

UNIT: 3

POLYMERIC MATERIALS

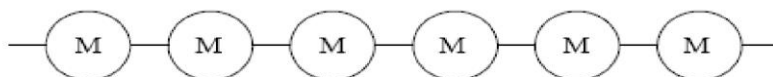
Polymers are made of two Greek words 'poly' means many and 'mers' means unit or part. A polymer is a high molecular weight compound formed by the joining of a large number of small units. Ex: Polystyrene and Polyethylene.

CLASSIFICATION OF POLYMERS

1. Based on Structure of Polymers: On the basis of the structures, polymers can be classified into three groups.

a. Linear chain polymer: In these polymers, monomers are joined together in a chain. They have high density and high melting point due to the well-packed structure.

Ex: polyethylene and nylon.

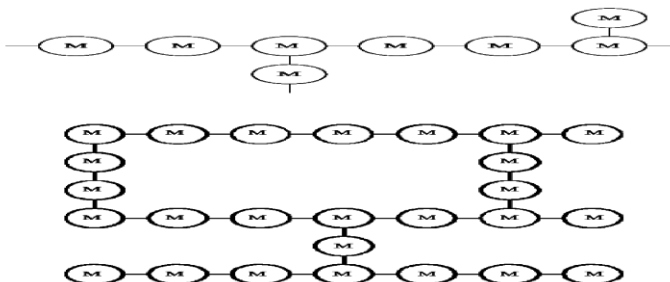


M = Monomer

b. Branched chain polymer: In these polymers, the chain of the polymer contains branches of monomers, which hinders the close packing of polymeric chains, and, hence, are less tightly packed in comparison to the linear chain polymers.

c. Crosslinked polymers: In the cross linked polymers, monomers are cross- linked together in all the three dimensions.

Eg: Bakelite.



2. Based on Types of Monomers: On the basis of monomers, polymers are classified into two groups:

a. Homo polymer: It is formed by the polymerization of one type of monomers.

$nA \rightarrow A_n$ (where A is a monomer)

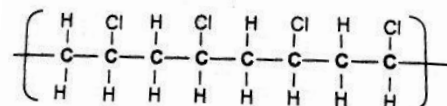
Ex: Polyethylene and PVC.

b. Copolymer: When two different types of monomers are joined in the same polymeric chain, the polymer is called a copolymer.

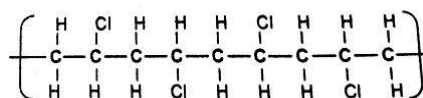
A—B—A—B—A—B—A—B—A—B—A—

3. Based on Tacticity (Configuration): There are three different types of polymers depending upon the relative geometric arrangement of the functional (side) groups.

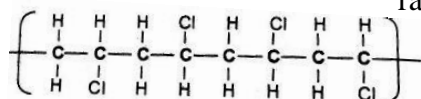
a. Isotactic polymer: All the functional groups are on the same side of the polymer chain.



b. Syndiotactic polymer: All the functional groups are arranged in regular on alternate sides of the polymeric chain.



c. Atactic polymer: All the functional groups are arranged randomly on both sides of the polymeric chain.

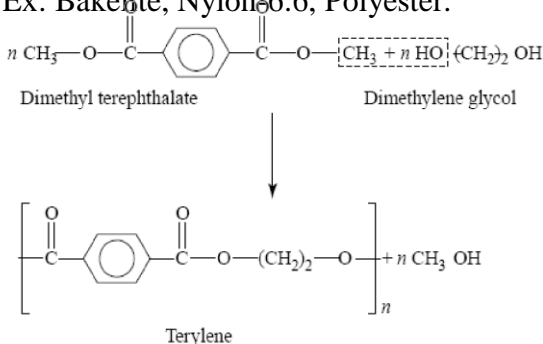
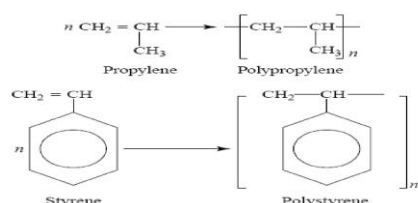


4. Based on Synthesis: On the basis of the synthesis, polymers are of two types:

1. Chain/Addition polymers
2. Step/Condensation polymers.

Differences between addition and condensation polymerization:

Chain/Addition Polymerization	Step/Condensation Polymerization
1. The functionality of the monomer is multiple bonds.	1. The functionality of the monomers is must be two or more than two.
2. It takes place without elimination of simpler molecule.	2. It takes place with elimination of simple molecule like H_2O , NH_3 , HCl .
3. Polymer has the same chemical composition as that of monomer.	3. Polymer has not same the chemical composition as that of monomer.
4. The molecular weight of the polymer is the exact multiple of the monomers.	4. The molecular weight of the polymer is not the exact multiple of the monomers.
5. The mechanism is carried out in three steps (Initiation, propagation, termination)	5. The mechanism is not carried out in three steps (Initiation, propagation, termination)
6. The mechanism is rapid	6. The mechanism is slow
7. This is exothermic (20KJ/Mole)	7. This is not exothermic (20KJ/Mole)
8. An initiator required to starts the reaction	8. An catalyst required to starts the reaction
9. Ex: Polyethylene, Polyvinyl chloride, teflon	9. Ex: Bakelite, Nylon-6:6, Polyester.



1. Mechanism of Addition Polymerization (Chain Growth Polymerization):

Addition or chain growth polymerization is the linking of molecules having multiple bonds. These unsaturated monomers have extra internal bonds which are able to break and link up with other monomers to form repeating chain. All the addition polymers are chain growth polymers, but few examples of condensation polymers are also present those mechanism proceed through chain growth polymerization.

a. Initiation step: This step involves the formation of a reactive particle.

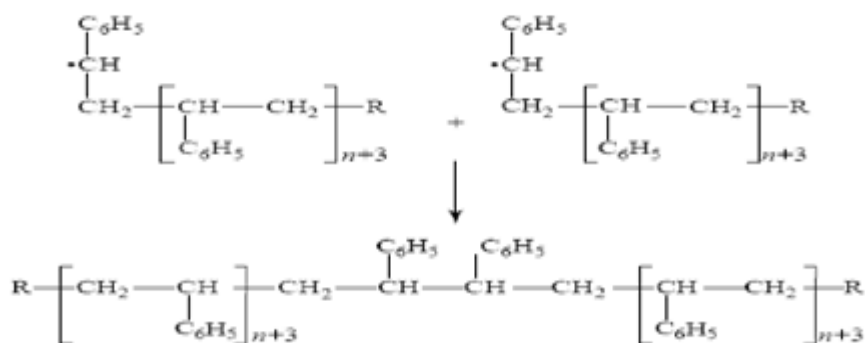
c. Termination step: In this step, the growth of the chain is finally terminated.

i. Free Radical Polymerization

Examples of initiators are benzoyl peroxide and azobis isobutyronitrile (AIBN). The polymerization of styrene, initiated by benzoyl peroxide, is a typical example of free radical polymerization.

$$\begin{array}{c}
 \text{O} \qquad \qquad \text{O} \\
 || \qquad \qquad || \\
 \text{C}_6\text{H}_5 - \text{C} - \text{O} - \text{O} - \text{C} - \text{C}_6\text{H}_5 \longrightarrow 2\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{O}\cdot \\
 \text{Benzoyl peroxide} \qquad \qquad \qquad \text{Benzoyloxy free radical} \\
 \downarrow \\
 2\text{C}_6\text{H}_5\cdot + 2\text{CO}_2 \\
 \text{phenyl free radical} \\
 \downarrow \\
 \text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2 + \text{C}_6\text{H}_5\cdot \longrightarrow \text{C}_6\text{H}_5 - \dot{\text{C}}\text{H} - \text{CH}_2 - \text{C}_6\text{H}_5 \\
 \text{Styrene} \qquad (\text{R}') \qquad \qquad \qquad (\text{new free radical}) \\
 (\text{C}_6\text{H}_5' = \text{R}')
 \end{array}$$
$$\begin{aligned}
 & \text{C}_6\text{H}_5-\dot{\text{C}}\text{H}-\text{CH}_2-\text{R} + \text{C}_6\text{H}_5 \text{ CH}=\text{CH}_2 \longrightarrow \text{C}_6\text{H}_5-\dot{\text{C}}\text{H}-\text{CH}_2-\overset{\text{CH}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}_2-\text{R} \\
 & \text{C}_6\text{H}_5-\dot{\text{C}}\text{H}-\text{CH}_2-\overset{\text{CH}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}_2-\text{R} + \text{C}_6\text{H}_5 \text{ CH}=\text{CH}_2 \longrightarrow \text{C}_6\text{H}_5-\dot{\text{C}}\text{H}-\text{CH}_2-\left[\overset{\text{CH}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}_2 \right]_2-\text{R} \\
 & \xrightarrow{\text{C}_6\text{H}_5 \text{ CH}=\text{CH}_2} \text{C}_6\text{H}_5-\dot{\text{C}}\text{H}-\text{CH}_2-\left[\overset{\text{CH}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}_2 \right]_3-\text{R} \\
 & \quad \quad \quad \downarrow n \text{ C}_6\text{H}_5 \text{ CH}=\text{CH}_2 \\
 & \text{C}_6\text{H}_5-\dot{\text{C}}\text{H}-\text{CH}_2-\left[\overset{\text{CH}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}_2 \right]_{n+3}-\text{R} \\
 & \quad \quad \quad \text{Macro free radical}
 \end{aligned}$$

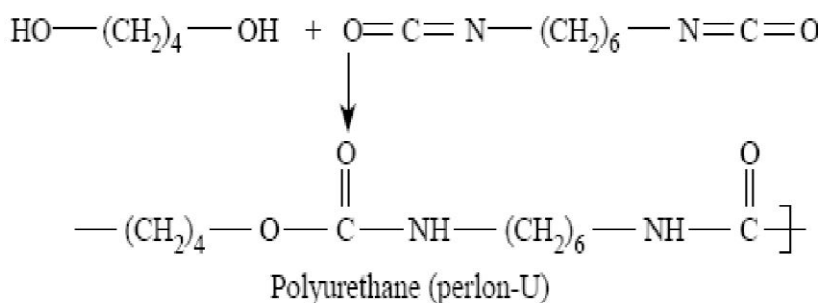
c. **Termination:** The macro-free radicals are deactivated by one of the following methods.



2. Condensation Polymerization or Step growth Polymerization

Step growth polymerization is defined as the polymerization in which polymers are formed by the stepwise reaction between functional groups of monomers. Step growth polymers increase in molecular weight at a very slow rate. Mostly condensation polymers are formed by step growth polymerization but few exceptions also exist.

Ex: Polymerization of polyurethane (addition polymer) proceeds through step growth mechanism.



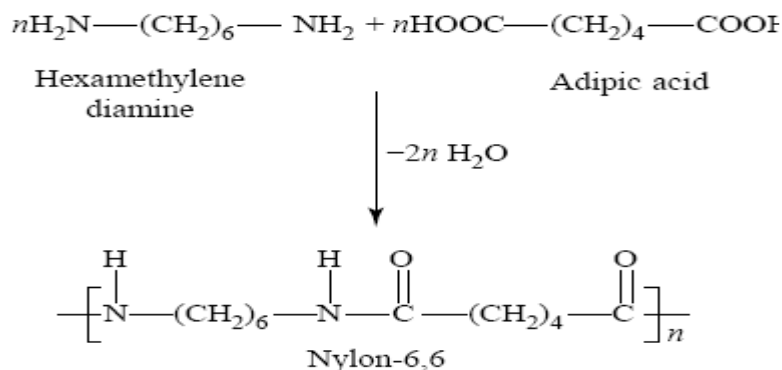
In the step growth polymerization, the monomer disappearance is very fast while in chain growth polymerization, it is slow. The functionality of the monomer must be two or more than two. The reactions are not exothermic. The molecular weight of the polymer is not the sum of the molecular weights of the monomers.

Fibers

Polyamides are polymers obtained by the condensation polymerization. The first number used in the suffix with the name of nylon represents the number of carbon atoms present in the amine monomer and the second number represents the number of the carbon atoms present in the acid monomer.

1. Nylon-6, 6:

It is obtained by the condensation of hexa methylene diamine and adipic acid. In 1:1 ratio.



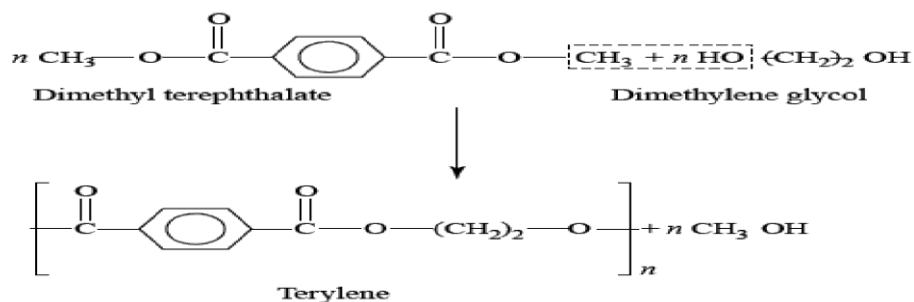
Properties:

1. Nylons show plastic and fiber property.
2. They possess good mechanical properties.
3. They are insoluble in organic solvents and soluble in formic acid and phenol.
4. They have strength and abrasive property.

Applications:

1. Nylon-6,6 is used as fibers for making socks, dresses, carpets and under garments.
2. Nylon-6, Nylon-11 are used for moulding purposes for gears and bearings.
3. Nylon is used in making filaments, films bristles and tooth brushes.

2. Dacron: Dacron or Terylene is a polyester fibre made from ethylene glycol and terephthalic acid.



Terephthalic acid required for the manufacture of Terylene is produced by the catalytic atmospheric oxidation of p-xylene.

Properties:

1. It is high tensile strength, high resistance to stretching, good resistance to degradation by chemical bleaches and it has abrasion resistance.
2. Due to cross linkage, it has high melting point (250°C).

Applications:

1. Decron is used in synthetic fiber.
2. It is applied in preparing sound recording tapes and photographic films.
3. It is used in textile industry with name polyester.
4. It is in preparing tapes, parachute cloth and wire insulators.

Plastics

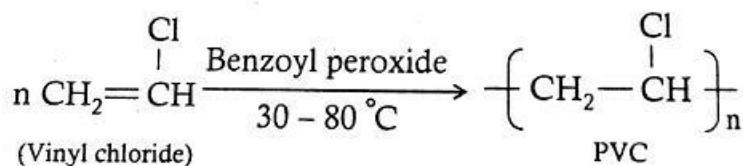
Polymers are classified based on thermal processing: On the basis of thermal processing behavior, polymers may be classified in two groups.

Differences between thermoplastic and thermosetting polymers:

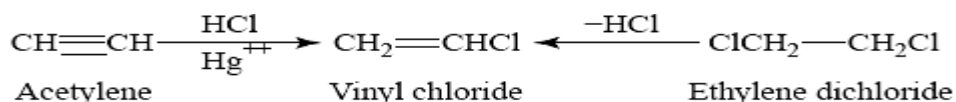
Thermoplastic polymers	Thermosetting polymers
1. On heating, they become soft. on cooling become hard.	1. They do not soften on heating and become hard.
2. These can be remoulded	2. They cannot be remoulded.
3. These have linear structures.	3. They have 3D crosslinked structures.
4. They are formed by addition polymerisation.	4. They are formed by Condensation polymerisation.
5. These can be reclaimed from waste.	5. These cannot be reclaimed from waste.
6. They are less brittle and are soluble in organic solvents.	6. They are more brittle and are insoluble in organic solvents.
Ex: PVC, Teflon and nylon.	Ex: Bakelite and Terylene.

Preparation, properties and Applications of some important polymers

1. Polyvinyl Chloride (PVC): It is obtained by heating vinyl chloride in an inert solvent in the presence of benzoyl peroxide.



The parent compound, vinyl chloride, may be prepared by the following two methods.

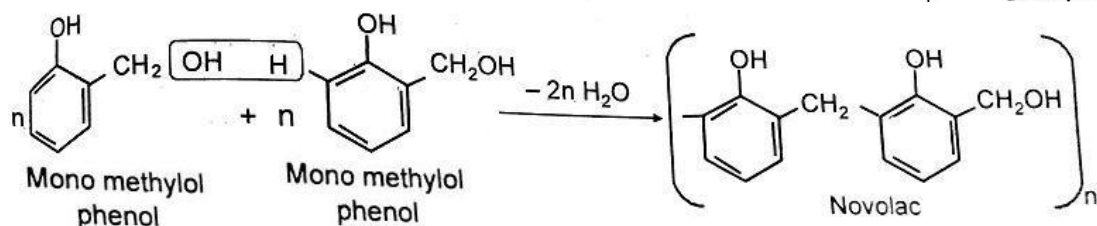
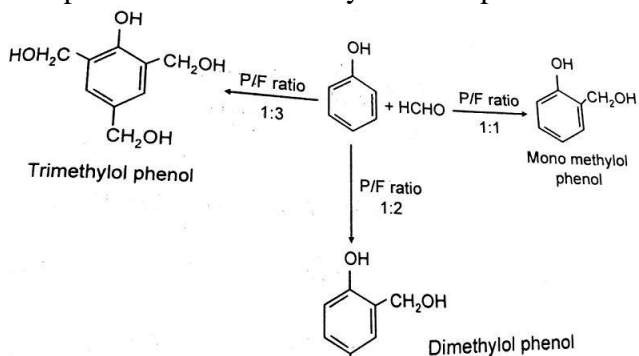
**Properties:**

1. It is colorless and odorless powder, Non-inflammable and chemically inert
- 2., It has high resistance to light, inorganic acids, alkalis and atmospheric oxygen.

Applications:

1. Making table cloths, rain coats, coating for electric wires, cables, toilet articles, and radio, TV Components.
2. PVC is also known as koroseal. Its plasticity can be increased by the addition of a plasticizer (ester of phthalic acid). It can be used in preparing refrigerator components, cycle mudguards, and tuber pipes.

2. Bakelite: These are the condensation product of phenol and formaldehyde in the presence of an acid or a base catalyst. Bakelite On further heating, in the presence of hexamethylene tetramine, Novolac produces 3D cross-linked networked thermosetting polymer which is known as bakelite. The hexamethylene tetramine decomposes into formaldehyde and ammonia, which is used as catalyst and HCHO, decreases the P/F ratio as 0.8.

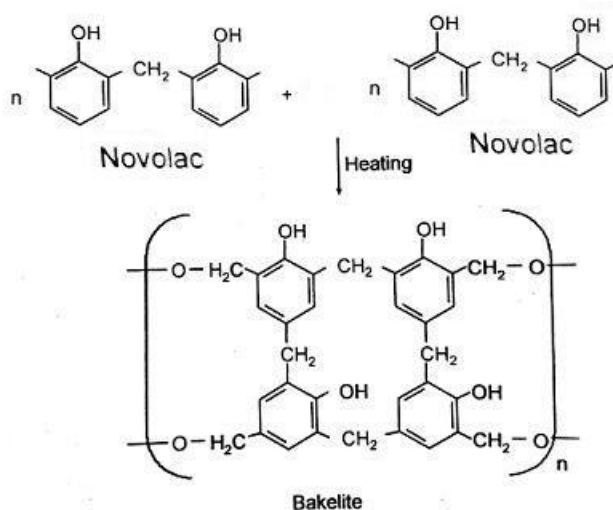


Properties:

1. Bakelite is rigid, hard, scratch resistant insoluble substance.
2. It is resistant to acids and salts, most organic solvents but attacked to alkali.
3. It possesses excellent insulating character.

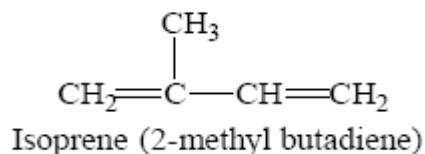
Applications:

1. It is used in preparing electrical equipments like switches, plugs, holders, switch boards and heater handles.
2. It is used in preparing paints, varnishes, resins, bearings and propeller shafts.
3. It is used in preparing telephone parts, radio and TV parts.



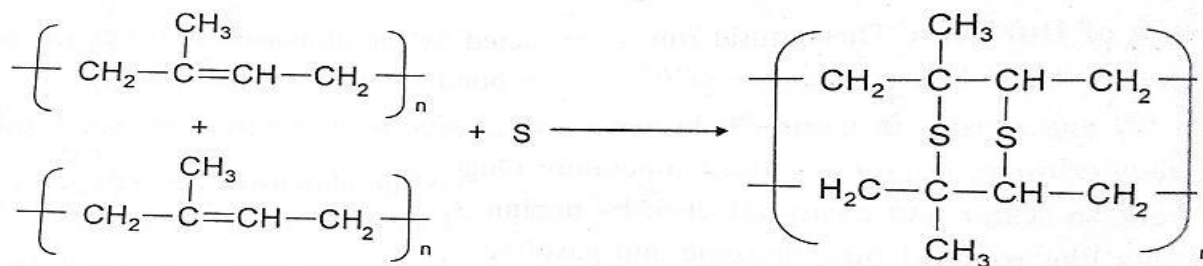
Rubbers

Natural rubber is obtained from nearly 500 different plants, but the main source from which the commercial natural rubber is obtained is the tree *Havea brasiliensis*. The rubber is obtained from latex (milky sap) collected from the cuts made in the bark of the tree. The obtained latex contains hydrocarbon with impurities such as fatty acids, proteins and resins in an emulsified form.



The latex is then coagulated with acetic acid or formic acid. The crude or raw rubber is composed of 95% hydrocarbons, 4% protein and 1% of resins. Destructive distillation of natural rubber gives isoprene as the main product.

Vulcanization: The raw or crude rubber is very little useful because it has very undesirable properties, such as low tensile strength, possesses elasticity only over a limited range of temperature and becomes softer, more plastic and sticky on heating and brittle on cooling. Its solubility in organic solvents (such as CHCl_3 , benzene and petrol) is of advantage for preparing rubber derivatives and adhesive solutions. In order to give more strength and more elasticity, natural rubber is heated with sulphur or sulphur compounds at 150°C temperature for a few hours. The sulphur combines chemically at double bonds of different rubber springs and a cross linked network is formed. The vulcanization can also be accomplished with certain peroxides, gamma radiation and several other organic compounds. The vulcanization process can be enhanced in the presence of certain organic substances known as accelerators. The common accelerators contain nitrogen, sulphur or both.



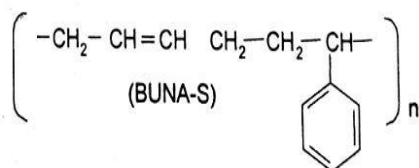
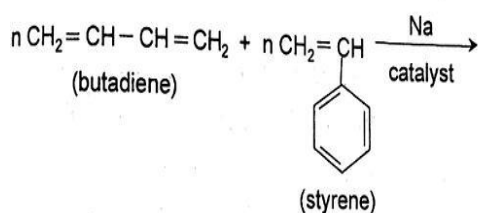
Advantages of Vulcanized Rubber:

1. Vulcanized rubber has good tensile strength.
2. The working temperature of vulcanized rubber is enhanced up to 100°C . Temperature range of raw rubber is $10-60^\circ\text{C}$.
3. The elasticity of vulcanized rubber is very low.
4. It has good resistance to organic solvents.

(Elastomers) Preparation, properties and uses of synthetic rubbers

1. Buna-S (Styrene Butadiene Rubber: SBR):

Buna is a copolymer of 75% butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) and 25% of styrene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$).



The polymerization is carried out at 50°C in the presence of peroxide catalyst. In Buna-S, 'Bu' stands for butadiene, 'na' for the symbol of sodium (Na), which is a polymerizing agent, and 'S' stands for styrene.

Buna-S is generally compounded with carbon black and vulcanized with

sulphur. It is used in manufacturing footwear components, motor tyres and other mechanical rubber goods.

Properties:

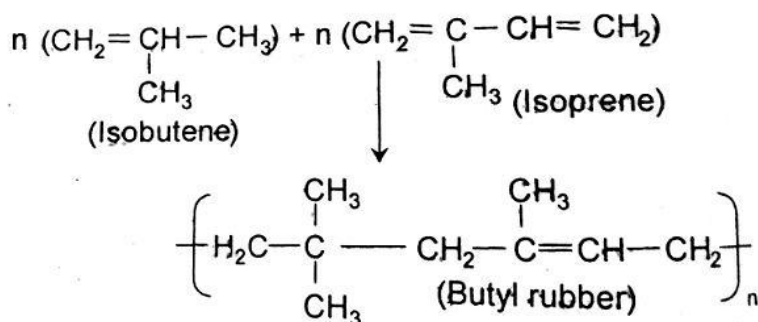
1. It is a strong and tough polymer
2. It is good electrical insulator and possesses excellent abrasion resistance.

Applications:

1. Styrene rubber is majorly used in manufacturing of tyres.
2. It is used in foot wear industry.
3. It is also used for making wires and cable insulators.

2. Butyl Rubber (Polyisobutylene):

It is a copolymer of 98% isobutene and 2% butadiene or isoprene. The butadiene is added to introduce the necessary ethylenic linkages for vulcanization. Butyl rubber is soluble in hydrocarbon solvents, such as benzene, but highly insoluble in polar solvents, such as alcohol and acetone. It has low degree of unsaturation and it is quite resistant to oxidation and chemicals.



Because of the above properties, it is used in manufacturing the inner tubes for automobile tyres. It is also used for insulation of high voltage wires and cables.

Properties:

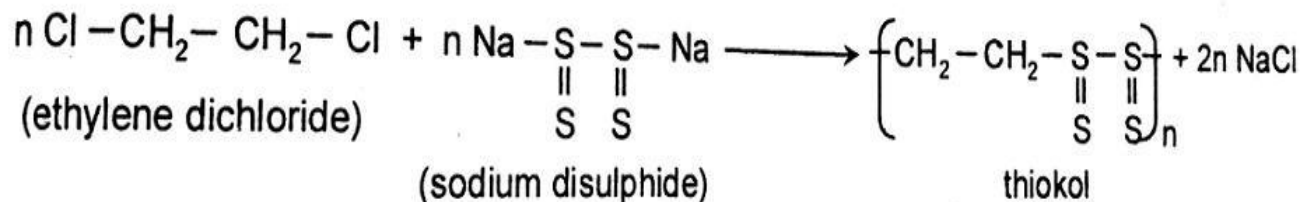
1. It is strong and tough synthetic rubber with low permeability to air and other gases.
2. It has good resistance to heat, abrasion.
3. It is good electrical insulator.
4. Though it is vulcanized with sulphur due to less number of double bonds it possesses low hardness.

Applications:

1. Butyl rubber is used for making cycle tyres and tubes
2. It is used for making automobile parts
3. it is used as an insulator for high voltage wires and cables.
4. It is used as linings of the tanks where chemicals are stored.

3. Thiokol (Polysulphide Rubber or GR-P):

Polysulphide rubbers are the condensation product of ethylene dichloride and sodium tetrasulphide.

**Properties:**

1. It is also resistant to the action of petrol lubricants and organic solvents
2. Thiokols outstanding resistance to swelling by organic solvents and impermeable to gases
3. Thiokols are vulcanized with metal oxides such as zinc oxide.
4. Thiokol has poor heat resistance and low tensile strength. The odour of thiokol is very bad. It tends to lose its shape under continuous pressure.

Applications:

1. Thiokol mixed with oxidizing agents is used as a fuel in rocket engine.
2. It is used to engine gaskets and other such products that come into contact with oil.
3. Thiokol's are used for hoses and tank lining for the handling and storage of oils and solvents.

Conducting polymers

The polymers which conduct electricity are called conducting polymers. The conductance is due to the presence of externally added ingredients or due to unsaturation.

Classification of conducting polymers: Two types:

1. Intrinsic conducting polymers 2. Extrinsic conducting polymers

1. Intrinsic conducting polymers

- i. Intrinsic polymers with conjugation
- ii. Doped conducting polymers

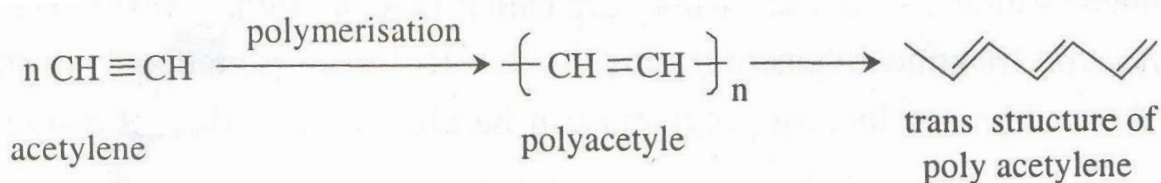
2. Extrinsic conducting polymers

- i. conductivity element
- ii. Blended conducting polymers

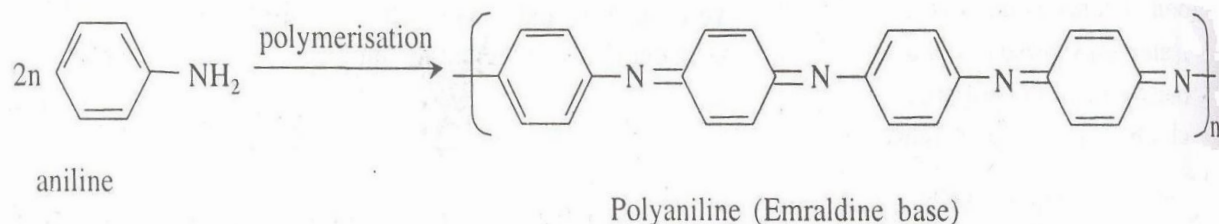
i. Intrinsic polymers with conjugation: The conductivity of such polymers having conjugated double bond is due to pi electrons in the back bone.

Ex: poly acetylene

a. Poly acetylene: Polymerization of acetylene over Ziegler natta catalyst get poly acetylene which is predominantly in cis form. By rising the temperature more stable form (Trans) is formed.

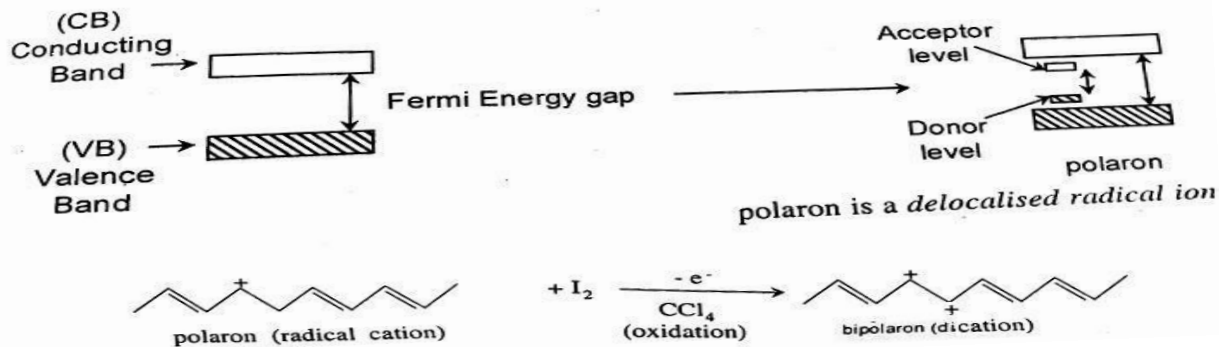


b. Poly aniline: Reaction of aniline with ammonium persulfate in aqueous HCl produces as a dark blue powder.



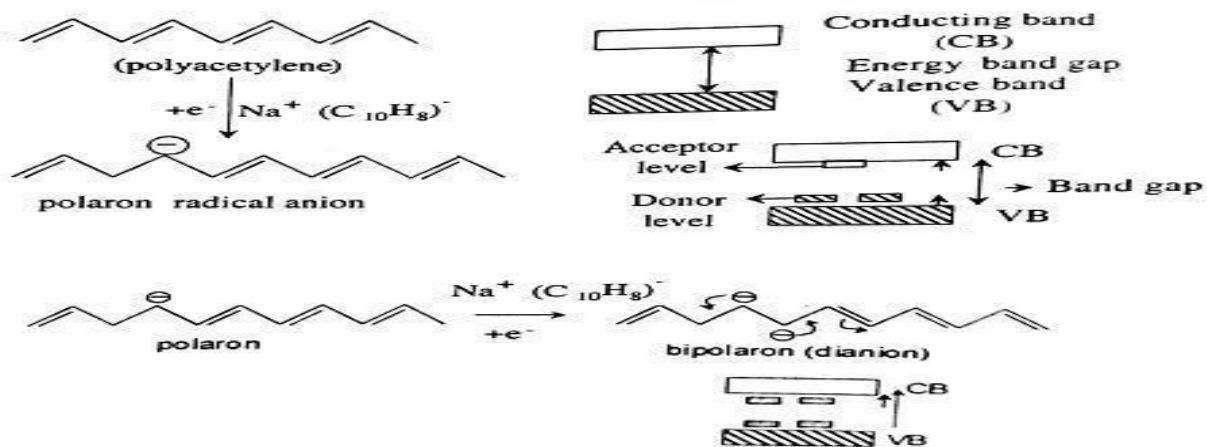
ii. Doped conducting polymers: The conductance of conducting polymers can be increased by introducing a positive or negative charge on polymer back bone by oxidation or reduction. This process is called doping. Doping happens in two ways.

- a. Creating a +ve site on polymer back bone-P-doping.
- b. Creating a -ve site on polymer back bone-P-doping

$$\text{Polyacetylene} + \text{I}_2 \xrightarrow[\text{(oxidation)}]{\text{CCl}_4, -e^-} \text{polaron (radical cation)}$$


removal of pi electrons from polymer back bone results in the formation of a radical ion called polaron (having a hole in between valency band and conducting band) Further oxidation of polaron results in two positive charge carries in each chain called bipolaron (which are mobile because of delocalization). These bipolarons are responsible for conductance when placed in electric field.

b. n-doping: n-doping is carried out by the addition of an electron to polymer back bone by using reducing agents like sodium naphthalide. Here the bipolaron contains electrons within the band gap and the bianion lowers its energy by segregating into two $-ve$ solitons in the energy level. The presence of holes in the band gap helps in the jumps of electrons from valency to conduction band. Hence conductivity increases.



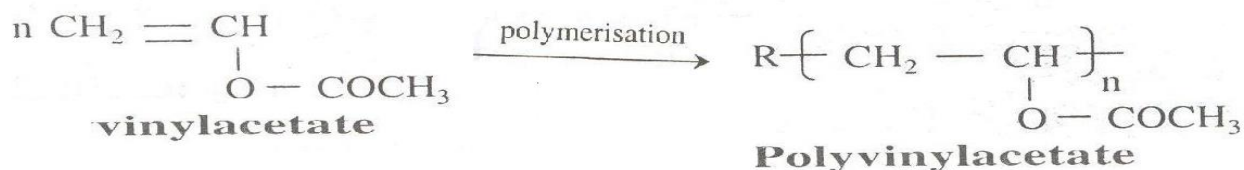
Applications:

1. Conducting polymers are used in rechargeable batteries
2. These are also used for making analytical sensors for pH, O₂, NO_x, SO₂, NH₃ and glucose.
3. These are used for making ion exchangers, these membranes with conducting polymers show selective permeability for ions and gases hence they are used for control release of drug.
4. These are used in making electron displays and optical fibers.
5. These are applied in photovoltaic devices.

Biodegradable polymers

These are degradable polymers in which degradation is caused by the action of naturally occurring microorganisms such as algae, fungi and bacteria. Biodegradable polymers are naturally occurring or may be synthesized chemically. Naturally occurring biodegradable polymers constitute polysaccharides, proteins, polyesters. Whereas synthetic biodegradable polymers constitute polyalkane esters, polyamide esters, polyvinyl esters and polylactic acid.

1. Poly vinyl acetate: The monomer of polyvinyl acetate is prepared by bubbling acetylene through hot glacial acetic acid in the presence of mercuric salts and sulfuric acid catalyst.

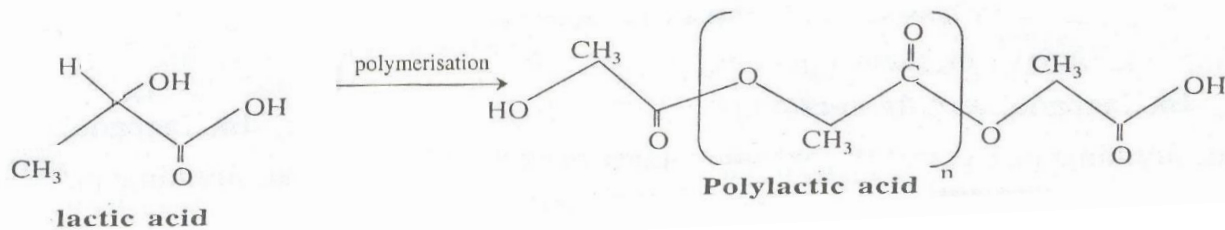


Applications:

1. It is used in the manufacture of polyvinyl alcohol
2. It is used in the production of water based emulsion paints and additives
3. It is used for finishing of textile and other fabrics and for bonding papers, textiles and leathers.

2. Polylactic acetate:

Lactic acid is produced by bacterial ferments of sugarcane or from the starch obtained from corn. Oligomerisation and catalyst dimersation of lactic acid results in the formation of lactide monomer which then undergoes polymerisation in the presence of stannous octate to give poly lactic acid.



Applications:

1. It is used in number of biomedical applications such as stents, drug delivery devices and dialysis media
2. It is used in the preparation of bio plastics for packing foods.

Essay questions

1. Write down different types of Polymerization and their mechanism?
2. Explain thermo plastics and thermosetting resins with examples?
3. Write down preparation, properties and applications of the following?
a) Polyethylene (b) PVC (c) Poly Styrene (d) Teflon (e) Bakelite & Nylon
4. Write down vulcanization of rubber and its advantage?
5. Write down properties and applications of Buna-S, Butyl rubber and Thiokol rubbers?
6. What is FRP and what are its applications?
7. Write down preparation properties and applications of Plastics?
8. What are the characteristics and uses of natural rubber?

Short questions

1. What is a polymer?
2. What are resins?
3. What is a natural rubber?
4. Why does rubber become stiff on stretching?
5. What is a thermosetting resin?
6. Name two natural polymers which are used as textile fibres.
7. Why nylons possess high melting point?
8. How is Teflon synthesized?
9. How are conducting polymers classified?
10. Why stabilizers are added to PVC?
11. What are biodegradable polymers?

Multiple choice questions

1. Polymerization in which two or more chemically different monomers takes part is called: [b]
(a) Homopolymers (b) Copolymer (c) Solids (d) Fabrics
2. A thermoplastic is formed by the phenomenon of [d]
(a) Chlorination (b) Condensation polymerization
(c) Nitration (d) Chain polymerization
3. Phenol-formaldehyde resin is commercially known as: [c]
(a) PVC (b) Elastomer (c) Bakelite (d) Nylon

4. Polymer commonly used for making fiber/cloth is: [c]
 (a) Rubber (b) PVC (c) Nylon (d) Bakelite
5. Bakelite is prepared by the condensation of: [b]
 (a) Benzene and formaldehyde (b) Phenol and formaldehyde
 (c) Phenol and acetaldehyde (d) Glycerol and phthalic acid
6. A high molecular weight material that can easily be molded in any desired shape is [b]
 (a) Graphite (b) Resin (c) Jelly (d) Grease
7. A plastic which can be softened on heating and hardened on cooling is called [b]
 (a) Thermo-elastic (b) Thermoplastic (c) Thermosetting (d) Thermite
8. Phenol-formaldehyde (bakelite) is an example of [c]
 (a) Thermo-elastic (b) Thermoplastic (c) Thermosetting (d) Thermite
9. Natural rubber is basically a polymer of [b]
 (a) Propylene (b) Isoprene (c) Ethylene (d) Propane
10. Which one of the following is an elastomer? [d]
 (a) PVC (b) Bakelite (c) Natural rubber (d) Nylon
11. The raw material used for the manufacture of polyester are [c]
 (a) Vinyl chloride (b) Urea + formaldehyde
 (c) Glycol + terephthalic acid (d) Phenol + formaldehyde
12. One of the important uses of bakelite is for making: [b]
 (a) Cables (b) Electrical switches (c) Cloth (d) Hose pipe
13. The fiber obtained by the condensation of hexamethylenediamine and adipic acid is [b]
 (a) Dacron (b) Nylon (c) Rayon (d) Terylene
14. Nylon is a [c]
 (a) A polythene derivative (b) A polyester fiber
 (c) A polyimide fiber (d) none of these
15. Bakelite is a copolymer of [b]
 (a) Urea and formaldehyde (b) Phenol and formaldehyde
 (c) Urea and formaldehyde (d) Urea and phenol

Fill in the blanks

1. Latex is the dispersion of isoprene molecules.
2. LDPE has less meltinor specific gravity than HDPE.
3. An example of thermosetting homo-polymer is nylon-6.
4. Stereo-specific polymers are obtained by coordination chain polymerization.
5. The plastic used for making optical lenses is PMMA.
6. Buna-S is a co-polymer of butadiene & styrene.
7. Caprolactum is a monomer of nylon-6.
8. Polyacetylene is a conducting polymer.
9. Nylon-6 is a polyamide.

-----The End-----