MACROMOLECULES

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<u>Syllabus</u>:- Macromolecules - Nomenclature, Classification, properties of polymer, mass of macromolecules, number average and weight average molecular mass, determination of molecular weight by osmotic pressure, viscosity and light scattering and sedimentation (ultra centrifuge) method

Introduction

The term macromolecule (macro- + molecule) was coined by Nobel laureate Hermann Staudinger in the 1920s, whose molecular weight is found to be more than 10,000 (in excess of 1,0000 atoms). According to the standard IUPAC definition, the term macromolecule as used in polymer science refers only to a single molecule. For example, a single polymeric molecule is appropriately described as a "macromolecule" or "polymer molecule" rather than a "polymer," which suggests a substance composed of macromolecules.[

What are Polymers?

A polymer is a large molecule or a macromolecule which essentially is a combination of many subunits. The term polymer in Greek means ‘many parts’. Polymers can be found all around us. From the strand of our DNA which is a naturally occurring biopolymer to polypropylene which is used throughout the world as plastic.

Polymers may be naturally found in plants and animals (**natural polymers**) or may be man-made (**synthetic polymers**). Different polymers have a number of unique physical and chemical properties due to which they find usage in everyday life.

Polymers are all created by the process of polymerization wherein their constituent elements called monomers, are reacted together to form polymer chains i.e 3-dimensional networks forming the polymer bonds.

The type of polymerization mechanism used depends on the type of functional groups attached to the reactants. In biological contexts, almost all macromolecules are either completely polymeric or are made up of large polymeric chains.

Classification of Polymers

Polymers cannot be classified under one category because of their complex structures, different behaviours, and vast applications. We can, therefore, classify polymers based on the following considerations.

Classification of Polymers based on the Source of Availability

There are **three types of classification** under this category, namely, Natural, Synthetic, and Semi-synthetic Polymers.

Natural Polymers:

They occur naturally and are found in plants and animals, for example proteins, starch, cellulose and rubber. To add up, we also have biodegradable polymers which are called biopolymers.

Semi-synthetic Polymers:

They are derived from naturally occurring polymers and undergo further chemical modification. For example, cellulose nitrate, cellulose acetate.

Synthetic Polymers:

These are man-made polymers. Plastic is the most common and widely used synthetic polymer. It is used in industries and various dairy products. For example, nylon-6, 6, polyether's etc.

Classification of Polymers based on the Structure of the Monomer Chain

This category has the following classifications:

Linear Polymers

The structure of polymers containing long and straight chains fall into this category. PVC, i.e. poly-vinyl chloride is largely used for making pipes and electric cables is an example of a linear polymer.

Branched-chain Polymers

When linear chains of a polymer form branches, then, such polymers are categorized as branched chain polymers. For example, Low-density polythene.

Cross-linked Polymers

They are composed of bifunctional and trifunctional monomers. They have a stronger covalent bond in comparison to other linear polymers. Bakelite and melamine are examples in this category.

Classification Based on Polymerization

- **Addition Polymerization:** Example, poly ethane, Teflon, Polyvinyl chloride (PVC)
- **Condensation Polymerization:** Example, Nylon -6, 6, perylene, polyesters.

Classification Based on Monomers

- **Homomer:** In this type, a single type of monomer unit is present. For example, Polyethene

- **Heteropolymer or co-polymer:** It consists of different type of monomer units. For example, nylon -6, 6

Classification Based on Molecular Forces

- **Elastomers:** These are rubber-like solids weak interaction forces are present. For example, Rubber.

- **Fibres:** Strong, tough, high tensile strength and strong forces of interaction are present. For example, nylon -6, 6.
- **Thermoplastics:** These have intermediate forces of attraction. For example, polyvinyl chloride.
- **Thermosetting polymers:** These polymers greatly improve the material's mechanical properties. It provides enhanced chemical and heat resistance. For example, phenolics, epoxies, and silicones.

Structure of Polymers

Most of the polymers around us are made up of a **hydrocarbon backbone**. A Hydrocarbon backbone being a long chain of linked carbon and hydrogen atoms, possible due to the tetravalent nature of carbon.

A few examples of a hydrocarbon backbone polymer are polypropylene, polybutylene, polystyrene. Also, there are polymers which instead of carbon have other elements in its backbone. For example, Nylon, which contains nitrogen atoms in the repeated unit backbone.

Types of Polymers

On the basis of the type of the backbone chain, polymers can be divided into:

- **Organic Polymers**: Carbon backbone.
- **Inorganic Polymers**: Backbone constituted by elements other than carbon

Natural polymers

Synthetic Polymers

On the basis of their synthesis:

- Natural Polymers
- Synthetic Polymers

Biodegradable Polymers

The polymers which are degraded and decayed by microorganisms like bacteria are known as **biodegradable polymers**. These types of polymers are used in surgical bandages, capsule coatings and in surgery. For example, Poly hydroxybutyrate co vel [PHBV]

High-Temperature Polymers

These polymers are stable at high temperatures. Due to their high molecular weight, these are not destroyed even at very high temperatures. They are extensively used in the healthcare industries, for making sterilization equipment and in the manufacturing of heat and shock-resistant objects.

Few of the important polymers are:

Polypropylene: It is a type of polymer that softens beyond a specific temperature allowing it to be moulded and on cooling it solidifies. Due to its ability to be easily moulded into various shapes, it has a lot of applications.

A few of which are in stationary equipment's, automotive components, reusable containers speakers and much more. Due to its relatively low energy surface, the polymer is fused with the welding process and not using glue.

Polyethene: It is the most common type of plastic found around us. Mostly used in packaging from plastic bags to plastic bottles. There are different types of polyethene but their common formula being $(C_2H_4)_n$.

Properties of Polymers

Physical Properties

- As chain length and cross-linking increases the tensile strength of the polymer increases.
- Polymers do not melt, they change state from crystalline to semi-crystalline.

Chemical Properties

- Compared to conventional molecules with different side molecules, the polymer is enabled with hydrogen bonding and ionic bonding resulting in better cross-linking strength.
- Dipole-dipole bonding side chains enable the polymer for high flexibility.

- Polymers with Van der Waals forces linking chains are known to be weak, but give the polymer a low melting point.

Optical Properties

- Due to their ability to change their refractive index with temperature as in the case of PMMA and HEMA: MMA, they are used in lasers for applications in spectroscopy and analytical applications.

Some Polymers and their Monomers

- Polypropene, also known as polypropylene, is made up of monomer propene.
- Polystyrene is an aromatic polymer, naturally transparent, made up of monomer styrene.
- Polyvinyl chloride (PVC) is a plastic polymer made of monomer vinyl chloride.
- The urea-formaldehyde resin is a non-transparent plastic obtained by heating formaldehyde and urea.
- Glyptal is made up of monomers ethylene glycol and phthalic acid.
- Bakelite or polyoxybenzylmethylenglycolanhydride is a plastic which is made up of monomers phenol and aldehyde.

Types of Polymerization Reactions

Addition Polymerization

This is also called as chain growth polymerization. In this, small monomer units joined to form a giant polymer. In each step length of chain increases. For example, Polymerization of ethane in the presence of Peroxides

Condensation Polymerization

In this type small molecules like H_2O, CO, NH_3 are eliminated during polymerization (step growth polymerization). Generally, organic compounds containing bifunctional groups such as idols, -dials, diamines, dicarboxylic acids undergo this type of polymerization reaction. For example, Preparation of nylon -6, 6.

What is Copolymerization?

In this process, two different monomers joined to form a polymer. Synthetic rubbers are prepared by this polymerization. For example, BUNA–S.

How to Calculate Molecular Mass of Polymers?

There are two types of average molecular masses of Polymers:

- **Number Average Molecular Masses**
- **Weight Average Molecular Mass**

Number Average Molecular Masses:

If N_1, N_2, N_3…. are the number of macromolecular with molecular masses. M_1, M_2, M_3….. Respectively then the number average molecular masses of the polymer is given by

$$\bar{M}_n = \frac{N_1M_1+N_2M_2+N_3M_3+\ldots\ldots\sum N_iM_i}{N_1+N_2+N_3+\ldots\ldots\sum N_i}$$

The number average molecular mass M_n^- is determined by colligative properties such as Osmotic Pressure.

Weight Average Molecular Mass:

If m_1, m_2, m_3…. Are the masses of a macromolecule with molecular masses M_1, M_2, M_3… respectively, Then weight average molecular mass of the polymer is given by

$$\overline{M}_{\omega} = \frac{m_1M_1+m_2M_2+m_3M_3+\ldots\ldots}{m_1+m_2+m_3}$$

$$\Rightarrow = \frac{\sum miMi}{\sum mi}$$

$$\Rightarrow \overline{M}_{\omega} = \frac{\sum NiMi \times Mi}{\sum NiMi}$$

$$\Rightarrow \overline{M}_{\omega} = \frac{\sum NiMi^2}{\sum NiMi}$$

Polydispersive index: It is the ratio of weight average molecular mass and number average molecular mass of Polymers.

$PDI = \frac{\overline{M}w}{\overline{M}n}$. For natural polymers PDI = 1.

Uses of Polymers

Here we will list some of the important uses of polymers in our everyday life.

- Polypropene finds usage in a broad range of industries such as textiles, packaging, stationery, plastics, aircraft, construction, rope, toys, etc.
- Polystyrene is one of the most common plastic, actively used in the packaging industry. Bottles, toys, containers, trays, disposable glasses and plates, tv cabinets and lids are some of the daily-used products made up of polystyrene. It is also used as an insulator.
- The most important use of polyvinyl chloride is the manufacture of sewage pipes. It is also used as an insulator in the electric cables.
- Polyvinyl chloride is used in clothing and furniture and has recently become popular for the construction of doors and windows as well. It is also used in vinyl flooring.
- Urea-formaldehyde resins are used for making adhesives, moulds, laminated sheets, unbreakable containers, etc.
- Glyptal is used for making paints, coatings, and lacquers.
- Bakelite is used for making electrical switches, kitchen products, toys, jewellery, firearms, insulators, computer discs, etc.

Commercial Uses of Polymers

Polymer	Monomer	Uses of Polymer
Rubber	Isoprene (1, 2-methyl 1 – 1, 3-butadiene)	Making tyres, elastic materials
BUNA – S	(a) 1, 3-butadiene (b) Styrene	Synthetic rubber
BUNA – N	(a) 1, 3-butadiene (b) Vinyl Cyanide	Synthetic rubber
Teflon	Tetra Flouro Ethane	Non-stick cookware – plastics
Terylene	(a) Ethylene glycol (b) Terephthalic acid	Fabric
Glyptal	(a) Ethylene glycol (b) Phthalic acid	Fabric
Bakelite	(a) Phenol (b) Formaldehyde	Plastic switches, Mugs, buckets
PVC	Vinyl Cyanide	Tubes, Pipes
Melamine Formaldehyde Resin	(a) Melamine (b) Formaldehyde	Ceramic plastic material
Nylon-6	Caprolactum	Fabric