UNIT-II
POLYMERS

Basic terms and definition:

Polymer	Polymer is defined as a chemical substance of a high molecular mass formed by the combination of a large number of simple molecules.
Polymerization	The process by which the monomers get combined and transformed into polymers. is known as polymerization.
Functionality	The number of binding sites or reactive sites of monomer.
Tacticity	The orientation of functional groups in polymer in orderly or dis orderly manner.
Isotactic polymer	If the functional groups are arranged on the same side of the chain.
Atactic polymer	The functional groups are arranged at random around the chain.
Syndiotactic polymer	The functional groups are arranged in alternative fashion with respect to main chain.
Plastics	Plastics are high polymers which can be moulded into any desired form by application of heat and pressure in presence of a catalyst.
Thermo plastics	There the polymers which become soft on heating and hard on cooling. On reheating, they become soft again and can be remoulded to any desired shape.
Thermosetting plastics	These are the polymers which are fusible on initial heating, but further heating become set insoluble, infusible, rigid and hard.
Elastomer	Any rubber line elastic polymer, which can be stretched to at least three times, but it returns to its original shape and size as soon as stretching force is removed.
Natural rubber	It consists of long coiled chains of polymers isoprene.
Compounding of rubber	Compounding is mixing of raw rubber with different substances to impart special properties to an application.
Vulcanization	The process by which sulphur is added to raw rubber at 110^0C - 140^0C to improve the quality of rubber is called vulcanization.
Conducting polymer	An organic polymer with highly delocalized pi-electron system, having electrical conductance on par with metallic conductor is called a conducting polymer.
Inorganic polymer	The polymer chain back bone made without carbon-carbon links is called Inorganic polymer.

Concepts:

The word polymer has a Greek origin. Which means many units (parts)? Polymer is defined as a chemical substance of a high molecular mass formed by the combination of a large number of simple molecules, called monomers. e.g.,

$$\underset{\text{ethylene}}{n(CH_2{=}CH_2)} \longrightarrow \underset{\text{polyethylene}}{[-CH_2-CH_2-]_n}$$

Polymerization: The process by which the monomers get combined and transformed into polymers is known as polymerization.

Difference between Polymers and Macromolecules: Polymers are also called macromolecules due to their large size but converse is not always true. A macromolecule mayor may not contain monomer units, e.g., chlorophyll ($C_{55}H_{72}O_5N_4Mg$) is a macromolecule but not a polymer since there are no monomers units present so we can conclude that all polymers are macromolecules while all macromolecules may not be polymers in nature.

Classification of Polymers Based on Source of Origin:

(i) Natural polymers: Those polymers which occur in nature. i.e., in plants or animals are called natural polymers.

(ii) **Synthetic polymers:** The polymers which are prepared in the laboratory are known as synthetic polymers or man-made polymers, e.g., polythene, synthetic rubber, PVC, nylon-66, Teflon, etc.

(iii) **Semi synthetic polymers:** Polymers obtained by making some modification in natural polymers by artificial means, are known as semi synthetic polymers, e.g., cellulose acetate (rayon), vulcanized rubber etc.

Classification of Polymers Based on Structure:

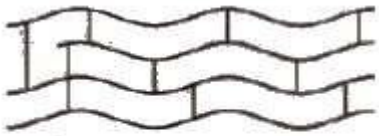
(i) **Linear polymers:** These are the polymers in which the monomer units are linked to one another to form long linear chains. These linear chains are closely packed in space. The close packing results in high densities, tensile strength and high melting and boiling points. e.g., high density polyethene, nylon and polyesters are linear polymers.

Linear chain polymer

(ii) **Branched chain polymers:** In such polymers, the monomer units are linked to form long chains with some branched chains of different lengths with source. As a result of branching, these polymers are not closely packed in space. Thus, they have low densities, low tensile strength as well as low melting and boiling points. Some common examples of such polymers are low density polyethene, starch, glycogen etc.

Branched chain polymer

(iii) **Cross-linked polymers or network polymers** In such polymers, the monomer units are linked together to form three dimensional network. These are expected to be quite hard, rigid and brittle. Examples of cross linked polymers are Bakelite, glyptal, melamine-formaldehyde polymer etc.



Cross linked polymer

Classification of Polymers Based on Mode of Polymerization:

(i) Addition polymerization: The polymers formed by the polymerization of monomers containing double or triple bonds (unsaturated compounds) are called addition polymers. Addition polymers have the same empirical formula as their monomers.

$$\underset{\text{ethylene}}{n(CH_2{=}CH_2)} \longrightarrow \underset{\text{polyethylene}}{[-CH_2-CH_2-]_n}$$

(ii) Condensation polymerization: The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers, e.g., nylon 6, 6 is formed by the condensation of hexa methylene diamine with adipic acid.

$$nH_2N(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \longrightarrow \underset{\text{nylon 6,6}}{+NH(CH_2)_6NHCO(CH_2)_4CO\,\tfrac{}{}_n} + nH_2O$$

(iii) **Copolymerization:** The polymers which are obtained by the polymerization of two or more monomers are called copolymers. E.g. BuNa- S, BuNa- N.

Mechanism of polymerization: Depending upon the nature of the reactive species involved. Chain growth polymerization occurs by the following mechanisms:

(i) Free radical addition polymerization

(ii) Cationic polymerization

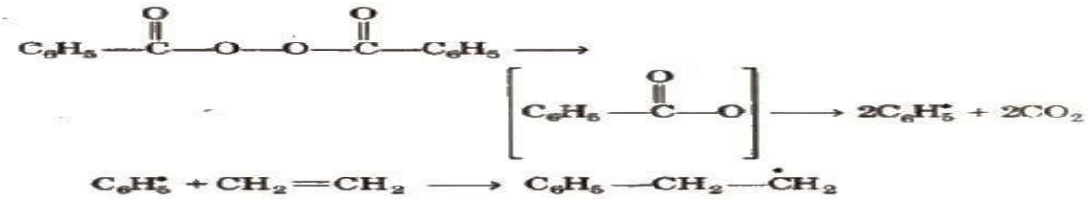
(iii) Anionic polymerization

(iv) Co ordination covalent polymerization

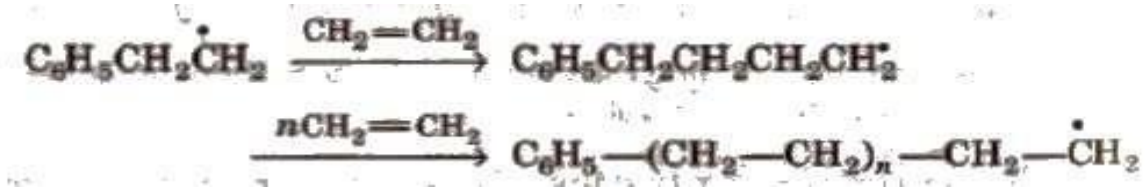
(i) Free radical addition polymerization: The monomers used are generally mono substituted alkenes. The most commonly used catalysts are benzyl peroxide, hydrogen peroxide or t-butyl peroxide etc.

Mechanism: The reaction involves the following steps;

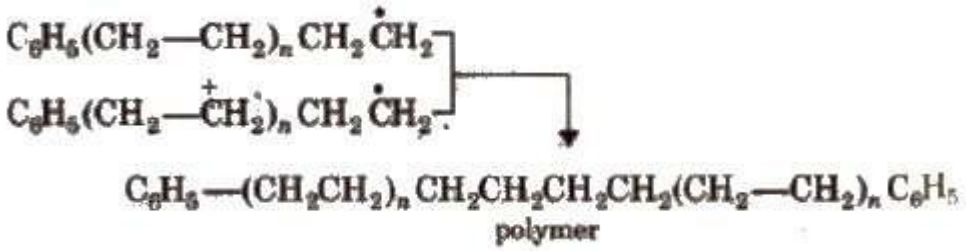
Step I: Chain initiation step: In this step, peroxide undergoes homolytic fission, e.g., benzyl peroxide on heating produces phenyl initiator free radical.



Step II: Chain propagation step: The new free radical adds to another molecule of monomer to form a larger free radical.



Step III: Chain termination step: There are three ways of chain termination: Coupling reaction, disproportionate reaction, chain transfer reaction. One mode of termination of chain is shown as under:



Plastics:

Thermoplastics: These are linear polymers and have weak Vander Waals' forces acting in the various chains. These forces are intermediate of the forces present in the elastomer and in the fibers. When heated, they melt and form a fluid which sets into a hard mass on cooling. Thus, they can be cast into different shapes by using suitable moulds, e.g., polyethene and polystyrene.

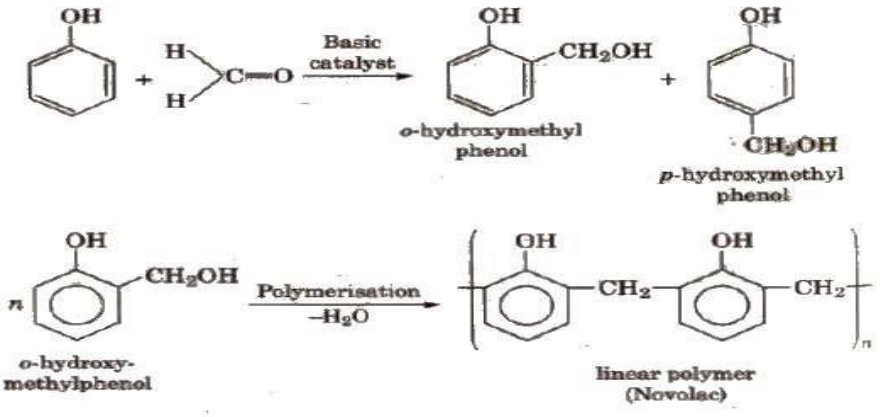
Thermosetting plastics: These are normally semi fluid substances with low molecular masses. When heated, they become hard and infusible due to the cross-linking between the polymer

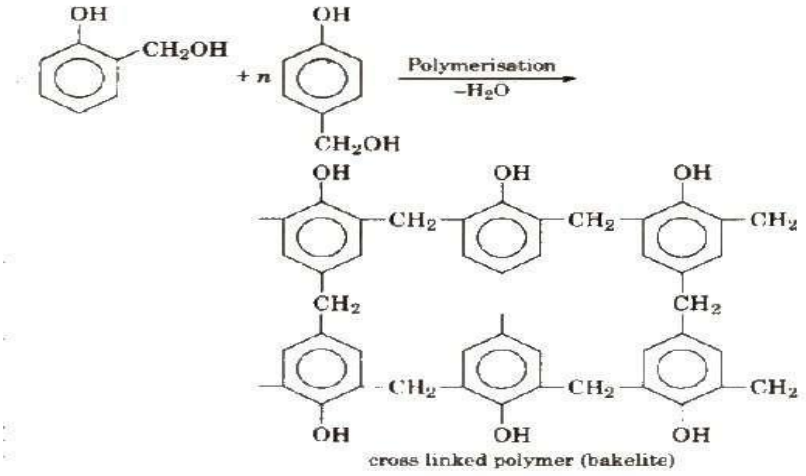
chains. As a result, they also become three dimensional in nature. A few common thermosetting polymers are Bakelite and urea formaldehyde resin.

Thermo plastics	Thermosetting plastics
These are produced by addition polymerization	These are produced by condensation polymerization
The resins are made of long chains attached by weak Vander Waal's force of attraction	The resins have three dimensional network structure connected bonds.
On heating they soften and on cooling become stiff chemical nature won't change	On heating they become stiff & hard. No change on cooling Chemical nature changes.

Some important polymers:

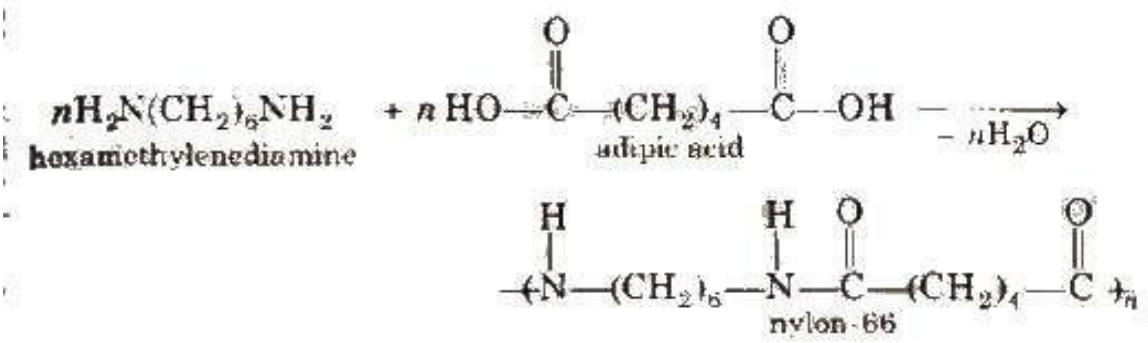
1. Bakelite (or) Phenol-Formaldehyde Polymer: These polymers are obtained by the condensation reaction of phenol with formaldehyde in the presence of either acid or a base catalyst. The reaction involves the formation of methylene bridge at ortho, para or both ortho and para positions. A linear or cross linked material is obtained depending upon the condition of reaction.





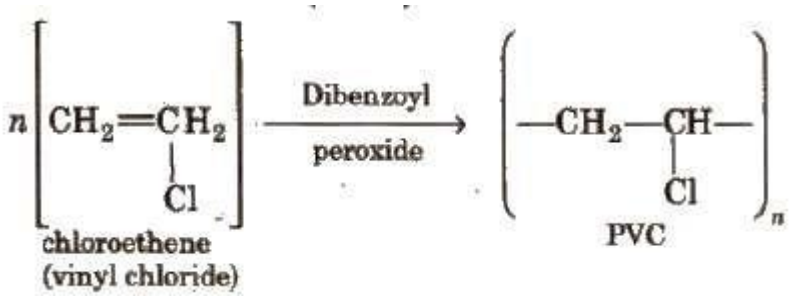
Uses: Bakelite is used for making combs, photograph records, electrical switches etc. Soft bakelites with low degree of polymerization are used as binding glue for laminated wooden plants, in varnishes and lacquers.

2) Nylon-6,6: It is obtained by the condensation of adipic acid and hexa methylene diamine with the elimination of water molecule.



Properties and uses: Nylon-6, 6 is a linear polymer and has very high tensile strength. It shows good resistance to abrasion. Nylon-6, 6 is usually fabricated into sheets. It is used in bristles for brushes and in textile.

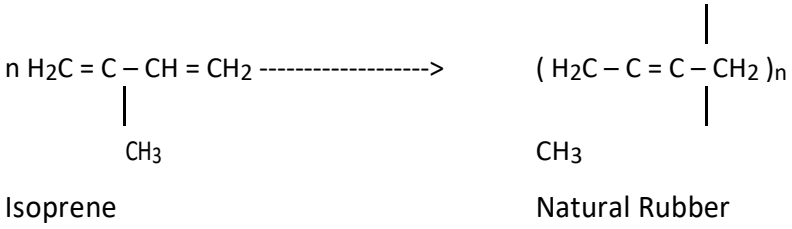
3) Poly vinyl chloride (PVC):



It is used for making rain coats, toys and electrical insulation. It is hard and resistant to heat and chemicals.

Rubbers: Rubbers also known as elastomer, they are high polymers, which have elastic properties in excess of 300%.

Natural Rubber:- Natural Rubber is a high molecular weight hydrocarbon polymer represented by the formula $(C_5H_8)_x$. it is obtained from a milk emulsion called latex by tapping the bark of the tree. "Hevea brasiliensis". It is a polymer of isoprene units.



Isoprene Natural Rubber

Processing of Natural Rubber:- By cutting the bark of rubber tree the milky colloidal rubber milk is obtained. The main constituent of rubber latex is 25-45% of rubber and the remaining are water, protein & resinous materials. The rubber latex is coagulated by using 5% acetic acid and made in to sheets. The rubber sheets are cured under mild heat and then subjected to further processing.

Crepe rubber:- To the rubber latex a small amount of sodium bisulphate is added to bleach the color and feed in to roller which produce 1mm or more thickness sheets which are dried in air at about 40-50^0 C. the dried thin sheet of rubber are known as "smoked crepe rubber".

Mastication:- Rubber becomes soft and gummy mass when subjected to severe mechanical agitation. This process is known as mastication. Mastication followed by the addition of certain chemical (compounding) which is carried out on roll mills or internal mixers. After mastication is comp etc, the rubber mix is prepared for vulcanization.

Compounding of plastics:- Compounding of plastics may be defined as the mixing of different materials like plasticizers, fillers of extenders, lubricants, pigments to the thermoplastic & thermosetting resins to increase their useful properties like strength, toughness, etc. Resins have plasticity or binding property, but need other ingredients to be mixed with them for fabrication into useful shapes. Ingredients used in compounding o plastics are

(1)Resins (2) Plasticizers (3) fillers (4) pigments (5) Stabilizers.

Resins:- The product of polymerization is called resins and this forms the major portion of the body of plastics. It is the binder, which holds the different constituents together.

(1) Thermosetting resins are usually, supplied as linear – polymers of comparatively low molecular weight, because at this stage they are fusible and hence, moldable. The conversion of this fusible form into cross-linked infusible form takes place, during moulding itself, in presence of catalysts etc.

(2) Plasticizers: - Plasticizers are substances added to enhance the plasticity of the material and to reduce the cracking on the surface.

(3) Fillers (or) extenders: - Fillers are generally added to thermo setting plastics.
E.g.:- Mica, cotton, carbon black, graphite, $BaSO_4$ etc.

(4) Dyes and pigments:- These are added to impart the desired c ur to the plastics and give decorative effect.
e.g.:- Lead chromate (yellow), Ferro cyanide (blue)

(5) Stabilizers:- Stabilizers are used to improve the thermal stability of plastics, e.g.:- PVC. At moulding temperature, PVC undergoes decomposition & decolourisation. So during their moulding, stabilizers are used. E.g.:- white lead, head chromate.

Synthetic Rubber:-

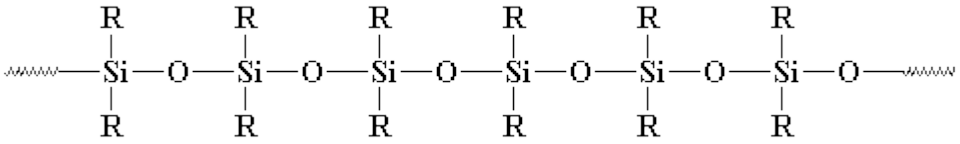
(1) Buna-S Rubber:-sodium was used as the catalyst. Hence the name bu (butadiene), Na (symbol Na for sodium) and S (for styrene). It is also called GRS (government rubber styrene) SBR (styrene butadiene Rubber). The Buna-S-Rubber is the first synthetic rubber developed during the second time of world war by US in order to overcome the scarcity of natural rubber. It is prepared by the copolymerization of butadiene & styrene.

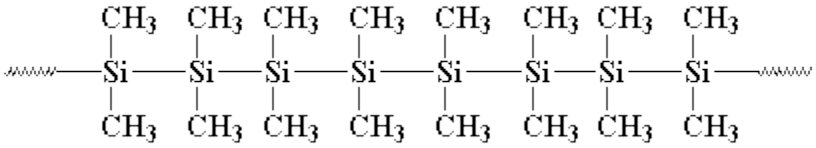
Conducting polymers:- An organic polymer with highly delocalized pi-electron system, having electrical conductance on par with metallic conductor is called a conducting polymer.
Intrinsically conducting polymers (ICPs) have been the subject of intense research. They are oligomeric or polymeric materials composed of phenylene rings and related units such as naphthalene, anthracene or hetero aromatic rings such as pyrrole and thiophene, which are connected to one another through carbon-carbon single bonds or through vinylene groups (-C=C-). These polymers have unique electrical and thermo physical properties. Due to the low hydrogen content and aromatic structure, they show excellent chemical, thermal, and oxidative stability and are practically insoluble in all common solvents. They are also potentially electrical conducting materials, particularly when doped. Due to the fully aromatic ring structure and absence of freely rotating groups, the mobility of the repeat units is highly

restricted which results in very high melting and softening points. This makes the synthesis and processing of these resins difficult and expensive. In fact, their melt viscosities are often so high that injection molding and similar processing methods are not feasible or practical.

Inorganic polymers:-The polymer chain back bone made without carbon-carbon links is called Inorganic polymer. On most of these pages we've been talking about polymers whose backbone chains are made mostly of carbon atoms, if not entirely of carbon atoms. These we call *organic* polymers. But now we're going to leave convention behind and talk about some polymers that don't have any carbon atoms in the backbone chain. These are called, as if you couldn't guess, inorganic polymers.

e.g. Silicones, Polysilanes, Polygermanes and poly phospahazenes.





Important Questions:

1. Distinguish between addition (or) Chain and condensation (or) Step wise polymerization.
2. Define and explain co-polymerization method by taking suitable example.
3. Discuss the mechanism of cationic and anionic addition polymerization.
4. Discuss the mechanism of free radical and co-ordination covalent addition polymerization.
5. Distinguish between thermo plastics and thermo setting plastics with examples.
6. Explain preparation, properties & uses of Bakelite and Poly ester.
7. Write preparation, properties & uses of PVC, Poly styrene, Poly ethylene, Teflon and nylons?
8. Give brief account on natural rubber and explain the processing and compounding of natural rubber.
9. Write preparation, properties & uses of any one Elastomer. (BuNa-S, BuNa-N, Poly urethane rubber, Butyl rubber, Thiokol rubber, Silicone rubber)
10. What are conducting polymers? Discuss various types of conducting polymers with examples.
11. Discuss the synthesis or mechanism of Poly acetylene and Poly aniline.
12. What are inorganic polymers? Write classification and applications of silicone and poly phospahazenes?