VELLORE INSTITUTE OF TECHNOLOGY, BHOPAL

Chapter-VI
Industrial & Conducting Polymer

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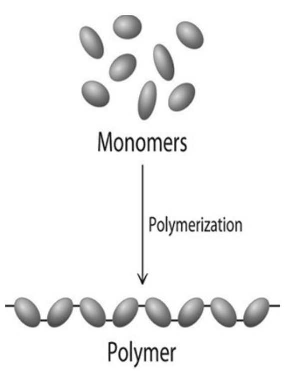
Syllabus of Engineering Chemistry (Theory)

Module No	Module Description	Hrs.
6	**Industrial and Conducting polymers:** Introduction to Polymers- Classification. Types of Polymerization (Chain & Step growth); Properties and engineering applications of BS, PVC, PMMA, PET, Teflon and Bakelite. Compression, injection, extrusion, Transfer moulding methods of plastics. Fiber reinforced composites - Properties and applications in automobiles and aerospace. Second Law of thermodynamics and entropy in recycling of plastics like PMMA. Introduction to metallic conductors. Conducting polymers: Polyacetylene and Polyaniline - Mechanism of Conduction, doping, Electrical characterization, applications of conducting polymers in semiconductor field.	9

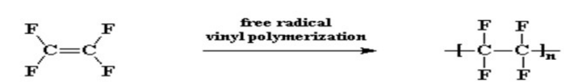
Polymer

Made up by linking together large number of small molecular units by chemical bonds.

The repeating small molecules which combine with each other to form a polymer are called monomers & due to large size polymers are also known as **Macromolecules.**



Degree of polymerization means the number of repeating units in the polymer chain.



tetrafluoroethylene   polytetrafluoroethylene

Degree of polymerization = n

Degree of Polymerization (n) = M / m
M = Mass of polymer, m = mass of monomeric unit

$$3\ CH_2 = CH_2 \rightarrow -[-CH_2\text{-}CH_2\text{-}]\text{-}_3$$

Ethylene   Polyethylene

Mass of polymer = 28*3 = 84
Degree of polymerization = 3

Polymers with high degree of polymerization are called **High polymer** and those with low degree of polymerization are called **oligopolymers.**

Polymers are semi-crystalline material i.e. they have both crystalline & amorphous regions. Crystallinity provide strength & hardness while amorphous regions provide flexibility to the polymeric material.

The intermolecular forces in a polymer can be Vander waal force, dipole-dipole attraction, hydrogen bonding and covalent bonds.

Classification of Polymer

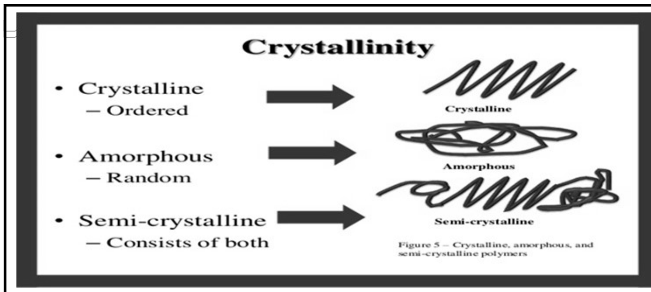
- **Classification of Polymer**
  - Based on Origin
    - Natural Polymer
    - Synthetic Polymer
  - Based on Physical State
    - Amorphous Polymer
    - Crystalline Polymer
  - Based on Structure
    - Linear Polymer
    - Branched Polymer
    - Cross-Linked Polymer
  - Based on Number of Monomers
    - Homopolymer
    - Copolymer
  - Based on Tacticity
    - Isotactic
    - Syndiotatic
    - Atactic
  - Based on Polymerization
    - Addition Polymer
    - Condensation Polymer

Based on Origin:

Polymer may be classified into
Natural Polymer: Polymers having origin in plants & animals. E.g.-Carbohydrates, Proteins, DNA
Synthetic Polymer: Plastic, Fibres, Rubber etc.

Based on Physical State:

Polymer may be classified into
Amorphous Polymer: Polymer chains are flexible and easily folded. For e.g.- Rubber, LDPE.
Crystalline Polymer: Polymer chains are ordered structure. Degree of crystallinity depends on the amount of ordering in polymer. For e.g.-
Semicrystalline Polymer: Polymers are amorphous as well as crystalline. For e.g.- HDPE, Nylon, Polyester.

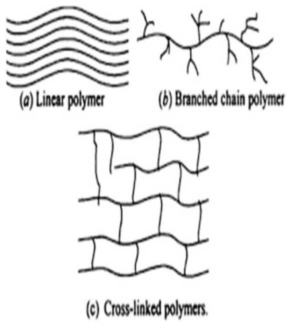


Based on Structure:

Polymer may be classified into:
1) Liner Polymer: Monomeric units are joined in the form of straight chain. Linear structure allows close packing of polymer chains. Posses high melting point, density & tensile strength.

2) Branched Polymer: Polymer which are linear and possess branches along the main chain. Branched chain polymer do not allow efficient packing of polymer chains. Posses low melting point, low density & low tensile strength.

3) Cross-linked Polymer: Polymer which are 3-D structure. They are hard, rigid, do not melt on heating but decomposes & burn on excessive heating.
Posses strong covalent bond between the polymer chains.



Based on Monomers:

Polymer may be classified into:

1) **Homopolymer:** Polymer obtained by the repeated combination of only one type of monomeric units. For e.g.- PVC
2) **Copolymer:** Polymer obtained by the repeated combination of two or more type of monomeric units. For e.g.- Styrene, Nylon, Bakalite, Dacron, Buna-S etc.

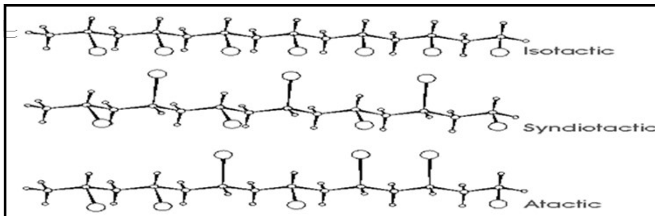
Copolymer can be further classified as-
Random Copolymer: -A-B-B-B-A-B-A-B-A-A-B-B-
Alternating Copolymer: -A-B-A-B-A-B-A-B-
Block Copolymer: -A-A-A-B-B-B-A-A-A-B-B-B
Graft Copolymer: -A-A-A-A-
|
B

Based on Tacticity:

Tacticity is defined as the spatial arrangement of the substituent groups on the asymmetric carbon atom. Based on the orientation of the group in space polymer can be of three type.

a) Isotactic Polymer
b) Syndiotactic Polymer
c) Atactic Polymer

1) **Isotactic polymer:** When the orientation of side groups on all carbon atom is same.
2) **Syndiotactic polymer:** When the orientation of side groups is alternating.
3) **Atactic polymer:** When the orientation of side groups is random.



Based on Polymerization:

Polymer may be classified into:

1) **Addition Polymerization:** In this type of Polymerization the monomers are added to eachother without the formation of byproduct. The elemental composition of polymer is same as that of monomer and its molecular weight is exact multiple of the original monomeric molecule.

1) **Condensation Polymerization:** In condensation polymerization reaction proceeds step by step through reaction between functional groups of the monomer with formation of byproduct.

Based on Molecular Force:

Polymer may be classified into:
Elastomer: Polymers held together by weakest intermolecular force and have elastic behavious.

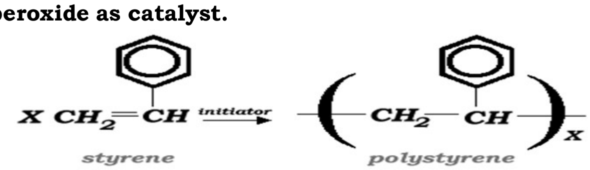
Fibre: Polymers whose polymeric chains are held together by strong intermolecular force like hydrogen bonding or dipole-dipole interaction. They are crystalline in nature and have high tensile strength.

Thermoplastic: They are long chain polymers that can be softened on heating and harden when cooled. The intermolecular force of these polymer are intermediate between those of elastomer and fibre.
For e.g.- Polystyrene, PVC, Polypropylene.

Thermosetting: The polymers that can change irreversibly into hard and rigid material on heating and cooling & cannot be reshaped once they set. They form hard, infusible, insoluble products because of cross-linkage.
For e.g. –Bakalite, Melamine.

Polystyrene

Preparation: Prepared by the free radical polymerization of styrene in the presence of benzoyl peroxide as catalyst.



Properties:

Due to the presence of bulky phenyl group packing of PS is not efficient & hence it is amorphous.

It has good optical properties & allow the transmission of all wavelength.

Due to chain stiffening effect of benzene ring, PS is hard & brittle.

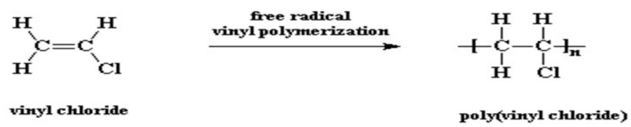
It is a non polar amorphous polymer with low moisture absorption and good electrical insulation characteristic, having low softening point (80-100°C), .

Application:

Used in the manufacturing of containers for talcum powder, housewares (Jars & containers), Bottle caps, Combs and brush handles.

Polyvinyl Chloride (PVC)

Preparation:
Vinyl Chloride is mixed with water in equal parts, small amount of catalyst and an emulsifier. The polymerization takes place at 40-45°C



Properties:

It is colourless, odourless and non-inflammable, excellent oil resistance and resistance to weathering.

It has superior chemical resistance but soluble in ethyl chloride. The presence of chlorine atom makes it hard and stiff.

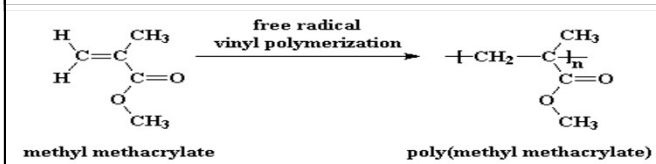
Application:

Used in acid recovery plants and in plants for handling hydrocarbons.

Used in the manufacturing of pipes, toys, tumbler, buckets, bottles.

Polyacrylate: Polymethyl Methaacrylate (PMMA) / Lucite / Plexiglass

Preparation:
It is prepared by the polymerization of methyl methacrylate in the presence of acetyle peroxide or hydrogen peroxide as catalyst.



Properties:

It is colourless, light, hard, transparent thermoplastic with high optical transparency.

It is has high softening point and having total internal reflection & allow the transmittance of light of all the wavelength.

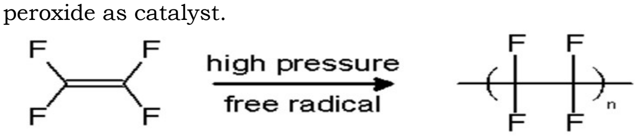
Application:

Used in light fittings for street lamp housing, automobile rear lamp housing, cock pit of helicopter.

Used in the manufacturing of motorcycle windscreens, optical fibres.

Polytetra Fluroethylene / Teflon / PTFE

Preparation:
It is prepared by the polymerization of tetrafluoro ethylene under pressure in the presence of benzoyl peroxide as catalyst.



Properties:

Due to the presence of highly electronegative fluorine atom there are very strong attractive force between the chains.

It is dense, chemically inert and high softening temperature.

Application:

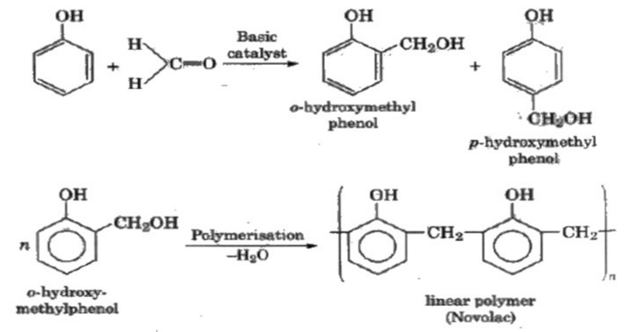
Used in the manufacturing of wire and cable insulation, coating of frying pans, Non lubricating bearings.

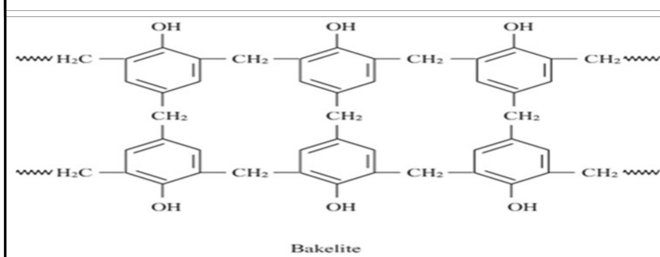
Used in the manufacturing of gaskets, pump parts, stop cock, insulators for capacitors motorcycle windscreens, optical fibres, coating on automobile body.

Phenolic Resins: Bakelite

Preparation:

The reaction mixture is heated and allowed to reflux under atmospheric pressure at about 100°C. The vacuum is applied for the removal of volatiles.





Properties:

It is hard, rigid, and strong. They have excellent heat and moisture resistance, good abrasion resistance.

They have good electrical insulation characteristics.

Application:

Used in the manufacturing of electrical plugs and switches. Handles of cooker.

Used in the manufacturing of varnishes, electrical insulation and protective coating.

Conducting Polymer

Conductive polymer (Intrinsically conducting polymer) are organic polymer that conduct electricity.

Conducting polymers have conjugated π-bonds between carbon atoms on the polymer backbone.

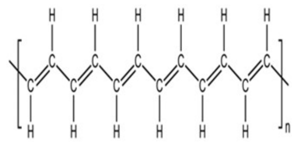
Such compounds may have metallic conductivity or can be semiconductors.

A polymers is a long chain having repeating units and to become a electrically conductive it should imitate like a metal i.e. it should have free electrons.

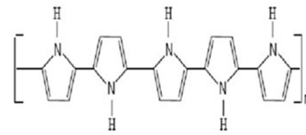
Condition to become conductive:

1) A polymer should have conjugated π-bonds.
2) The plastic has to be disturbed either by removing electrons from (oxidation) or by inserting them into (reduction) the material. This process is known as Doping.

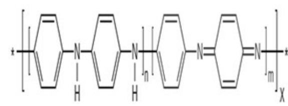
Polyacetylene



Polypyrrole



Polyaniline

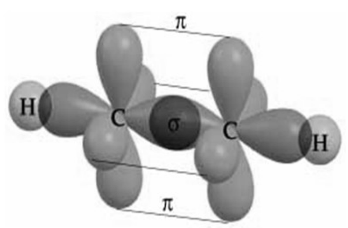


Graphite

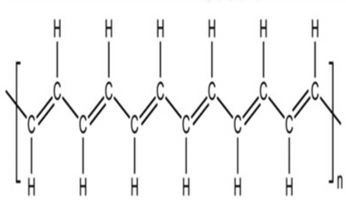
Diamond (Insulator)

Conduction Mechanism of Polyacetylene

The poly unsaturated hydrocarbon consist of hydrogen atom and sp2 hybridized carbon atom.



The localised electrons in the s bonds form the backbone of the polymer chain while the electrons in the π bonds are delocalised along the chain and responsible for electrical properties.



Before the current flow along the molecule one or more electrons have to be removed or inserted.

Polyacetylene has alternating single and double bond that give rise to mobile π-electrons. When doped become highly anistropic metallic conductor.

There are two types of doping

1) **Oxidation with halogen (or *p*-doping).**

$$(CH_n)+\frac{3x}{2}I \rightarrow (CH_n)^{+}+I_3^{-}$$

2) **Reduction with alkali metal (or *n*-doping).**

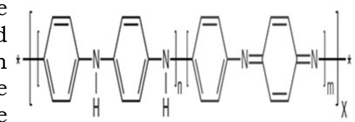
$$(CH_n)+xNa \rightarrow (CH_n)^{x-}+xNa^{+}$$

In the oxidation reaction the iodine molecule attracts an electron from the polyacetylene and becomes I_3^-. The polyacetylene molecule is positively charged is termed as **radical cation or polaron.**

The polarons created on doping may change into (p or n) **solitons** for polyacetylene.

Conduction Mechanism of Polyaniline (PANI)

In Polyaniline the conjugated double bond permits easy electron mobility throughout the molecule because electrons are delocalised.



Delocalisation is the condition in which the p-bonding electrons are spread over a number of atoms rather than localised between two atoms. Thus making the polymer electrically conducting.

Conjugated double bond “benzenoid ring” between the benzenoid amine and quinoid imine makes it electrically conductive polymer.

Polyaniline exists in three forms of oxidation states:
1) Leuco emeraldine- Fully reduced or only benzenoid amine structure.
2) Eneraldine- Neutral / Partially reduced and partially oxidised.
3) Pernigraniline- Fully oxidised or only quinoid imine structure.

Polyaniline is doped with para-hydroxybenzene sulphonic acid (PHBSA) & the conductivity is increased due to delocalisation.

APPLICATIONS OF CONDUCTING POLYMERS

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes their electroactivity.

Group 1	**Group 2**
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical biochemical and thermal sensors
Printed circuit boards	Rechargeable batteries and solid electrolytes
Artificial nerves	Optical computers
Antistatic clothing	Ion exchange membranes
Piezoceramics	Electromechanical actuators
Diodes/Transistors	'Smart' structures
Aircraft structures	Switches

Thank You