers or copolymers. This method is often used in the synthesis of biodegradable polymers like polylactic acid (PLA).
5. **Living Polymerization:** This controlled polymerization method allows for precise control over the polymer's molecular weight and structure. It includes techniques like atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization.

Importance of Polymers:

1. **Material Versatility:** Polymers are incredibly versatile materials, with applications ranging from packaging and textiles to electronics and biomedical devices. Their diverse properties make them suitable for various industrial and consumer applications.
2. **Resource Efficiency:** Polymers allow for the efficient use of resources due to their lightweight nature and ability to be molded into complex shapes. This helps in reducing material wastage and energy consumption during manufacturing processes.
3. **Durability and Longevity:** Many polymers exhibit excellent durability and longevity, making them ideal for long-term applications such as construction materials, automotive parts, and infrastructure components. This contributes to sustainability by reducing the need for frequent replacements.
4. **Customizability:** The chemical structure of polymers can be tailored to achieve specific properties such as strength, flexibility, and thermal stability. This customization ability enables the development of materials optimized for particular applications, leading to enhanced performance and efficiency.
5. **Environmental Benefits:** With growing concerns about environmental sustainability, the development of biodegradable and eco-friendly polymers has gained significant attention. Biopolymers derived from renewable resources offer alternatives to traditional petroleum-based plastics, reducing reliance on fossil fuels and minimizing environmental impact.
6. **Medical and Healthcare Applications:** Polymers play a crucial role in various medical and healthcare applications, including drug delivery systems, medical implants, and tissue engineering scaffolds. Their

biocompatibility, tunable properties, and ability to mimic biological structures make them indispensable in modern healthcare.

7. **Economic Impact:** The polymer industry contributes significantly to the global economy by generating employment opportunities, driving innovation, and supporting various sectors such as manufacturing, construction, and healthcare. The widespread use of polymers in diverse industries fuels economic growth and development.

Molecular Weight of Polymers:

1. Introduction to Polymers:

- Polymers are large molecules composed of repeating structural units called monomers.
- They are ubiquitous in everyday life, found in materials ranging from plastics and rubber to biological macromolecules like proteins and DNA.

2. Molecular Weight (MW) of Polymers:

- Molecular weight refers to the sum of the atomic weights of all the atoms in a molecule.
- For polymers, molecular weight is often expressed in terms of "average molecular weight" due to their polymeric nature.

3. Types of Molecular Weight:

- **Number Average Molecular Weight (Mn):**
  - Calculated by summing up the molecular weights of individual polymer chains and dividing by the total number of chains.
  - $Mn = \Sigma(Ni * Mi) / \Sigma Ni$, where Ni is the number of polymer chains with molecular weight Mi.
- **Weight Average Molecular Weight (Mw):**
  - Calculated by multiplying the molecular weight of each chain by the number of repeat units in that chain, summing these products, and dividing by the total number of repeat units.
  - $Mw = \Sigma(Ni * Mi^2) / \Sigma(Ni * Mi)$, where Ni is the number of polymer chains with molecular weight Mi.
- **Z-Average Molecular Weight (Mz):**
  - Reflects the weight average molecular weight of the largest molecules in the polymer sample.
  - Provides information about the size distribution of macromolecules.

Number Average Molecular Weight (*Mn*):

Number Average Molecular Weight (M_n):

The number average molecular weight (M_n) is calculated by summing the products of the number of molecules of each different molecular weight (M_i) present in the sample and their respective molecular weights, then dividing by the total number of molecules in the sample.

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

Where:

- N_i = Number of molecules of molecular weight M_i present in the sample.

Characteristics of Number Average Molecular Weight:

1. **Sensitive to Low Molecular Weight Species:** M_n is more sensitive to low molecular weight species, as it is influenced more by the presence of a few high molecular weight chains rather than the majority low molecular weight chains.
2. **Direct Relationship with Polymerization Conditions:** M_n is directly related to the polymerization conditions, such as monomer concentration and reaction temperature. Higher concentrations or temperatures often lead to higher M_n val

Weight Average Molecular Weight (*Mw*):

Weight Average Molecular Weight (M_w):

The weight average molecular weight (M_w) takes into account both the number of molecules of a particular molecular weight (M_i) and the contribution of each to the overall weight of the sample.

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Where:

- N_i = Number of molecules of molecular weight M_i present in the sample.
- M_i = Molecular weight of the i^{th} species.

Characteristics of Weight Average Molecular Weight:

1. **Sensitive to High Molecular Weight Species:** *Mw* is more sensitive to high molecular weight species. This means that larger polymer chains contribute more significantly to *Mw* than smaller chains.
2. **Reflects Distribution of Chain Lengths:** Unlike *Mn*, *Mw* reflects the distribution of chain lengths in the polymer sample, giving more weight to longer chains.
3. **Influenced by Polydispersity:** Polydispersity index (PDI), which is the ratio of *Mw* to *Mn*, provides information about the breadth of the molecular weight distribution. A higher PDI indicates a broader distribution of chain lengths

Determination of molecular weight by osmometry

1. **Introduction to Osmometry**:
   - Osmometry is a technique used to determine the molecular weight of macromolecules, such as polymers or proteins, based on their osmotic pressure behavior.
   - It relies on the principle that the osmotic pressure exerted by a solution is directly proportional to the concentration of solute particles in the solution.
2. **Principle of Osmometry**:
   - According to van't Hoff equation, $\pi = iCRT$, where π is the osmotic pressure, i is the van't Hoff factor (the number of particles into which the solute dissociates), C is the molar concentration of the solute, R is the gas constant, and T is the temperature in Kelvin.
   - By measuring the osmotic pressure of a solution containing the macromolecule and comparing it with the osmotic pressure of a solution containing known concentrations of standard molecules, the molecular weight of the macromolecule can be determined.
3. **Experimental Setup**:
   - A semipermeable membrane, such as Visking tubing or a dialysis membrane, is used to separate the solution containing the macromolecule from the solvent.
   - The solution is placed in a chamber with the semipermeable membrane and immersed in a pure solvent.
   - Osmotic pressure is measured using an osmometer, which typically involves a pressure sensor connected to the chamber.
4. **Procedure**:
   - Prepare solutions of known concentrations of standard molecules (e.g., sucrose or glucose) and the solution containing the macromolecule.

- Fill the osmometer chamber with the solvent and calibrate the instrument.
- Place the semipermeable membrane between the solvent and the solution containing the macromolecule.
- Measure the osmotic pressure of the solution containing the macromolecule.
- Repeat the measurements for solutions of known concentrations of standard molecules.
- Plot a graph of osmotic pressure versus concentration for the standard solutions.
- Determine the molecular weight of the macromolecule from the graph by extrapolating the osmotic pressure of the macromolecule solution to the concentration axis.

5. **Factors Affecting Accuracy**:
    - Temperature: Osmotic pressure measurements should be conducted at a constant temperature to ensure accuracy.
    - Presence of impurities: Impurities in the solvent or the solution containing the macromolecule can affect the osmotic pressure measurements.
    - Choice of solvent: The choice of solvent should be such that it does not interact with the macromolecule or the solute molecules.
6. **Applications**:
    - Determination of the molecular weight of polymers, proteins, and other macromolecules.
    - Quality control in industries producing polymers and biopharmaceuticals.
    - Research in polymer chemistry, biochemistry, and biotechnology.

light scattering, viscosity and sedimentation methods

1. **Introduction to Macromolecules:**
    - Macromolecules are large molecules typically composed of repeating subunits called monomers.
    - Examples include proteins, nucleic acids, carbohydrates, and synthetic polymers.
2. **Light Scattering Methods:**
    - Utilized for determining the molecular weight and size of macromolecules in solution.

- Based on the principle of scattering of light by particles suspended in a medium.
- Different types of light scattering methods include static light scattering (SLS) and dynamic light scattering (DLS).
- SLS measures the intensity of scattered light at a fixed angle and is used for determining molecular weight.
- DLS measures the fluctuations in scattered light intensity over time and provides information on particle size and diffusion coefficients.

3. **Viscosity Methods:**
    - Viscosity measurements are used to determine the hydrodynamic properties of macromolecules in solution.
    - Viscosity is a measure of a fluid's resistance to flow.
    - Macromolecules in solution increase the solution viscosity due to their size and shape.
    - Viscosity methods, such as viscometry or rheology, measure the flow properties of solutions containing macromolecules.
    - The relationship between viscosity and molecular weight can be used to estimate the size and conformation of macromolecules.
4. **Sedimentation Methods:**
    - Sedimentation techniques involve the separation of macromolecules based on their sedimentation rates in a centrifugal field.
    - Sedimentation velocity analysis measures the rate of movement of macromolecules in a centrifugal field.
    - Sedimentation equilibrium analysis measures the distribution of macromolecules between the solution and sediment phases at equilibrium.
    - These methods provide information about the molecular weight, size, shape, and conformation of macromolecules.
5. **Applications:**
    - These methods are widely used in biochemistry, biophysics, polymer science, and material science.
    - They are essential for characterizing the properties of macromolecules, understanding their structure-function relationships, and studying their interactions with other molecules.

Polymerisation Reactions:

- Polymerisation is the process of joining together monomers to form a polymer.
- It can proceed via various mechanisms, including addition polymerisation and condensation polymerisation.
- Addition polymerisation involves the repetitive addition of monomers without the elimination of any byproducts.
- Condensation polymerisation involves the formation of a polymer along with the elimination of small molecules such as water or alcohol.

Kinetics of Polymerisation Reactions:

- Kinetics studies the rates of chemical reactions and the factors affecting them.
- In polymerisation kinetics, the rate of polymerisation, degree of polymerisation, and molecular weight distribution are key parameters.
- Factors affecting polymerisation kinetics include temperature, concentration of monomers and initiators, and presence of inhibitors or catalysts.

Example: Free Radical Polymerisation of Ethylene

Reaction:

Ethylene (C2H4)→Polyethylene

Initiation: Initiator→Free RadicalInitiator→Free Radical

Propagation:
Free Radical+Ethylene→Polymer Chain with Ethylene Unit+New Free Radic
al

Termination: Two Free Radicals Combine→End of Polymer Chain

<u>**Polycondensation Reactions:**</u>

- **Definition:** Polycondensation is a polymerisation process where monomers react with each other, usually with the elimination of small molecules like water or alcohol.
- **Example Reaction:** Polyester formation through the condensation of a dicarboxylic acid and a diol.

$$\text{Dicarboxylic Acid} + \text{Diol} \rightarrow \text{Polyester} + \text{Water}$$

Example:

$$\text{HOOC-(CH}_2)_4\text{-COOH} + \text{HO-(CH}_2)_2\text{-OH} \rightarrow (\text{HOOC-(CH}_2)_4\text{-COO-(CH}_2)_2\text{-O})_n + H_2O$$

- **Explanation:**
  - The carboxylic acid (–COOH) group of one monomer reacts with the hydroxyl (–OH) group of another monomer, resulting in the elimination of a water molecule (H_2O).
  - This process continues, leading to the formation of a long-chain polyester polymer.

2. Ionic Polymerisation:

- **Definition:** Ionic polymerisation involves the formation of polymers through the reaction of monomers with ionic initiators or catalysts.
- **Example Reaction:** Polymerisation of styrene using anionic initiators like n-butyllithium.

Reaction:

Styrene+Anionic Initiator→Poly(styrene)

Example:

Styrene+n-BuLi→(Poly)styrene+LiH

- **Explanation:**
  - The anionic initiator (e.g., n-butyllithium) reacts with the monomer (styrene) to form a reactive species called a carbanion.

- This carbanion initiates the polymerisation reaction by attacking the double bond of another monomer molecule, leading to chain growth.

3. Free Radical Polymerisation:

- **Definition:** Free radical polymerisation involves the formation of polymers through the reaction of monomers with free radicals, which are highly reactive species with unpaired electrons.
- **Example Reaction:** Polymerisation of ethylene using a peroxide initiator like benzoyl peroxide.

Reaction:

$$\text{Ethylene} + \text{Peroxide Initiator} \rightarrow \text{Poly(ethylene)}$$

Example:

$$\text{Ethylene} + \text{Benzoyl Peroxide} \rightarrow \text{(Poly)ethylene} + \text{Benzoic Acid} + \text{Radical Species}$$

- **Explanation:**
  - The peroxide initiator (e.g., benzoyl peroxide) decomposes to form free radicals.
  - These free radicals attack the double bond of ethylene monomer molecules, initiating chain growth by bonding with the carbon atoms and forming new radicals.

4. Copolymerisation:

- **Definition:** Copolymerisation involves the polymerisation of two or more different monomers to form copolymers, which contain repeating units of more than one type of monomer.
- **Example Reaction:** Copolymerisation of styrene and acrylonitrile to form styrene-acrylonitrile copolymer.

Reaction:

$$\text{Styrene} + \text{Acrylonitrile} \rightarrow \text{Styrene-Acrylonitrile Copolymer}$$

Example:

$$\text{Styrene} + \text{Acrylonitrile} \rightarrow \text{(Styrene-Acrylonitrile) Copolymer}$$

- **Explanation:**
  - The monomers (styrene and acrylonitrile) undergo simultaneous polymerisation, resulting in the formation of copolymer chains containing both types of repeating units.

- The properties of the copolymer can be tailored by adjusting the ratio of the monomers in the reaction mixture.

Coordination Polymers:

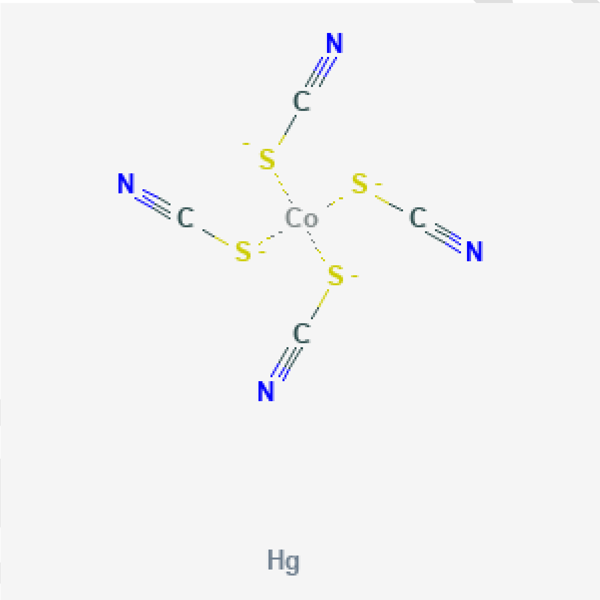
1. **Definition**: Coordination polymers are a class of macromolecules formed through the coordination bonding between metal ions and ligands.

2. **Formation**:

   - Metal ions act as coordination centers, binding with multiple ligands.
   - Ligands are typically organic molecules with multiple donor atoms (e.g., nitrogen, oxygen) capable of forming coordination bonds.
   - Coordination bonds form between the metal ions and the ligands, leading to the formation of extended networks or chains.

3. **Example Reaction**:

   - **Poly[mercury(II) tetrakis(thiocyanato-N)cuprate(II)]**



4. **Properties**:

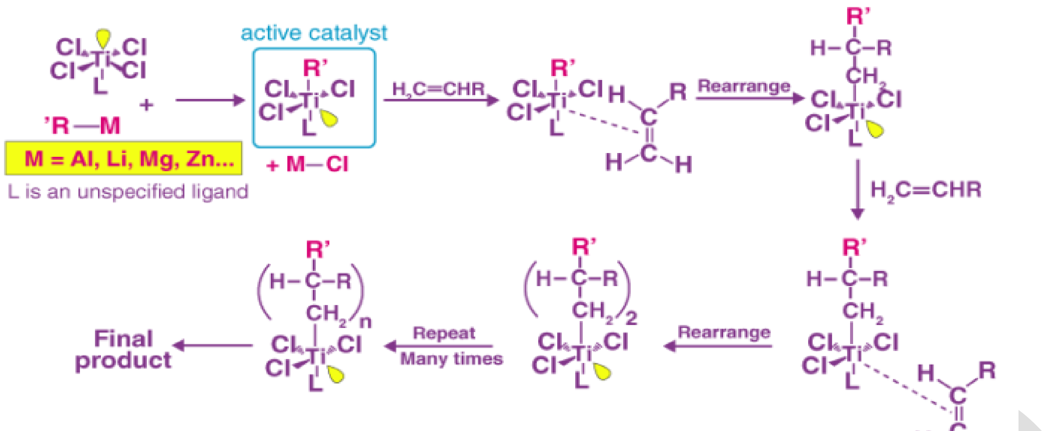
   - Often exhibit porous structures, making them useful in applications such as gas storage and separation.
   - Can display interesting magnetic, optical, and electronic properties, depending on the metal-ligand combinations and the arrangement of the coordination polymer.

Conducting Polymers:

1. **Definition**: Conducting polymers are a special class of macromolecules that exhibit electrical conductivity similar to metals or semiconductors.
2. **Formation**:
   - Typically synthesized through chemical polymerization of monomers containing π-conjugated systems.
   - π-conjugated systems allow delocalization of electrons along the polymer backbone, facilitating electrical conductivity.
3. **Example Reaction**:
   - **Polyaniline Synthesis**: Aniline monomers undergo oxidative polymerization in the presence of an oxidizing agent like ammonium persulfate.
   - nC6H5NH2 + nH2O + oxidant→ (C6H4NH)n + $n$$NH_4^+$ + $n$$SO4^{2-}$
4. **Properties**:
   - Exhibits both electrical conductivity and mechanical flexibility.
   - Applications include organic light-emitting diodes (OLEDs), sensors, and conductive coatings.

Ziegler-Natta Catalyst:

1. **Definition**: Ziegler-Natta catalysts are transition metal-based catalysts used in the polymerization of olefins, particularly in the production of polyethylene and polypropylene.
2. **Function**:
   - Coordinate with monomers to form an active species capable of initiating polymerization.
   - Control the stereochemistry and molecular weight of the resulting polymer.
3. **Example Reaction**:
   - **Polypropylene Synthesis**: Propylene monomers polymerize in the presence of a Ziegler-Natta catalyst, typically based on titanium compounds supported by aluminum alkyl co-catalysts.
   - CH2=CHCH3+Catalyst→(CH2CHCH3)n



A mechanism for ziegler natta catalysis

4. **Properties**:

- Enables the production of polymers with tailored properties, such as high-density polyethylene (HDPE) and isotactic polypropylene.
- Widely used in the plastics industry for various applications due to their high strength, chemical resistance, and processability.