

UNIT – III

POLYMERS

INTRODUCTION:

- Matter is composed of many small units called molecules, which are in different sizes and shapes and associated with atoms. Polymers are giants or macro molecules which play a vital role in our daily life and provide the basic needs of our life (food, clothing and shelter).

- The word polymer was derived from Greek word 'poly' = 'many' and 'mers' = 'parts /units'.

Polymer: It is defined as a high molecular weight compound (macro molecule) made by linking together a large number of small molecules called **monomers**.

Ex: PVC, Polyethylene, Starch, Poly styrene, Proteins, DNA etc

Monomer: The basic repeating units present in a polymer are called monomer.

Ex: Vinyl chloride is a monomer of PVC.

Ethylene is a monomer of poly ethylene.

Glucose is a monomer of starch.

Styrene is a monomer of polystyrene.

Amino acids are the monomers of proteins.

Nucleotides are the monomers of Nucleic acids.

Degree of polymerization: The number of repeating units (or) monomers present in the polymer is called as degree of polymerization. They may be hundreds (or) thousands (or) ten thousands.

$$\text{Degree of polymerization (D.P)} = \frac{\text{Mol.wt of polymer}}{\text{Mol.wt of monomer}}$$

Molecular wt of polymer = D.P × Mol.wt of monomer.

Classification of Polymers:

1. Based on degree of polymerization:

- Polymers having high DP (having of more number of monomers) are called **High polymers**. Their molecular weight range is about 10,000 to 10,00,000 Daltons.
- Polymers with low DP are called **Oligopolymers**. Their molecular weight ranges from 5,000 to 2,00,000 Daltons.

2. Based on occurrence:

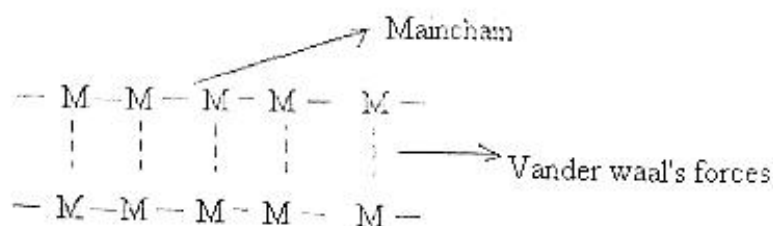
- Polymers may be either **Natural** (natural rubber, proteins, cellulose, starch etc) (or) **Synthetic** (PVC, PE, PS, Teflon, Nylon, Bakelite etc.....).

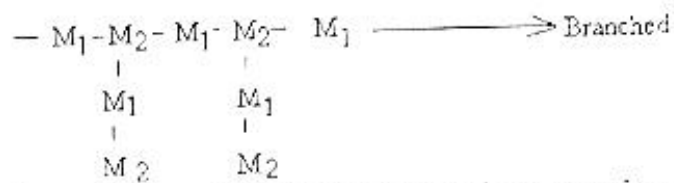
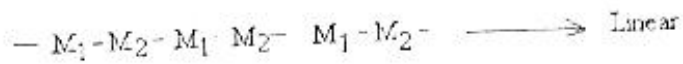
Basic Concepts:

1) Functionality:

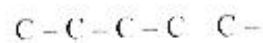
- The number of bonding sites (or) reactive sites present in a monomer is called as functionality.
- Each monomer should have minimum two bonding sides for polymerization.
 - a) If the functionality of monomer is 2, the resulting polymer is linear (or) straight chained.

Ex: Ethylene, styrene, vinyl chloride.





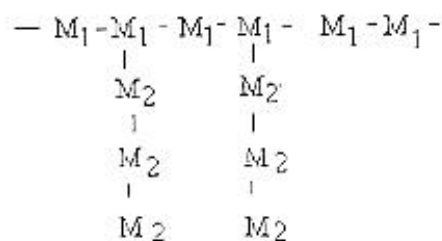
c) **Homo chain polymer:** If the main chain is made up of same species of atoms is called homo chain polymer.



d) **Hetero chain polymer:** If main chain is composed of different atoms is said to be Hetero chain polymer

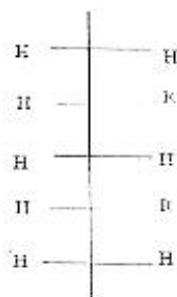


e) **Graft co-polymers:** These polymers are branched structures in which the monomer units on the branches and back bone differ.

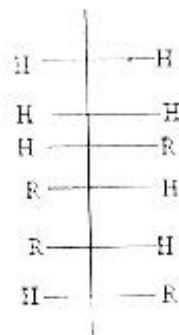


3) **Tacticity:** The orientation of functional groups in polymer is called as configuration. The difference in configuration of polymers because of the difference in arrangement of functional groups around main chain is called as Tacticity. Based on tacticity, polymers are of three types.

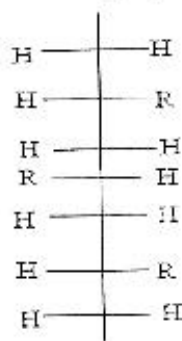
a) **Isotactic:** If all the functional groups are arranged on the same side of the chain, the polymer is called Isotactic polymer.



b) **Atactic:** If all the functional are arranged randomly around the main chain, the polymer is called Atactic polymer.



c) **Syndiotactic:** If all the functional groups are arranged alternately with respect to the main chain, the polymer is called syndiotactic polymer.



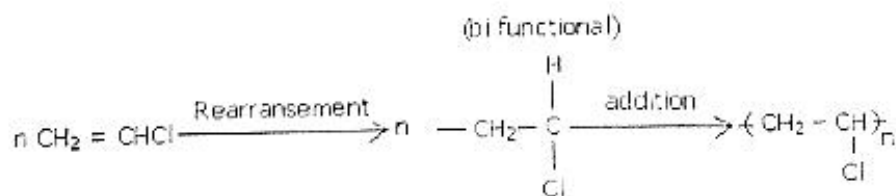
Polymerization:

1) Addition Polymerization:

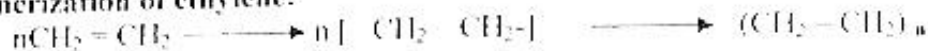
- This polymerization takes place between monomers that are bifunctional and contains double bonds in its structure.
- This can be defined as binding of several bifunctional monomers to form polymers without elimination of by products by addition reactions.
- This polymerization results in the formation of linear polymers.
- The produced polymer has same chemical composition as that of monomers.
- The molecular weight of polymer is an integral multiple of the monomer.

Examples:

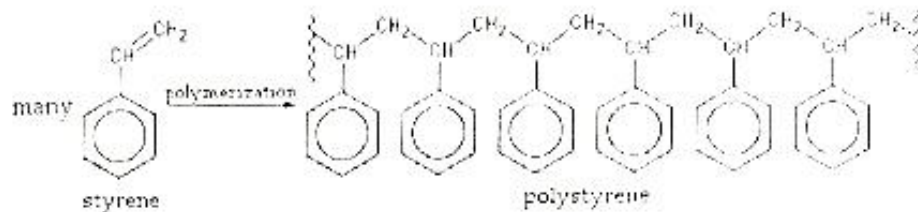
1. Formation of PVC:



2. Polymerization of ethylene:



3. Polymerization of Styrene:

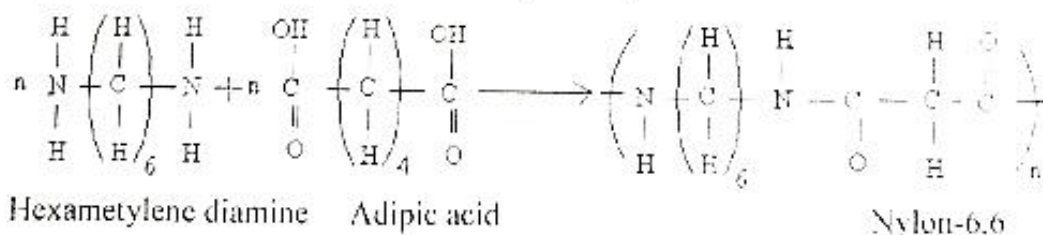


2) Condensation Polymerization:

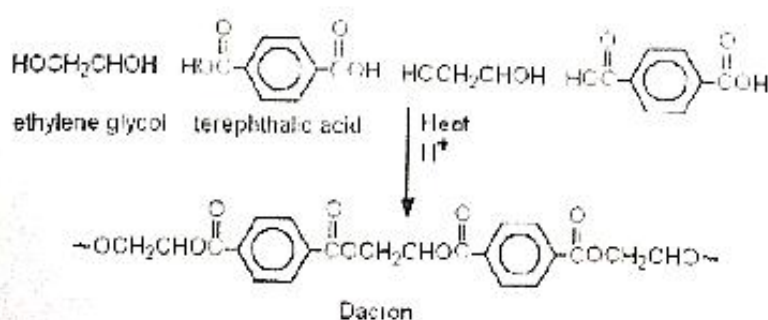
- This is also called Step-wise polymerization.
- This occurs between monomers that contain polar side groups.
- A reaction occurring between the same (or) different polar groups containing monomers with elimination of small molecules like ammonia, water, HCl etc. ... and forms linear (or) Cross - linked polymers is called condensation polymerization.
- The molecular weight of polymer is not an integral multiple of the mol-wt of monomer.
- The chemical composition of monomer and polymer are different.
- It results in the formation of linear or cross linked polymers.

Example:

1. **Formation of Nylon-6,6:** Formed by the condensation of Hexamethylene diamine with adipic acid (Tetra methylene dicarboxylic acid)



2. **Formation of Polyester:** Formed by the condensation between ethylene glycol and Terephthalic acid



- Transparent
- Low maintenance cost
- Chemically inert
- Corrosion resistance
- Insect resistance
- Easy transportability
- Easy workability
- Impermeable to water
- High resistance to abrasion

Disadvantages:

- Low heat resistance, so combustible
- High softness
- Poor ductility
- Major pollutant not degraded by soil

Uses:

- For Making many house hold articles
- For making furniture
- For making electric goods

Types of Plastics: Plastics are classified in to two types

- Thermo plastics
- Thermo setting plastics.

THERMOPLASTICS

THERMO SETTING PLASTICS

- They are formed by addition reactions (some times formed by condensation r/n)
- They become softened on heating & hardened on cooling
- They are soft, weak and less brittle.
- Adjacent polymer chains are held together by weak Vanderwaal's forces



- They have either linear (o) branched structures
 - The chemical nature is not altered during heating & cooling.
 - They can be remoulded, reshaped & reused so they can be reclaimed from waste.
 - Low molecular weight thermoplastics are soluble in suitable organic solvents
- Ex: PE, PVS, PS, Nylon Teflon etc...

- Formed by condensation reactions.
- They become soft on initial heating and hard on cooling. On reheating they become harder.
- They are hard, strong and more brittle.
- Adjacent polymer chains are held together by strong covalent bonds.



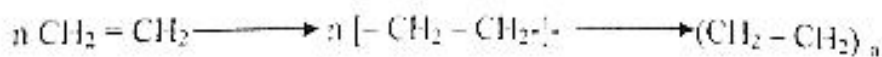
- Due to strong bonds, they exhibit cross-linked 3D-structure.
 - Chemical changes takes place during moulding process.
 - They cannot be remoulded and reused so they cannot be reclaimed from the waste.
 - Due to strong bonds and cross links, they are not soluble in almost all organic solvents.
- Ex: Bakelite, amino resins, poly ester resins, poly urethanes epoxy resins etc.....

Important plastics: Polythene, PVC, Polystyrene, Teflon, Nylon, Bakelite

1. Polythene:

Preparation:

Polythene is obtained by the addition polymerization of Ethylene under high pressure (1500 atm) and temperature range of 180-250°C and in the presence of oxygen.



There are two kinds of polythene

(a) Low Density Polyethylene (LDPE)

(b) High Density Polyethylene (HDPE)

HDPE is formed by using ionic catalyst like Zeigler - Natta catalyst or Chromium or Molybdenum oxides.

Properties:

- Polyethylene is a rigid, waxy, white, translucent material.
- It crystallizes very easily.

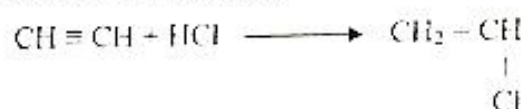
- It has high chemical resistance to acids, alkalis, and salt solutions at room temperature.
- LDPE melts at 110-125°C while HDPE melts at about 144-150°C.
- HDPE is completely linear in structure.

Uses:

- LDPE is used for packing purpose in the form of films, sheets, bags etc.
- HDPE is used in the manufacture of pipes, bottles, toys, industrial cloths, household articles, etc.

2. Poly Vinyl Chloride (PVC):

Preparation: Vinyl chloride is used as monomer for the manufacture of polyvinyl chloride. Vinyl chloride is prepared by reacting acetylene with hydrogen chloride at 100-150°C in the presence of metal salt catalyst.



PVC is prepared by heating a water-emulsion of vinyl chloride in presence of Benzoyl Peroxide in a autoclave under pressure



Properties:

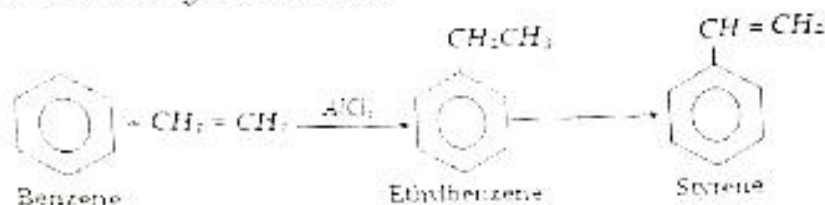
- PVC is colorless and odorless Powder.
- It is non-inflammable and chemically inert.
- It is soluble in chlorinated hydrocarbons like ethyl chloride, etc. and ketones.
- It has high resistance to light, inorganic acids, alkalis, and atmospheric oxygen.

Uses:

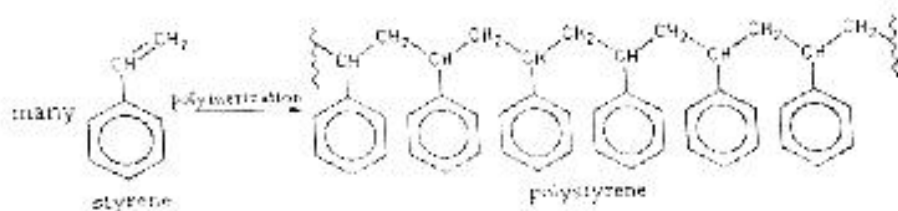
- Plasticized PVC is used for making table cloths, rain coats, coatings for electric wire and cables, toilet articles, radio, T.V components, pipes, coupling valves, etc.
- Un-plasticized PVC or rigid PVC is used for making refrigerator components, cycle and motor cycle mudguards, tubes, pipes, etc.

3. Polystyrene:

The monomer styrene is obtained from benzene and ethylene under pressure at 90°C, in the presence of a catalyst and the resulting ethyl benzene is dehydrogenated to styrene in presence of iron oxide or magnesium oxide.



Polystyrene is obtained by polymerization of styrene in the presence of Benzoyl peroxide catalyst.



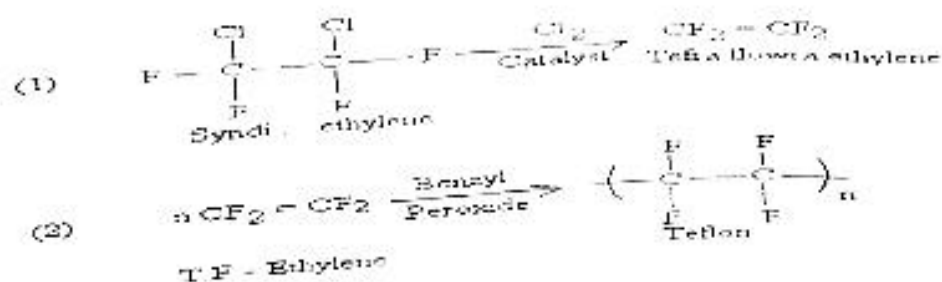
Properties:

- Polystyrene is light, transparent, and resistant to alkalis, oxidizing agents, etc.
- It is chemically inert.
- It is a good electrical insulator.

Uses: Polystyrene is used in the manufacture of moulded articles like toys, jars, bottles, radio and T.V parts, high frequency insulators, etc.

4. Teflon: (Fluon / Poly Tetra Fluoro Ethylene): $(-\text{CF}_2-\text{CF}_2)_n$

Teflon is obtained by the polymerization of water emulsion of Tetra fluoro ethylene in the presence of benzoyl peroxide as catalyst. The monomer Tetra fluoro ethylene is obtained by de-chlorination of syn-dichloro tetra fluoro ethane in presence of catalyst.



Preparatio

ii:

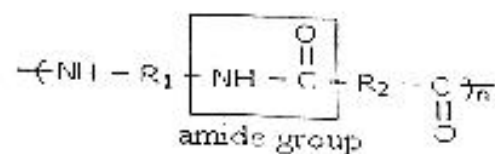
Properties:

- It is a thermo plastic resin.
- Having high melting point - 330°C
- High density - 2.1 to 2.3 gr / CC
- Highly resin - 93 to 98%
- High chemical resistance
- Good electrical and mechanical properties
- Not soluble in any solvent

Applications:

- For insulation of motors, generators, capacitors, transformers etc...
- Used in making stop cocks for hurettes, non-lubricating bearings, gaskets, pump parts etc...
- Used for coating on articles like bakery trays, frying pans etc.

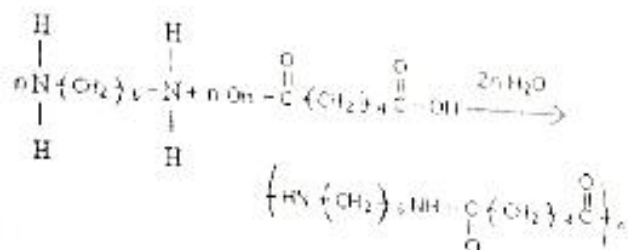
5. Nylon: (Poly Amid Resin)



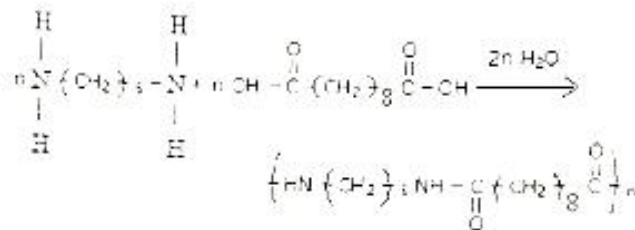
Nylon is a poly amide resin consists of amide group produced by condensation polymerization of diamine with di-acid. The Nylon has been named on the basis of the number of carbon atoms in the monomer chain.

Ex: Nylon 6:6, Nylon 6:10, Nylon 6, Nylon 11 etc. Where the first number indicates that the number of carbon atoms in diamine and the second number indicates that number of carbon atoms in diacid.

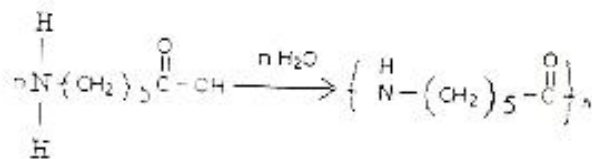
a) Nylon 6:6: Nylon 6:6 is produced by the condensation polymerization of hexa methylene di-amine with adipic acid.



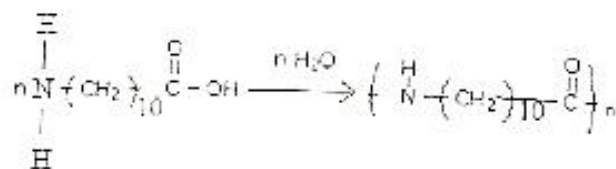
b) **Nylon 6:10**: Condensation of hexa methylene di amine with sebacic acid (octa methylene di acid) to form Nylon 6:10.



c) **Nylon 6**: It is produced by the self condensation of α -amino caproic acid (α - amino hexanoic acid).



d) **Nylon 11**: It is made by self - condensation of ω - amino undecanoic acid.



Properties:

- It show plastic and fibre property
- Insoluble in common solvent and soluble in pharmonic acid and phenol
- Posses high strength and high melting point (160 - 264°C)
- They absorb little moisture
- Possess resistance to environmental conditions and chemicals.
- They are good electrical insulators.

Applications:

- Nylon 6:6 is used as fiber for making socks, dresses, lady's hoses, carpets, under garments etc. (i.e., Used in textile industry)

- Nylon 6 and Nylon 11 are mainly used for moulding purposes of gears and bearings etc.
- They are also used for making filaments, films, Tire cords, bristles for tooth brushes etc.

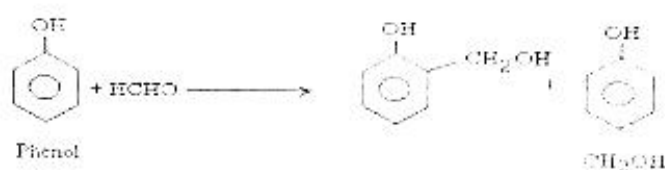
BAKELITE: (Phenol formaldehyde resin / phenolic resin / phenoplasts)

Bakelite is an important thermosetting resin named after the scientist Bakeland, who synthesized this resin in they year 1909.

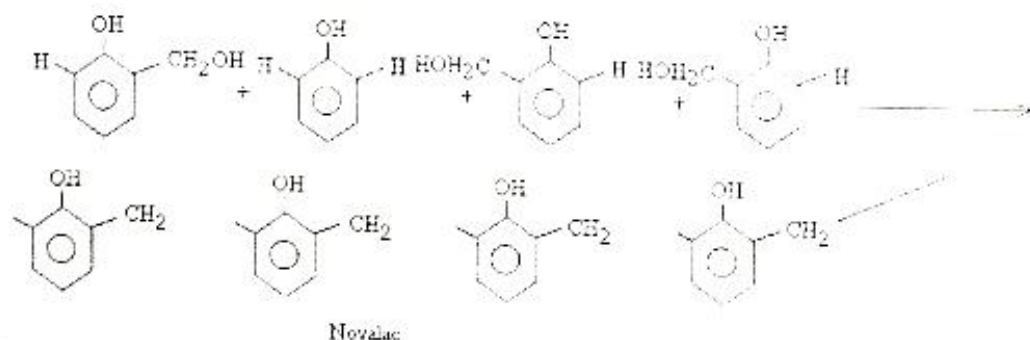
It is prepared by the step polymerization of phenol with formaldehyde in presence of an acid (or) Alkali as a catalyst.

This polymerization takes place in three steps:

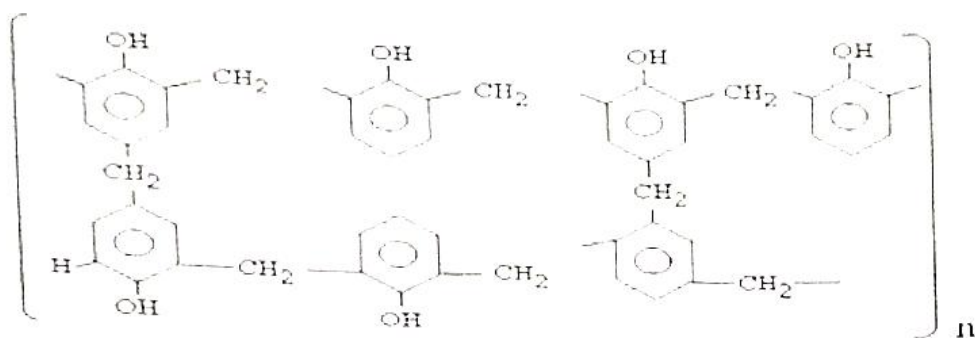
Step I: Phenol can condense with formaldehyde to produce O – hydroxy methyl phenol and P – hydroxy methyl phenol



Step II: condensation takes place b/n hydroxy methyl phenol and phenol to give linear polymer called Novalac



Step III: During moulding, hexa methylene tetraamine ((CH₂)₆ N₄) are added. it produces formaldehyde and ammonia. Formaldehyde converts the soluble and fusable Novalac in to a hard infusible and insoluble solid of cross - linked structure called Bakelite, whereas NH₃ Nuetralises the acid.



Properties:

- Bakelites are rigid, hard, scratch resistant, infusible, water resistant, solid substance.
- Resistant to acids, salts and most organic solvents but attacked by alkali due to the presence of hydroxyl groups
- Good electrical insulator

Applications:

- For making electric insulator parts like switches, plugs, holders, switch boards, heater etc.
- For making moulded article like telephone parts, cabinets for radio and T.V.
- Used in paints and varnishes
- as adhesives for grinding and wheels.
- In the product of ion exchange resin
- For making bearings used in propeller shops, for paper industry and Rolling mills.

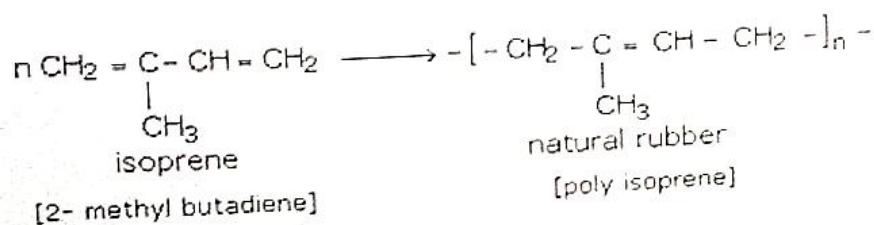
RUBBER (ELASTOMERS):

The polymers which pass the property of elasticity is called as rubber i.e., rubbers are high polymers, which have elastic properties in excess of 300%. The molecular weight of raw rubber is about 1,00,000 to 1,50,000 Daltons.

Most of the Indian production comes from Kerala state.

Natural rubber: It is a high polymer of cis - Isoprene, which are arranged in Cis - Configuration (functional groups are arranged on the same side).

Studied by X - ray diffraction. It having 2000 to 3000 monomer units.



Milk of rubber latex	Draw backs of crude rubber (or) raw rubber Crude rubber has following drawbacks.
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Natural rubber is mainly produced from the milk of the rubber tree “*hevea Brasiliensis*”. Small quantities of natural rubber are also produced from the milk of a shrub known as “guayule”.

Processing of natural rubber:

The milk of rubber tree is called latex. It is a colloidal emulsion consists a 25 – 45% of rubber and the remainder is protein and resinous materials

- The Latex was collected by cutting the bark of rubber trees.
- There after the Latex is diluted with water and filtered to eliminate dirt present in it. The Latex then coagulates by the addition of acetic acid (or) formic acid.
- The coagulated rubber is called as crude rubber. It is then made (or) rolled out in to sheets.
- The rubber sheets are dried under sunlight or mild heat and then subjected to further processing of rubber.

a) Crepe rubber: To the crude rubber, a small amount of sodium bi-sulphite is added to bleach the colour and passed into rollers which produce one mm or more thickness sheets which are dried in air about 40 to 50^oC. The dried thin sheet of rubber is known as crepe rubber.

b) Smoked rubber: The crepe rubber sheets are placed inside smoke rooms maintaining a temperature 40 to 50^oC for 4 days. The dried rubber sheets are called smoked rubber, which are sent to rubber factories for further processing.

Diluted & filtered to remove dirt	1. Soft at high temperature and brittle at low temp.
Coagulation $\text{CH}_3\text{COOH} / \text{HCOOH}$	2. It shows large water capacity
Crude rubber (coagulation)	3. Shows little durability
Passed in to roller	4. Shows high elasticity
Rolled sheet dried at $40^\circ - 50^\circ\text{C}$	5. Attacks easily by oxidizing agents
Crepe rubber $40^\circ - 50^\circ\text{C} / 4$ days	6. Swells in organic solvents
Smoked rubber	7. Possess tackiness
	8. Shows low tensile strength.

The draw backs can be crude are rectified by the process of vulcanization.

Vulcanization: This was discovered by "charles Good year" in 1839. The process to improve the quality and properties of rubber are compounded at 110°C to 140°C by addition of sulphur is called "Vulcanization".

The added sulphur combines at the double bonds of rubber chains and cross – links of the linear polymer chains, resulting in a three dimensional network structure. Thus the rubber loses plastic state and acquires elastic state. The stiffness of vulcanized rubber depends on the amount of the sulphur added.

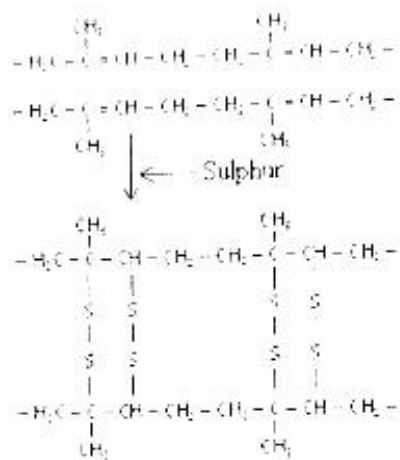
A flexible tyre rubber contains about 3 – 5% if sulphur whereas hard rubber contains 32% of sulphur.

Advantages of Vulcanization:

Vulcanization process brings excellent changes in the properties of rubber.

A Vulcanized rubber has

- (i) Low water absorption tendency
- (ii) Higher resistance to oxidation
- (iii) High stiffness
- (iv) Slight tackiness
- (v) Good durability
- (vi) Good resistant to changing temperature
- (vii) Resistance to swelling in organic solvents etc.



Compounding of rubber:

Compounding is a process by which mixing of raw rubber with d/f substances to impart special properties to an application. The following substances are mixed with raw rubber.

(i) **Plasticizers and softeners:** They give greater plasticity and flexibility and to reduce the brittleness of the products

Ex: Waxes, Stearic acid and Vegetable oils.

(ii) **Vulcanizers:** When rubber is heated with sulphur, its tensile strength, elasticity and resistance to swelling are increased. The remaining Vulcanizing agents are hydrogen peroxide (H_2O_2), Sulphur mono-chloride (S_2Cl_2), Benzyl chloride, Benzyl peroxide etc.

(iii) **Anti-Oxidants:** Natural rubber has tendency for Oxidation, This Oxidation is prevented by added Anti-Oxidants like phenyl naphthyl amine and phosphates.

(iv) **Accelerators:** These shortened the time required for Vulcanization and give toughness to rubber.

Ex: z-mercaptanol and Benzothisol.

(v) **Fillers:** They give rigidity and strength to the rubber

Ex: Carbon black, Zinc oxide and CaCO_3

(vi) **Colouring substances:** these substances provides pleasing colour to the rubber product.

Ex:

Titanium Oxide - White

Ferric Oxide - Red

Lead Chromate	-- Yellow
Antimony Oxide	- Crimson
Chromic Oxide	- Green

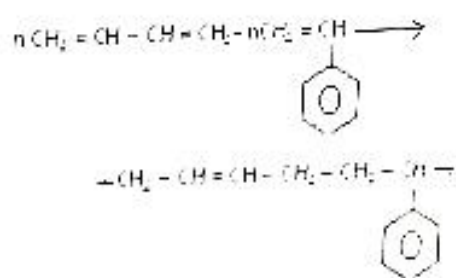
SYNTHETIC RUBBER: (ELASTOMERS):

The following rubbers are considered as synthetic rubbers.

1. Buna - S - Rubber
2. Buna - N - Rubber
3. Polyurethane rubber
4. Silicone rubber

1. Buna - S / Styrene / GR - S rubber:

Preparation: It is prepared by copolymerization of 1, 3 - butadiene and styrene.



Properties:

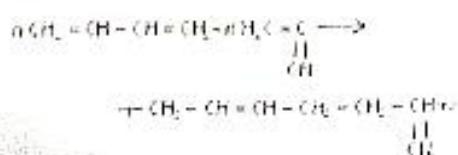
- a) It has high abrasion resistance and high load bearing capacity
- b) Easily oxidized in presence of ozone
- c) It swells in oils and organic solvents
- d) Its Vulcanization process is similar to natural rubber.

Applications / Uses:

1. It is mainly used for manufacture of tyres.
2. It is also used for floor tiles, shoe soles, gaskets, wire and cable insulations, tank linings etc.

2. Buna - N / Nitrile rubber: / GR - A rubber:

Preparation: It is formed by copolymerization of 1, 3 buta - diene and Acrylo Nitrile.



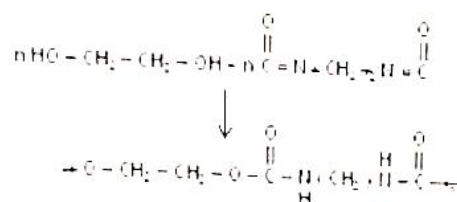
Properties:

- It can be vulcanized in same way as natural rubber.
- It has good oil resistance, heat resistance and abrasion resistance
- It is attacked by alkalis, due to presence of cynogroups.

Uses: making air craft components, conveyor belts, tank linings, gaskets, hoses, printing rollers, automobile parts etc.

3. Polyurethane / Isoocyanate rubber:

Preparation: It is obtained by polymerization of poly alcohol (ethylene glycol) with ethylene di isocyanide.



Properties:

- They are highly resistant to organic solvents – but are attacked by acids and alkalis
- They show good resistance to oxidation because of their saturation (single bond) character.
- Their foams are light, tough and resistant to heat, chemicals, weathering and abrasion

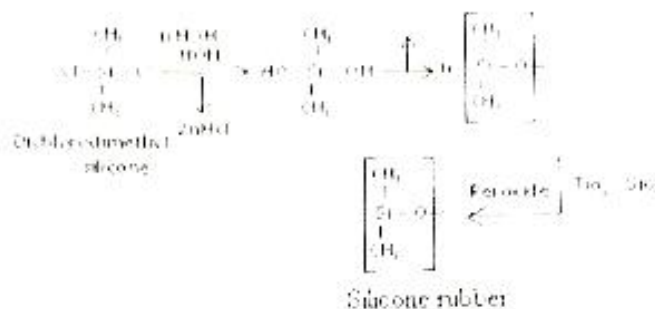
Uses:

They are used for surface coatings, manufacture of foams and spondex fibres.

4. Silicone rubber:

Preparation: It is formed by the polymerization of dihydroxy dimethyl silicon, which is formed by dichloro dimethyl silicon. This step requires water molecules and HCl elimination takes place.

Dihydroxy dimethyl silicon form an unstable silicon rubber by dehydration. Which yields silicon rubber in the presence of peroxide and in organic pillers like TiO_2 , SiO_2 etc..... by the polymerization.



Properties:

- It has good resistant to Oils, dilute acids, alkalis and sunlight.
- It retains rubber properties at elevated temperatures.
- It is also resistant to air and ozone at high temperature

Uses:

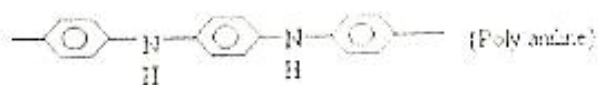
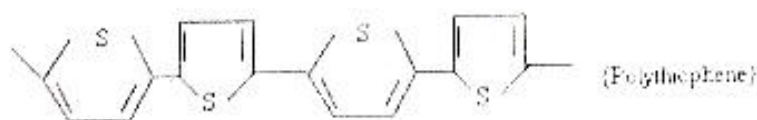
- It is mainly used in making lubricants, paints etc.
- For making artificial heart valves, transfusion tubings, for special boots to be used at low temperature.

CONDUCTING POLYMERS:

The polymers which conduct electricity are called as conducting polymers. Usually polymers are poor conductors of electricity. Hence, act as good electrical insulators due to non-availability of more electrons.

The conduction of the polymers may be due to unsaturation or by the addition of chemical ingredients such as copper, silver, etc. (conducting elements, metals).

Ex: Poly acetylene, poly aniline, polythiophene etc.





CLASSIFICATION:

Conducting polymers are classified in to two

1. Intrinsic
2. Extrinsic

1. Intrinsic: The conjugation of double bond present in the structure is responsible for conductance. Intrinsic again be classified in to two types.

(i) π electrons conducting polymers

(ii) Doped conducting polymers

(i) π electrons C.P: Conductance is due to positive (or) Negative charges present in the polymer back bone.

Ex: Poly acetylene

(ii) Doped C.P: Conductance is due to positive (or) Negative charges present in the polymer back bone.

Ex: Poly Naphthalene.

2. Extrinsic: An added ingredient is responsible for conductance. It is also are of two types.

(i) Conducting element filled polymer

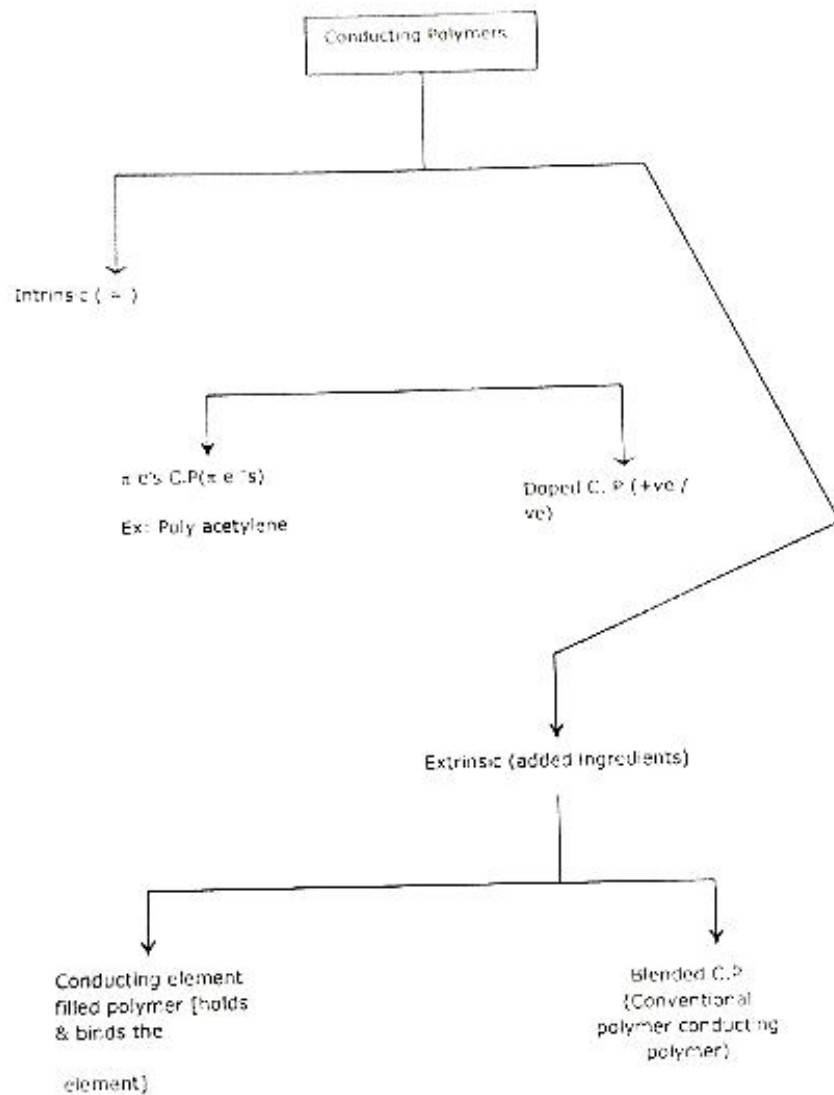
(ii) Blended polymer.

(i) Conducting element filled polymer:

A polymer holds (or) binds the conducting element such as metal oxide, metallic fibres and carbon black.

(ii) Blended C.P:

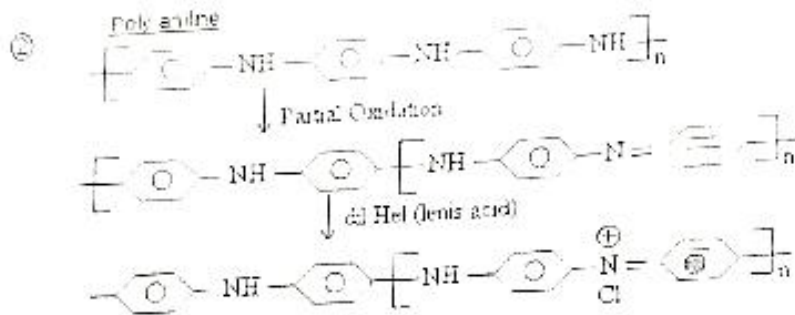
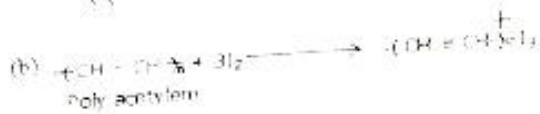
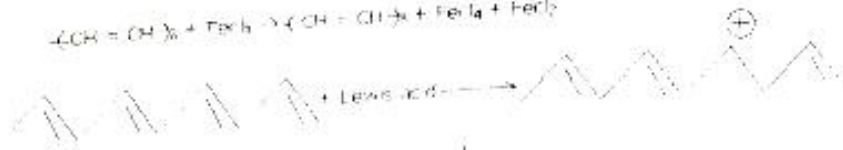
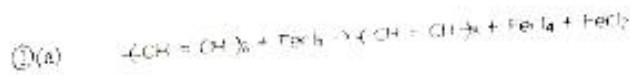
These are made by blending (mixing) a conventional polymer with a conducting polymer.



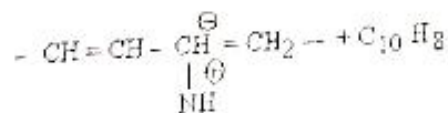
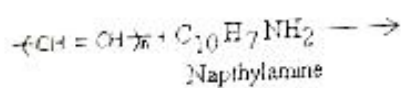
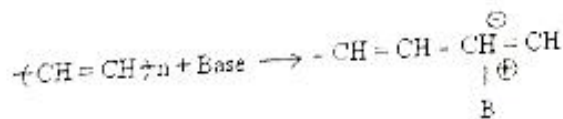
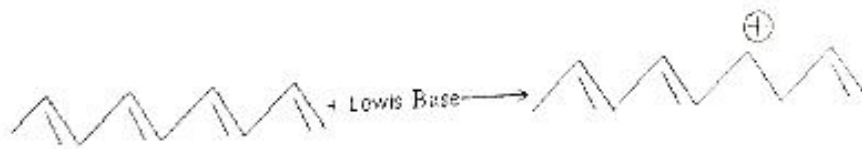
The conducting polymers having π 's in their back bone can easily be oxidized (or) reduced because they possess low ionization potential and high electron affinity. Hence their conductance can be increased by introducing a +ve / -ve charge on polymer back bone by oxidation (or) reduction. This synthetic process is called as Doping. Doping are of two types.

1. P – doping and 2. n – doping

1. P – doping: It is done by oxidation of conducting polymers like polyacetylene with Lewis acid (electron pair acceptor). (or) Iodine (or) Bromine vapors. By oxidation, a +ve charge is created on polymer back bone (oxidative doping)



2. n - doping: It is carried out by reduction process by the addition of lewis base (electron pair donor). There by negative sites are created on polymer back bone which is responsible for conductance. The used n - dopants are Lithium, Na, Ca, Tetra butyl ammonium etc.



Applications:

- Used in solar cells
- In photo voltaic devices
- In non - linear optical materials