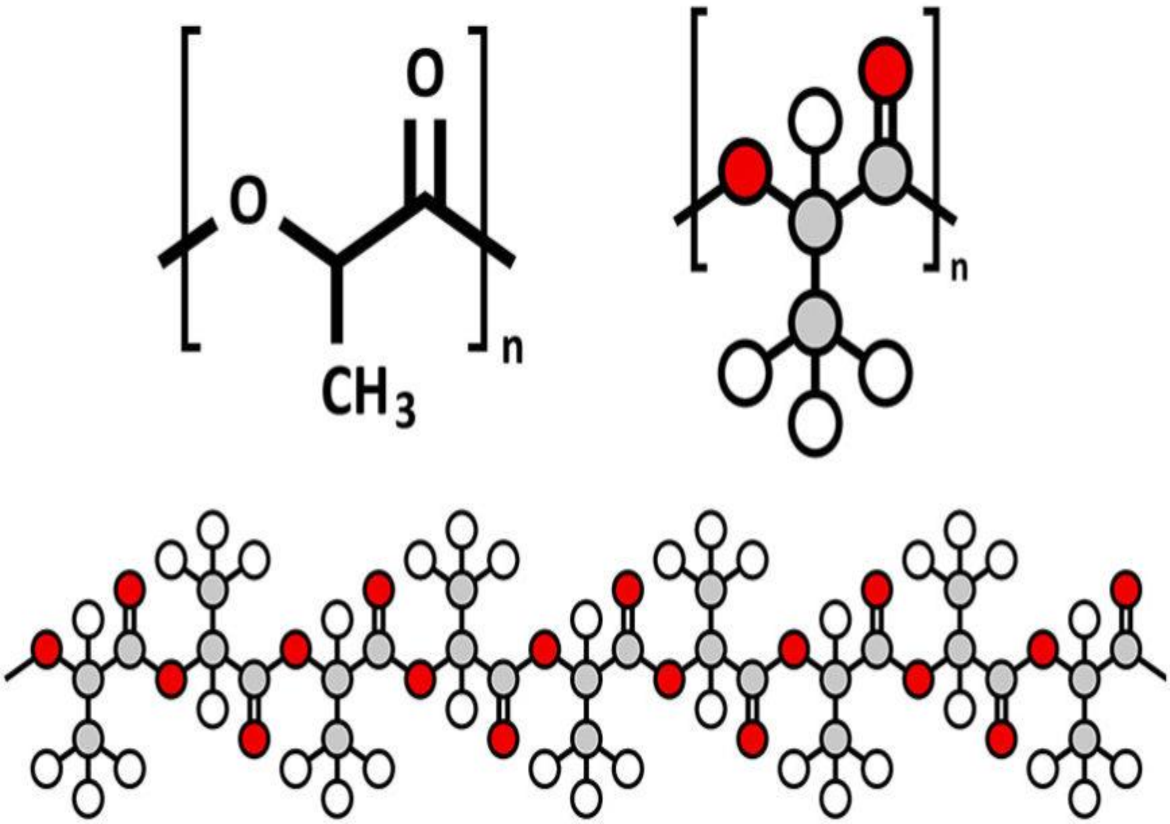
Introduction to Polymer Science

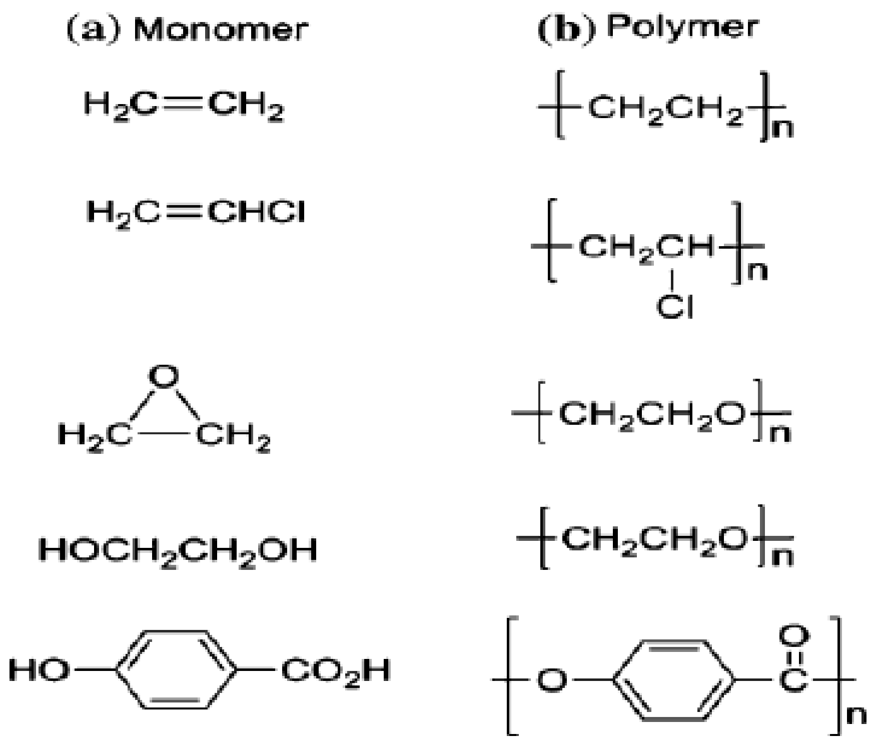


Definition of Polymer

A polymer is a **large molecule** of high molecular weight obtained by the **chemical interaction** of many **small molecules** of low molecular weight of one or more types. The process of manufacture of a polymer is called the **polymerization**.

A polymer (Greek poly means "many" + mer means "part") is a substance or material consisting of **very large molecules called macromolecules**, composed of many **repeating subunits**.

A polymer is a large **molecule or a macromolecule**, which essentially is a **combination of many subunits**.



History of Polymers

Polymer science is a relatively new discipline which deals with **plastics, natural and synthetic fibers, rubbers, coatings, adhesives, sealants, etc.**; all of these materials nowadays have become very common.

The concept of polymers is one of the great ideas of the **20th century**. It emerged in the **1920s** amid prolonged controversy and its acceptance is closely associated with the name of **H. Staudinger who received the Nobel Prize in 1953**.

Reference: Dorel Feldman (2008) Polymer History, Designed Monomers and Polymers, 11:1, 1-15, **DOI: 10.1163/156855508X292383**

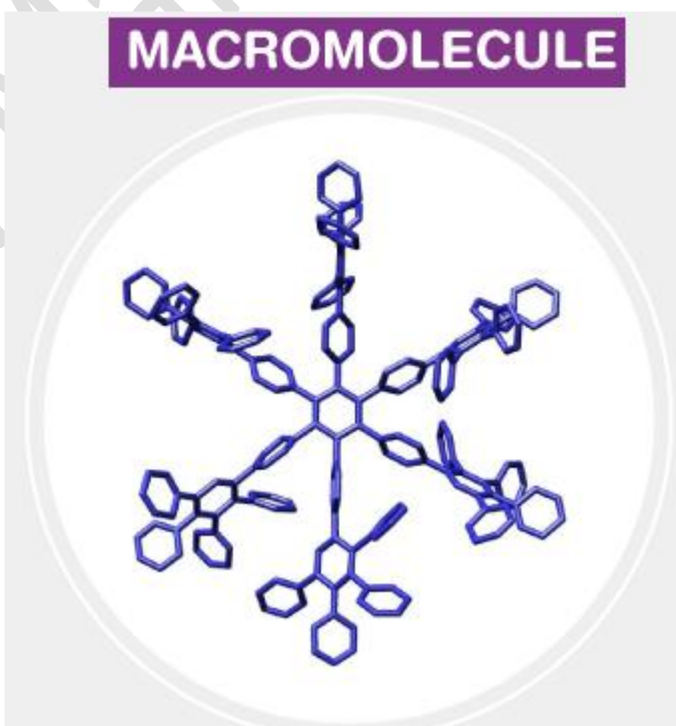
Important Terms to Understand

1. Molecule v/s Macromolecule

Macromolecule is a **very large molecule**, usually with a diameter ranging from about **100 to 10,000 angstroms (10^{-5} to 10^{-3} mm)**.

The term molecule refers to very large molecules and something that consists of more than one atom. **Herman Staudinger coined it in 1920**. Macromolecules are so huge that these are made up of more than **10,000 or more atoms. The term molecule here refers to a very big molecule and something that consists of more than one atom.**

Macromolecules are also termed as polymers. They are formed by the polymerization of molecules such as carbon, hydrogen and oxygen.



The molecule is the **smallest unit** of the substance that **retains its characteristic properties**. The macromolecule is considerably larger than the ordinary molecule, which usually has a diameter of less than **10 angstroms (10^{-6} mm).**

IUPAC (International Union of Pure and Applied Chemistry) definition of Macromolecule:

A molecule of **high relative molecular mass**, the structure of which essentially comprises the **multiple repetitions of units** derived, actually or conceptually, from molecules of **low relative molecular mass**.

Why all polymers are macromolecules but all macromolecules are not polymers?

The polymers are also called as macromolecules because of their big size. A polymer always consists of thousands of repeating monomers units. However a macromolecule is a giant molecule which may or may not contain monomer units. For example chlorophyll is a macromolecule but it is not a polymer as it does not contains monomer whereas polythene is a polymer as well as macromolecules as it contains large number of repeating monomers. Thus all the polymers are macromolecules but reverse is not true.

2. Monomers: Small molecules of low molecular weight, which combine to give a polymer, are called monomers.

3. Degree of polymerization: The number of monomers used in the process is called degree of polymerization.

4. Functionality: The total number of functional groups or bonding sites present in a monomer molecule is called the functionality of the monomer.

5. Reaction conditions: Temperature, pressure and catalysts affect the length and branching of the polymer chain.

Properties of Polymers

Physical Properties of Polymer

1. Tensile Strength – The strength of a polymer to elongate without breaking is its tensile strength. Physical strength and durability depend on this property of polymers.

2. Melting Point and Boiling Point – Polymers have a high melting point and boiling point. Greater the intermolecular forces, longer the chains, and hence higher the melting point and boiling point.

3. Hardness – Hard polymers resist the penetration of hard substances into them. They withstand wear and tear, scratches and are used in the manufacturing of constructing devices.

4. Density- Polymers are classified into high-density polymers and low-density polymers based on the density differences.

5. Heat Capacity / Heat Conductivity – This decides the extent to which a polymer acts as an insulator of heat. The stiffness of molecules decides whether a polymer is a good conductor of heat.

6. Thermal Expansion – The extent to which a polymer expands or contracts when subjected to heat or cold is measured by this property.

7. Crystallinity – Polymers with less crystallinity are more useful as they are brittle. This property is based on the type of arrangement of polymeric chains.

8. Elasticity– Polymers with weak intermolecular bonds stretch to a greater extent and are more elastic.

9. Permeability – This is the tendency of particles to pass through the polymers. For example, low density polyethylene is less permeable to air, so it is used to pack food items.

10. Refractive Index– The extent to which the light bends as it passes the polymer is measured as its refractive index. Polymers use this property in spectroscopy.

11. Resistance to Electric current – Most of the polymers are bad conductors of electricity. Nowadays, conductive polymers are used in semiconductor devices. Their conductivity arises due to conjugated carbon-carbon double bonds.

12. Crystallinity: In the crystalline phase, the intermolecular bonding is more strong and significant. Hence, the crystallinity of the polymer increases its strength.

13. Young's Modulus – It is the ratio of tensile stress and tensile strain. It determines how easily a polymer can stretch and deform. In short, it is the measure of the stiffness of a polymer. $E= \frac{\text{Tensile strength}(\alpha)}{\text{Tensile strain}(\varepsilon)}$

<u>Chemical Properties of a Polymer</u>

1. Bonding and reactivity – The strong covalent bond and other weak forces such as hydrogen bonding between the particles of polymers determine its property like reactivity. Generally, polymers are resistant to chemicals due to their low reactivity.

2. Interaction between the reactive groups – Intermolecular forces among the monomers is decided by their dipole. The carbonyl group (amide group) present at the side chains of the monomers is responsible for the formation of the hydrogen bond.

3. Adhesion of polymers on the surface, its interaction with coating, and the external environment also affects their quality, like paints.

4. Biodegradability– Polymers can degrade by the action of decomposers. Natural polymers like rubber are biodegradable, while synthetic polymers are non-biodegradable.

Factors Contributing to Polymer Properties

Properties of a polymer depend mainly on three factors:

1. **Chemicals** from which polymers are formed.

2. **Polymerization condition** such as chain length, type of bonds present between polymers, and nature of the functional group present at the end of the monomers.
3. The **type of monomer** units polymerized to form the repeating units in polymers is one of the critical factors that decide the properties of polymers.

Factors that Affect Properties of a Polymer

Properties of Polymer depend on several factors. Some of them are discussed below:

Temperature – Polymers are sensitive to temperature: the flexibility and compressive strength decrease as the temperature increases. The kinetic energy of the molecules increases with increasing temperature, and Young's modulus decreases.

Chain Length – It can be inferred that as the chain length of polymers increases, their strength also increases.

Branching – As branching increases, the mechanical strength of polymers also increases. For example, the degree of crystallinity is higher in density of polyethylene and has relatively poor mechanical properties. Thus branching makes polymers stiffer, harder and stronger.

Cross-linking: When polymer chains are cross-linked extensively by strong covalent bonds, their strength increases, making it difficult to melt them.

Nature of Side Groups – The presence of polar side-groups increases the strength of attraction between the polymeric chains, making them stronger due to hydrogen bonding and other attractive forces.