

POLYMER SCIENCE AND TECHNOLOGY

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INTRODUCTION:

The term polymer derived from the Greek words (Poly+mer). *Poly* means- many and *mer* means- parts or unit. Thus polymer is large molecule, formed by repeating linking of thousands of small molecular units by chemical bonds. Monomer is a small molecule which may react chemically to link together with other molecules of the same type to form a large molecule called polymer.

History of polymers starts with the formation of earth when basic elements such as C, H, O, N in the way of forming complex molecules, have formed polymers. From basic molecules to formation of human body is actually the story of formation of polymers. In the path of man living in the jungles to today's man living in modern worlds is the way of development from natural polymers (starch, cellulose, cotton etc) to man-made polymer known as synthetic polymer.

Discovery and use of synthetic polymers starts when we start using decorative article, textiles, building materials, packaging material and finally use of plastics in our day to day life that we cannot imagine our life without plastic.

Use of polymer like plastic, fibre and rubber came into human life in such a big way because of high strength, light weight, good flexibility, special electrical properties, resistant to chemicals etc.

The first modified natural polymers cellulose nitrate and casein-formaldehyde was commercially produced in the year 1860. The first fully synthetic polymer is phenol-formaldehyde resin called Bakelite was made by Leo Backeland in the year 1907. Cellophane was invented in the year 1908 by Jocques Brandenberger. The major development of polymer science and technology has taken place since about in the year 1920.

In 1922 Hermann Staudinger was the first to propose that polymers consist of long chains of atoms held together by covalent bonds. He also proposed to name this compound macromolecule. Before that, scientists believed that polymer were clusters of small molecules (called colloids) without definite molecular weight, held together by an unknown force. Staudinger received the Noble Prize in chemistry in the year 1953. Wallace Carothers invented the first synthetic rubber called neoprene in 1931 and invented nylon a true silk replacement in the year 1935. Stephanie Kwolek developed and aramid, or aromatic nylon named Kevlar.

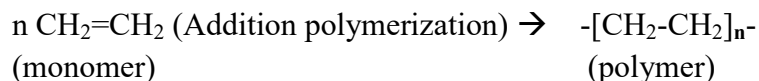
There are now a large number of commercial polymers, including composite material such as carbon fiber-epoxy, polystyrene-poly-butadiene (HIPS), Acrylonitrile-butadiene-styrene (ABS) and other such material which have best properties of their various components including polymer designed to work at high temperature in automobile.

MONOMER:

It is a simple molecule with two or more binding sites through which it forms covalent linkages with other monomer molecule to form polymer. Monomers are thus building block of polymers. All simple molecules cannot behave as monomers but only those with two or more building site can act as monomer.

POLYMER:

A polymer is a large molecule built by the repetition of small simple molecule called monomer. The repeating chemical units are covalently linked to each other in a macromolecule. The properties of a polymer are entirely different from those of the monomers from which it is formed. The molar masses of polymer vary from 10^3 to $m10^7$.



- Due to large size of polymer they are also some times called macromolecule.
- The chemical process leading to the formation of polymer is known as polymerization.
- The number of monomeric units contained in the polymer is known as Degree of Polymerization (DP)

$$\text{Molecular weight of polymer (M)} = \text{DP} \times \text{Molecular weight of monomer (m)}$$

CHARACTERSTICS OF POLYMERS:

1. Polymeric molecules are very big molecule. Their average molecular weight of the order of 10^5 or more. That's why they also known as Macromolecule.
2. Polymers are semi-crystalline material. It contains both the properties of amorphous as well as crystalline. Crystalline region provides strength and hardness and the amorphous region provide flexibility to polymeric material.
3. Inter molecular forces in polymers can be Vander Waals Forces, dipole-dipole attractions or hydrogen bonding.
4. The chemical, electrical, optical, mechanical and thermal properties of polymers depends mainly on (i) Size and shape of polymers and
(ii) The presence or absence of characteristics intermolecular forces
5. Polymer are combustible materials, have low densities and show excellent resistance to corrosion.
6. Polymer are thermal and electrical insulator and easily mouldable even into complex shapes.

CLASSIFICATION OF POLYMER:

There are several ways to classify polymers. The classification is based on several considerations. The source or origin, type of polymerization, nature, type of chain, solid state behavior etc. are shown in below figure.

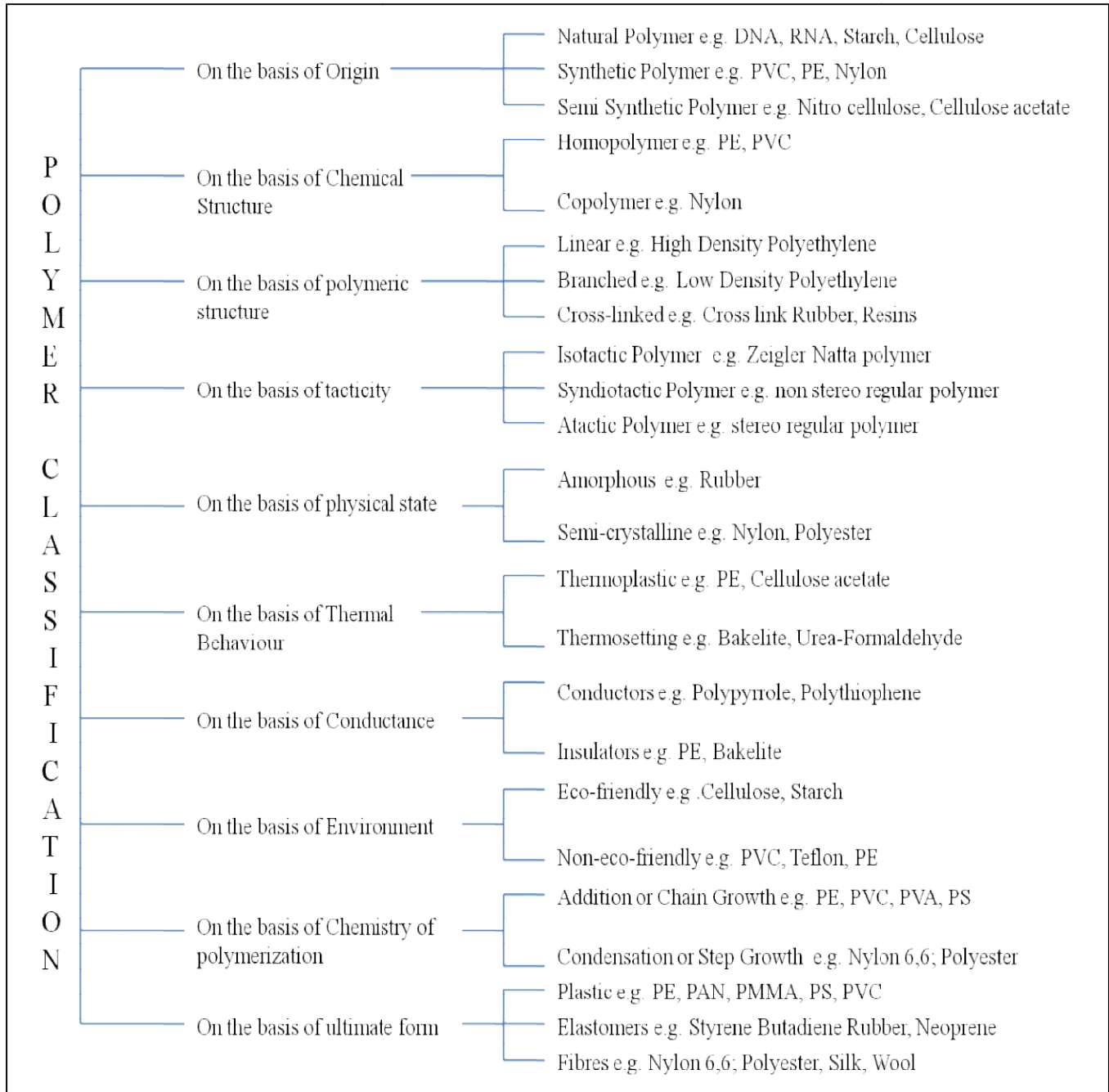


Figure: Classification of polymers

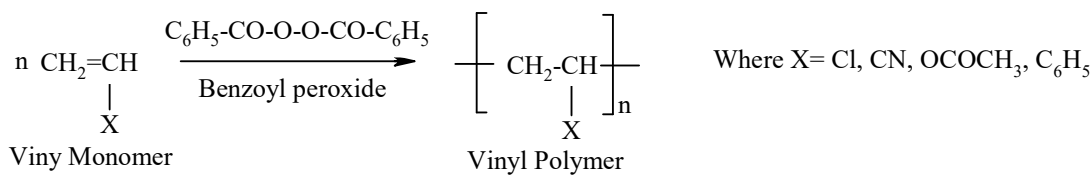
- b) Chain Propagation- Growth of polymer chain having active center is called propagation steps.
- c) Chain Termination- removal of active centre by coupling or by Disproportionation or by chain transfer is called chain termination step.

TYPES OF ADDITION POLYMERIZATION: Depending upon the nature of active centre or the chain carrier, the polymerization is classified as follows:

- (A) Free Radical Addition Polymerization
 (B) Ionic Addition Polymerization

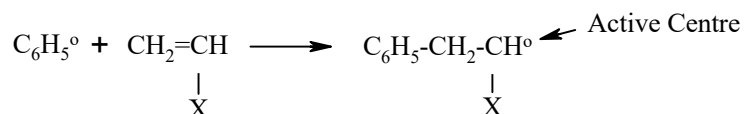
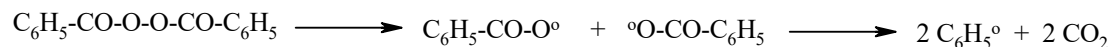
RADICAL OR FREE RADICAL CHAIN GROWTH ADDITION POLYMERIZATION:

In this polymerization process initiation of chain is brought about by either light radiation or by heat or by organic peroxides. e.g. Polymerization of vinyl compound in presence of benzoyl peroxide.

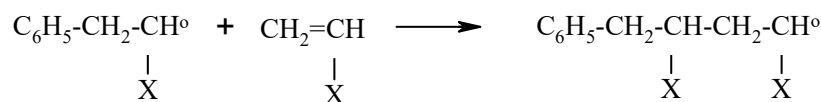


MECHANISM:

Chain initiation



Chain propagation



Chain Termination: removal of active centre is called chain termination.

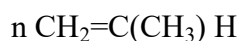
IONIC POLYMERIZATION: In ionic polymerization is of two types:

- (i) Cationic Polymerization
 (ii) Anionic Polymerization

- Anionic and Cationic polymerization are complex and more versatile than free radical chain polymerization.
- The initiation reaction of ionic polymerization requires only small amount of activation energy. Therefore, these types of reaction occur at very low temperature.
- Similar to radical polymerization, ionic polymerization has also the mechanism of chain reaction.

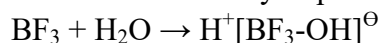
CATIONIC OR CATIONIC CHAIN GROWTH POLYMERIZATION:

- ✓ Cationic polymerization takes place in presence of acidic species e.g. HF, H₂SO₄, H₂O or by Lewis Acid AlCl₃, BF₃, SnCl₄.
- ✓ For cationic polymerization monomer should have electron releasing groups (+I Effect).
- ✓ For cationic polymerization carrier of chain is positively charge carbocation i.e. Active centre of carbocation.



MECHANISM:

- (i) Chain Initiation: Chain initiation is also brought about by Lewis acid e.g. AlCl₃, BF₃, but these halides are active only in presence of water.



- (ii) Carbonium ion salt are also used to initiate the chain e.g. (C₆H₅)C⁺ SbCl₆[⊖] (Trityl hexachloro antimonate)
- (iii) Chain Propagation:
- (iv) Chain Termination: