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## UNIT 5: MATERIALS CHEMISTRY (POLYMERS AND ORGANOMETALLIC COMPOUNDS)

This unit forms a foundational part of engineering chemistry, delving into the synthesis, properties, and applications of advanced materials like polymers and specific organometallic compounds. Understanding these concepts is crucial for various industrial and technological applications.

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### I. POLYMERS

#### 1. Definition and Introduction

- **POLYMERS** are defined as substances where many units of a single or two different molecules are united together by a covalent bond. The word 'polymer' is derived from Greek words: "poly" meaning many, and "mer" meaning unit or part.
- They are very large molecules with high molecular mass, formed by joining repeating structural units on a large scale.
- The repeating structural units are derived from simple and reactive molecules known as **MONOMERS**, which are linked by covalent bonds.
- **POLYMERIZATION** is the process by which monomers combine to form polymers.

#### 2. Key Concepts

- **MONOMER**: The starting molecule from which the polymer molecule is formed.
- **DEGREE OF POLYMERIZATION**: The number of monomer units united to form a polymer molecule.
  - Formula: Degree of polymerization = (Molecular weight of Polymer) / (Molecular weight of Monomer).
  - **HIGH POLYMERS** have a very high molecular weight, with more than 100 repeating units (also called **MACROMOLECULES**).
  - **OLIGOMERS** (or low polymers) have fewer than 100 repeating units.
- **Distinction between Polymers and Macromolecules**: While high polymers are macromolecules, not all macromolecules are polymers. For example, vitamins and carotene are macromolecules but not polymers because they are not composed of repeating units. Polymers specifically consist of repeating monomer units.

#### 3. Classification of Polymers

Polymers can be classified based on various criteria:

#### A. Based on Source

- **NATURAL POLYMERS:** Obtained from nature (e.g., rubber, cellulose, starch, proteins).
- **SYNTHETIC POLYMERS:** Man-made polymers (e.g., polyethylene, nylon, terylene, styrene).
  - Synthetic polymers can be linear, branched, or cross-linked.
- **SEMISYNTHETIC POLYMERS:** Derived from natural polymers through chemical modification (e.g., cellulose acetate, cellulose nitrate).

#### B. Based on Backbone Chain

- **ORGANIC POLYMERS:** Backbone chain primarily composed of carbon atoms.
- **INORGANIC POLYMERS:** Backbone chain made of atoms other than carbon.

#### C. Based on Monomers

- **HOMOPOLYMER:** Consists of only one type of monomer unit (e.g., polyethylene from ethylene, polyvinyl chloride (PVC) from vinyl chloride).
- **CO-POLYMER:** Composed of two or more different monomer units.
  - Can be **Random Co-polymer** (A-A-B-A-B-B-A) or **Alternating Co-polymer** (A-B-A-B-A-B-A-B).
  - Examples: Buna-S (from 1,3-Butadiene and Styrene), Nylon 6,6 (from hexamethylene diamine and adipic acid).

#### D. Based on Mechanical Properties / Behavior on Heating (Plastics)

- **THERMOPLASTIC POLYMERS:**
  - Soften and melt on heating, and become hard on cooling. This process is **REVERSIBLE**.
  - Can be molded, remolded, and reshaped multiple times, making them **RECYCLABLE**.
  - Typically formed by **ADDITION POLYMERIZATION**.
  - Generally have **LINEAR** or slightly branched structures.
  - Possess lower molecular weight and are often soft, weak, and less brittle.
  - Soluble in organic solvents.
  - Examples: Polyvinyl chloride (PVC), polyethylene, polypropylene, nylon:6,6, polystyrene.
- **THERMOSETTING POLYMERS:**
  - Soften on initial heating but undergo chemical changes, converting into infusible and insoluble masses. Once set, they cannot be softened again on further heating; the process is **IRREVERSIBLE**.
  - Cannot be molded, remolded, or reshaped after initial setting, making them **NON-RECYCLABLE**.
  - Typically formed by **CONDENSATION POLYMERIZATION**.

- Generally have **CROSS-LINKED** or three-dimensional network structures.
- Possess higher molecular weight and are typically hard, strong, and more brittle.
- Insoluble in organic solvents.
- Examples: Bakelite, melamine, urea-formaldehyde resin.

#### 4. Polymerization Processes (Synthesis of Polymer)

Polymer molecules can be synthesized by various methods, including Addition, Condensation, Ring Opening, and Oxidative Polymerization. The primary methods discussed are Addition and Condensation Polymerization.

##### A. Addition Polymerization (Chain Growth Polymerization)

- **Definition:** Monomer units are added together to form a polymer molecule **WITHOUT** losing any small molecules.
  - Example: Conversion of ethylene to polyethylene:  $n\text{CH}_2=\text{CH}_2 \rightarrow (-\text{CH}_2-\text{CH}_2-)_n$ .
- **Mechanism:** Consists of three steps:
  - **Initiation:** Formation of active centers (free radicals or ions).
  - **Propagation:** Active centers combine with monomers, causing chain growth.
  - **Termination:** Chain growth stops (e.g., by combination or disproportionation of active centers).
- **Types based on mechanism:**
  - **FREE RADICAL ADDITION POLYMERIZATION:** Initiated by free radicals formed from decomposition of organic/inorganic peroxides (e.g., benzoyl peroxide).
  - **IONIC ADDITION POLYMERIZATION:** Involves formation of ions using initiators (Lewis acids for cationic, Lewis bases for anionic).
    - **Cationic Polymerization:** Initiated by Lewis acids (e.g.,  $\text{A} + \text{CH}_2=\text{CH}_2 \rightarrow \text{A}:\text{CH}_3-\text{CH}_2^+$ ).
    - **Anionic Polymerization:** Initiated by Lewis bases (e.g.,  $\text{B} + \text{CH}_2=\text{CH}_2 \rightarrow \text{B}:\text{CH}_3-\text{CH}_2^-$ ).

##### B. Condensation Polymerization (Step Growth Polymerization)

- **Definition:** Many monomer molecules unite to form a large macromolecule with the **LOSS of some simple molecules** (e.g., water, carbon dioxide, alcohol, hydrogen chloride).
- **Monomers:** Uses bi-functional or multi-functional monomers.
- **Key Distinction from Addition Polymerization:**
  - Condensation polymers eliminate small molecules during formation, while addition polymers do not.
  - The molecular formula of the repeating unit is **NOT** the same as that of the monomer in condensation polymers.
  - No rapid loss of monomers at the beginning; oligomers are formed first and then combine.

- Does **NOT** require initiators.
- Does **NOT** show termination steps; continues to grow until monomers are consumed or external agents are added (like "living polymers").
- **Examples:**
  - **Nylon 6,6:** Prepared from hexamethylene diamine and adipic acid.
    - **Uses:** Fabrics, ropes, nets, threads for toothbrushes, carpets, parachutes, waterproof swimsuits.
  - **Dacron (Terylene):** Formed from Terephthalic acid and Ethylene glycol.
  - **Bakelite:** A thermosetting polymer formed from phenol and formaldehyde.
    - **Uses:** Electrical switches, handles of utensils, combs, jewelry, radio cabinets.
  - **Urea-formaldehyde resin:** Another thermosetting polymer.
    - **Preparation:** Can be prepared in the lab.
- **Important Polymers and their Applications:**
  - **Polythene (Polyethylene):** Monomer is Ethene.
    - **Uses:** Packing material, manufacture of bottles, toys, insulation for electric wires.
  - **PVC (Polyvinyl chloride):** Monomer is Vinyl chloride.
    - **Uses:** Pipes, roofing and flooring, raincoats and bags, cable insulation.
  - **Buna-S (Styrene-butadiene rubber):** Monomers are 1,3-Butadiene and Styrene.
    - **Uses:** Tyres, rubber tubes and hoses, conveyer belts, shoe heels, footwear.
  - **Buna-N (Acrylonitrile-butadiene rubber):** Monomers are 1,3-Butadiene and Acrylonitrile.
    - **Uses:** Oil seals, manufacture of hoses, tank linings.
  - **Neoprene:** A synthetic rubber.
  - **Teflon:** Industrial applications.
  - **Lucite:** Industrial applications.
  - **Kevlar:** Industrial applications.
  - **Thiokol:** Industrial applications.

## 5. Types of Specialty Polymers

### A. Conducting Polymers

- **Definition:** Polymers that can conduct electricity.
- **Advantages over Traditional Polymers:**
  - Can provide electromagnetic shielding for electronic circuits.
  - Used as antistatic coating material to prevent electrical discharge on photographic emulsions.
  - Used as hole injecting electrodes for OLEDs.
  - Used as emissive layer in full-color video displays.
  - Promising for field-effect transistors.
  - Some absorb microwaves.

- Can be used in PCB tracks.
- **Synthesis Example - Polyaniline:** Synthesized by chemical oxidative polymerization of aniline in sulfuric acid using ammonium persulfate as oxidant at room temperature.

## B. Biodegradable Polymers

- **Definition:** Polymers that can decompose naturally, reducing environmental impact. Their importance lies in addressing plastic pollution.
- **Example:** Polynucleotides.

## 6. Rubber (A Natural Polymer)

- **Natural Rubber:** Possesses elastic properties, manufactured from rubber latex. A linear polymer of isoprene (2-methyl-1,3-butadiene).
- **Limitations of Natural Rubber:**
  - Becomes soft at high temperatures (above 335 K) and brittle at low temperatures (below 280 K).
  - High water absorption capacity.
  - Soluble in non-polar solvents.
  - Non-resistant to attack by oxidizing agents.
- **VULCANIZATION:** Process to overcome the limitations of natural rubber.
  - **Process:** Heating natural rubber with sulfur in the presence of ZnO at a temperature range of 373 K to 415 K.
  - **Mechanism:** Sulfur forms cross-links at the reactive sites of double bonds, stiffening the rubber.
  - **Merits of Vulcanization:**
    - Increases tensile strength, elasticity, and extensibility.
    - Lowers water absorption tendency.
    - Higher resistance to oxidation, abrasion, and wear and tear.
    - Better electrical insulator.
    - Increases resistance to organic solvents, fats, and oils.
    - Makes rubber less sensitive to temperature changes.
- **Synthetic Rubber:** Man-made rubber-like polymers with elastomeric properties, monomers usually obtained from petroleum.
  - Examples: Neoprene, Buna-S, Buna-N.

## 7. Polymer Blends and Composites

- **Polymer Blends:** Mixtures of two or more polymers.
- **Polymer Composites:** Materials formed by combining a polymer matrix with another material (reinforcement) to enhance properties. Liquid crystals can be used as reinforcing fillers in thermoplastic fillers, providing strength and stiffness.

## Quick Revision Summary for Polymers:

- Polymers are macromolecules of repeating monomer units, formed by polymerization.

- Classifications: Natural/Synthetic, Homo/Co-polymer, Thermoplastic/Thermosetting.
  - **Thermoplastics** are recyclable (linear, Addition poly.), **Thermosettings** are not (cross-linked, Condensation poly.).
  - Polymerization types: **Addition** (no small molecule loss, 3 steps) and **Condensation** (small molecule loss, step-growth).
  - Specific examples: Nylon 6,6, Dacron, Bakelite, PVC, Polythene, Buna-S, Buna-N.
  - **Conducting Polymers** offer electromagnetic shielding, antistatic coatings, etc.
  - **Biodegradable Polymers** are environmentally friendly.
  - **Vulcanization** improves natural rubber properties by creating sulfur cross-links.
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## II. ORGANOMETALLIC COMPOUNDS

### 1. Definition and Introduction

- Organometallic compounds are chemical compounds containing at least one chemical bond between a carbon atom of an organic group and a metal. They are significant in synthesis and industrial processes.

### 2. Important Organometallic Reagents and Their Applications

The sources specifically highlight Grignard reagents and Lithium Aluminium Hydride ( $\text{LiAlH}_4$ ).

#### A. Grignard Reagent ( $\text{RMgX}$ )

- **General Method of Preparation:** Grignard reagents are typically prepared by reacting an alkyl or aryl halide ( $\text{RX}$ ) with magnesium metal in an ethereal solvent (like diethyl ether or tetrahydrofuran).
  - **Reaction:**  $\text{R-X} + \text{Mg} \rightarrow \text{R-Mg-X}$ 
    - **R:** Alkyl or Aryl group
    - **X:** Halogen (Cl, Br, I)
- **Applications (General):** Grignard reagents are highly versatile and are used in various organic synthesis reactions. They act as strong nucleophiles and strong bases.
  - Synthesis of alcohols from carbonyl compounds.
  - Synthesis of carboxylic acids (reaction with  $\text{CO}_2$ ).
  - Formation of alkanes (reaction with compounds containing active hydrogen).
  - Synthesis of other organometallic compounds.

#### B. Lithium Aluminium Hydride ( $\text{LiAlH}_4$ )

- **General Method of Preparation:** Prepared by the reaction of lithium hydride ( $\text{LiH}$ ) and aluminum chloride ( $\text{AlCl}_3$ ).
- **Applications (General):**  $\text{LiAlH}_4$  is a powerful, non-selective reducing agent widely used in organic chemistry. It effectively reduces various functional groups.

- **Specific Reactions / Examples:**  $\text{LiAlH}_4$  reacts with various organic compounds to reduce them:
  - **(i)  $\text{CH}_3\text{CHO}$  (Acetaldehyde):** Reduces aldehydes to **PRIMARY ALCOHOLS**.
    - $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$  (Ethanol)
  - **(ii)  $\text{CH}_3\text{CN}$  (Acetonitrile):** Reduces nitriles to **PRIMARY AMINES**.
    - $\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$  (Ethylamine)
  - **(iii)  $\text{CH}_3\text{COOC}_2\text{H}_5$  (Ethyl Acetate):** Reduces esters to **PRIMARY ALCOHOLS**.
    - $\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CH}_2\text{OH}$  (Ethanol) and  $\text{C}_2\text{H}_5\text{OH}$  (Ethanol, from the ester part)
  - **(iv)  $\text{CH}_3\text{COC}_2\text{H}_5$  (Ethyl Methyl Ketone):** Reduces ketones to **SECONDARY ALCOHOLS**.
    - $\text{CH}_3\text{COC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$  (Butan-2-ol)
  - **(v)  $\text{CH}_3\text{COOH}$  (Acetic Acid):** Reduces carboxylic acids to **PRIMARY ALCOHOLS**.
    - $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$  (Ethanol)
  - **(vi)  $\text{CH}_3\text{N}_3$  (Methyl Azide):** Reduces azides to **PRIMARY AMINES**.
    - $\text{CH}_3\text{N}_3 \rightarrow \text{CH}_3\text{NH}_2$  (Methylamine)
  - **(vii)  $\text{CH}_3\text{CHCH}_2\text{O}$  (Epoxide):** Reduces epoxides to **ALCOHOLS**.
    - $\text{CH}_3\text{CHCH}_2\text{O} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$  (Propan-2-ol, as  $\text{LiAlH}_4$  attacks the less hindered carbon)

#### Quick Revision Summary for Organometallic Compounds:

- Organometallic compounds contain a carbon-metal bond.
- **Grignard reagents ( $\text{RMgX}$ )** are prepared from alkyl/aryl halides and magnesium, used as nucleophiles/bases in synthesis.
- **$\text{LiAlH}_4$**  is a strong reducing agent for aldehydes, ketones, esters, carboxylic acids, nitriles, azides, and epoxides, typically yielding alcohols or amines.

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This comprehensive overview of Unit 5, covering Polymers and Organometallic Compounds, should be highly beneficial for your exam preparation. Remember to review the specific reactions and applications for each type of material. Good luck!