

UNIT-I

POLYMER CHEMISTRY

Introduction to polymers, functionality of monomers, chain growth and step growth polymerization, coordination polymerization, with specific examples and mechanisms of polymer formation

Plastics –Thermo and Thermosetting plastics, preparation, properties, and applications of –
PVC, Teflon, Bakelite, Nylon-6,6, carbon fibres.

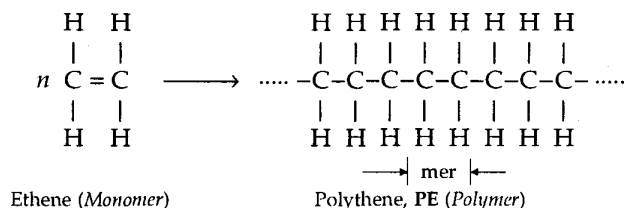
Elastomers–Buna-S, Buna-N–preparation, properties and applications

Conducting polymers – polyacetylene, polyaniline, – mechanism of conduction and applications Bio-Degradable polymers - Poly Glycolic Acid (PGA), Polyl Lactic Acid (PLA)

Introduction:

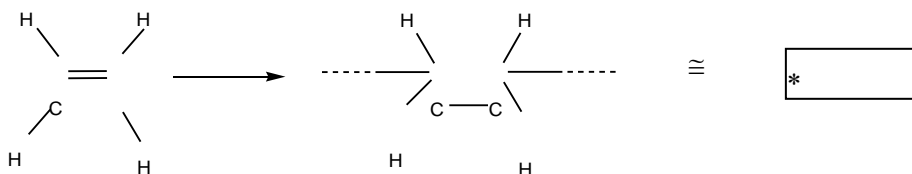
Polymers are macro molecules, built-up by the linking together of a large number of small molecules by covalent bonds. These small molecules are called monomers. The process of combining these monomers to form a macromolecule is called polymerization. The repeat units in a polymer chain are linked through strong covalent bonds.

Example: Polythene is a polymer formed by linking together of a large number of ethylene (C_2H_4) molecules.

**FUNCTIONALITY OF MONOMERS**

The number of reacting sites present in the monomer is known as functionality. A monomer having two reactive sites is called bi-functional, three reactive sites called tri-functional and more reactive sites called poly functional. A monomer should have at least bi-functionality to undergo polymerization reaction.

Example: An olefin like ethylene is considered bi-functional. It has two reactive sites, i.e. when the double bond is broken; two single bonds become available for undergoing polymerization.



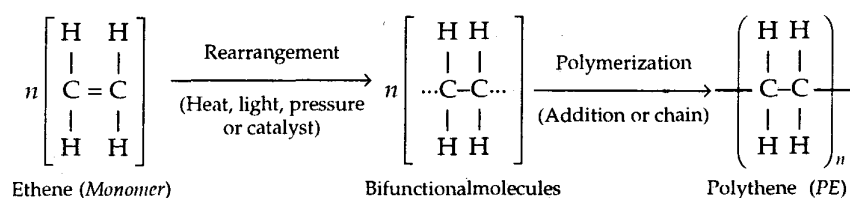
Depending on functionality of monomer, linear, branched or cross-linked polymers can be formed. A bifunctional monomer leads to formation of linear polymers. If a small amount of trifunctional monomer is added to bifunctional monomers, then it leads to formation of branched structure and with a greater number of trifunctional monomers cross linked polymers are also formed.

S. No	Name of The Monomer	Molecular Formula	Functionality
1	Vinyl chloride	$CH_2=CHCl$	02
2	Ethylene glycol	$HO-CH_2-CH_2-OH$	02
3	Phenol	C_6H_5OH	03

4	Adipic acid	HOOC-(CH ₂) ₄ -COOH	02
5	Ethylene	H ₂ C=CH ₂	02

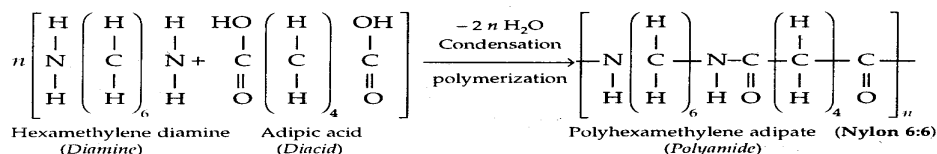
Chain growth or Addition polymerization: The fundamental chemical process by which the low molecular weight molecules are converted into high molecular weight molecule, without the elimination any small molecules like water, ammonia, ethyl alcohol etc. is called the addition polymerization. A chain polymerization is a reaction that yields a polymer product which is the exact multiple of monomers.

Ex: Polyethylene

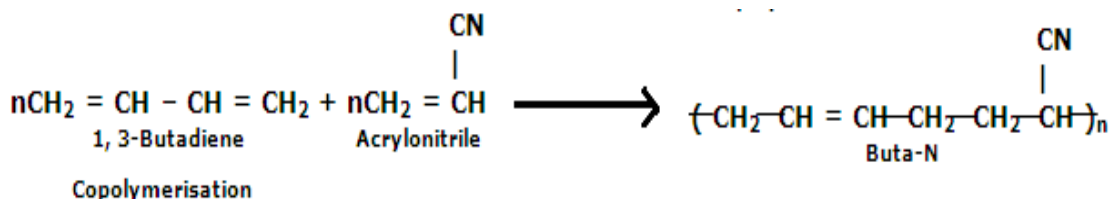


Step growth or Condensation polymerization: The fundamental chemical process by which the low molecular weight molecules are converted into high molecular weight molecule with the elimination any small molecules like water, ammonia; ethyl alcohol etc. is called condensation or step growth polymerization.

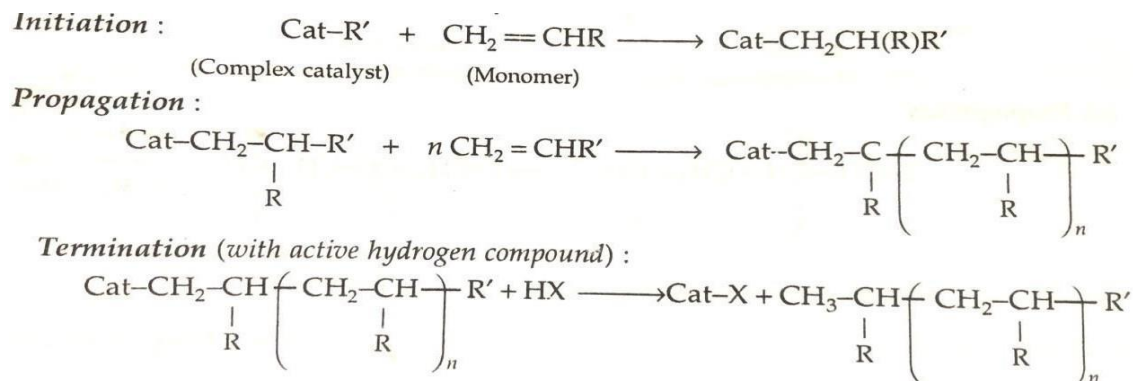
Example: Nylon 6:6



Copolymerization: The processes of simultaneous addition polymerization of two or more different types of olefinic monomers are called copolymerization. Ex: Nitrile Rubber or Buna-N Rubber: It is prepared by copolymerization of butadiene and Acrylonitrile



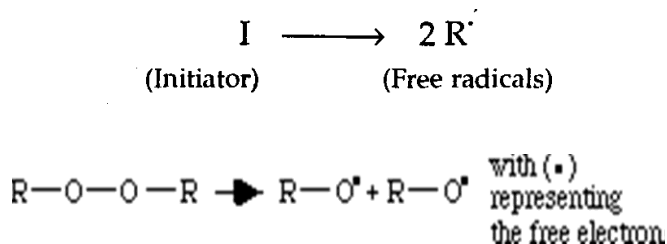
Coordination Polymerization or Ziegler-Natta Polymerization: Ziegler and Natta discovered that in the presence of combination of transition metal halide like TiCl_4 , TiCl_3 , ZrBr_3 , TiCl_2 , halides of V, Zr, Cr, Mo with an organo metallic compounds like Triethyl aluminium, Trimethyl aluminum, stereo specific polymers can be carried out. The mechanism of coordination polymerization may be illustrated as



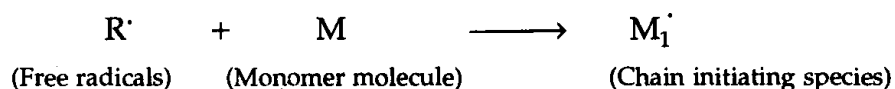
MECHANISM OF ADDITION POLYMERIZATION:

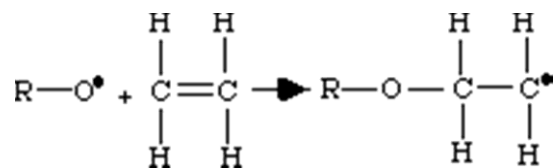
Free radical mechanism: In this mechanism, the reaction is initiated by a free radical resulting in the formation of a free radical as intermediate, thus known as free radical mechanism. The reaction can be terminated by a free radical. We can summarize that in this reaction, Initiator is Free radical, Intermediate is Free radical, and Inhibitor (Terminator) is Free radical. The mechanism can be shown as:

Chain Initiation: It is considered to involve two reactions. The first is the production of free R usually, by the hemolytic dissociation of an initiator (or catalyst) to yield a pair of radicals R

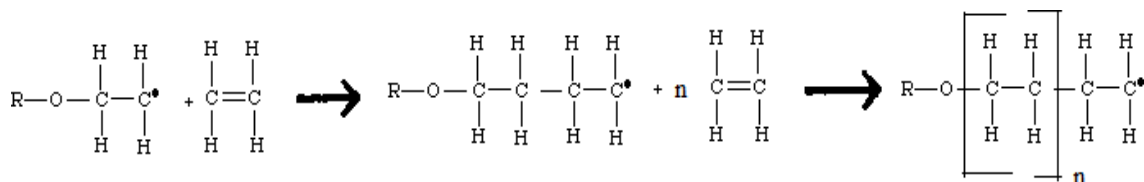
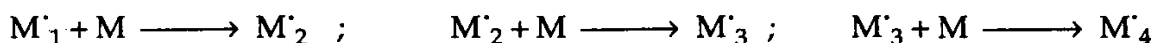


The second part of initiation involves the addition of this radical to the first monomer molecule (M) to produce the chain initiating species, M_1'



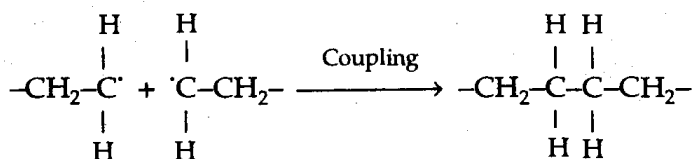


Chain Propagation: consists of the growth of M by successive additions of large numbers (hundreds, and perhaps, thousands) of monomer molecules according to equations:

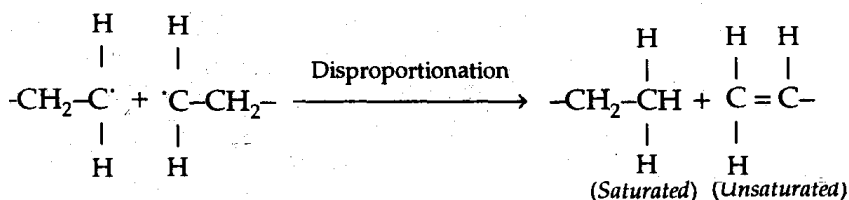


Chain Termination: At some point, the propagating polymer chain stops growing and terminates.

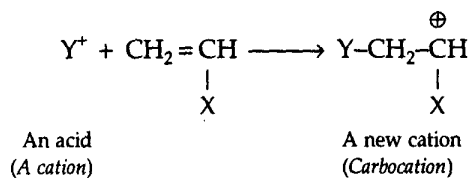
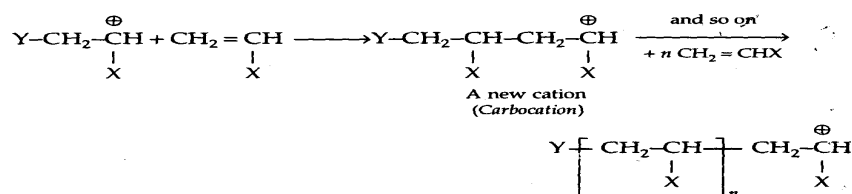
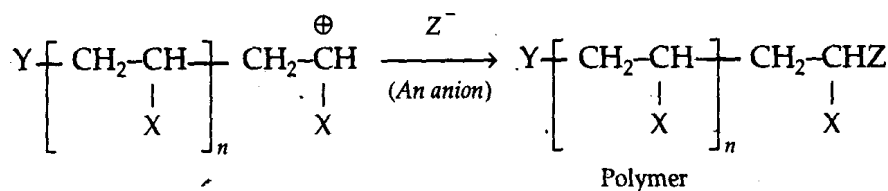
- By coupling or combination



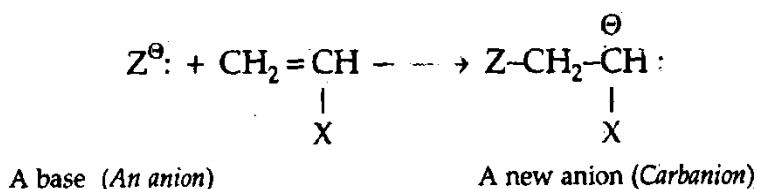
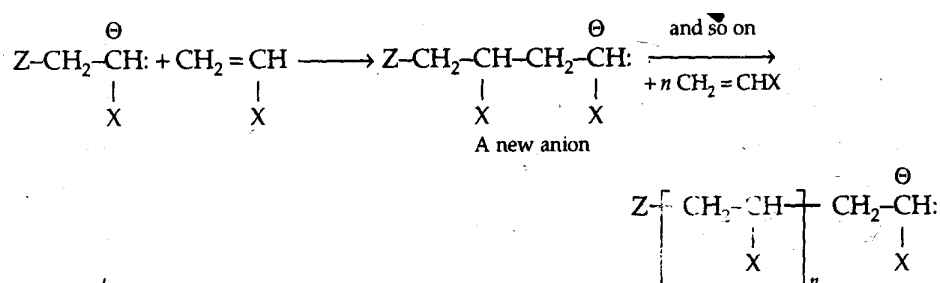
- By disproportionation

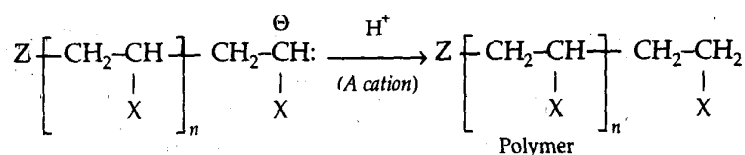


Cationic Mechanism: In this mechanism, the reaction is initiated by an electrophile resulting in the formation of a carbocation as intermediate, thus known as cationic mechanism. The reaction can be terminated by a nucleophile. We can summarize that in this reaction, Initiator is Electrophile, Intermediate is Carbocation; Inhibitor (Terminator) is Nucleophile. The mechanism can be shown as

Chain Initiation:**Chain Propagation:****Chain Termination:**

Anionic Mechanism: In this mechanism, the reaction is initiated by a nucleophile resulting in the formation of a carbanion as intermediate, thus known as anionic mechanism. The reaction can be terminated by an electrophile. We can summarize that in this reaction, Initiator is Nucleophile, Intermediate is Carbanion; Inhibitor (Terminator) is Electrophile. The mechanism can be shown as

Chain Initiation:**Chain Propagation:**

Chain Termination:**PLASTICS**

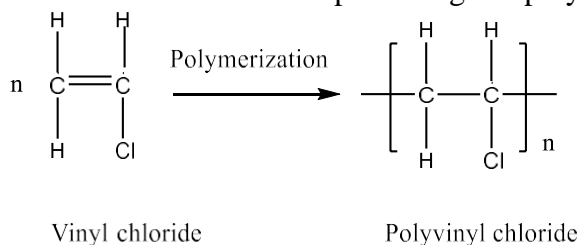
- Plastics are basically polymers.
- The word plastic is derived from ‘plastikos’ meaning capable of being shaped or moulded.
- It refers to their malleable nature which allows them to be cast, pressed or extruded into a variety of shapes – such as films, fibres, plates, tubes, bottles, boxes and much more.
- A plastic material should have sufficient rigidity, dimensional stability and mechanical stability (strength) at RT to serve as a useful article, gadget or structural part.

Types of plastics/resins:

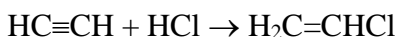
S.No.	Thermoplastics	Thermosettings
1	These resins become soft on heating and rigid on cooling	These resins are moulded by heating. Once they are solidified, they cannot be softened by heating again.
2	They are formed by addition (chain) polymerization only	They are formed by condensation (step) polymerization
3	They are linear polymers with negligible cross-links	They have three-dimensional structure
4	Heating and cooling does not alter the chemical nature of these resins, changes involved are purely physical in nature	These resins are permanent setting resins
5	They can be reshaped	They can't be reshaped
6	They can be reclaimed from waste	They can't be reclaimed from waste
7	These resins are usually soluble in suitable organic solvents. Ex: Polyethylene, Poly vinyl chloride etc.	Due to strong bonds and crosslinks, they are insoluble in all organic solvents. Ex: Bakelite, Nylon etc.

Polyvinyl chloride (PVC)

Preparation: Heating a water emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide (or) hydrogen peroxide in an autoclave under pressure gives poly vinyl chloride.



Vinyl chloride itself is prepared by treating acetylene at 1 to 1.5 atm. with hydrogen chloride at 60-80 °C in presence of metal oxide as catalyst

*Properties:*

- (i) PVC is colorless, odorless, non-flammable and chemically inert powder
- (ii) Resistant to light, atmospheric oxygen
- (iii) Resistant to acids and alkalis, but soluble in hot chlorinated hydrocarbons High Softening point (148 °C)
- (iv) Greater stiffness and rigidity compared to polyethylene, but is brittle

PVC is of two types

1. Rigid PVC (or) Unplasticized PVC
2. Plasticized PVC: PVC is treated with the plasticizers like tri cresyl phosphate, and then it is called as plasticized PVC

Applications:

Unplasticized PVC applications:

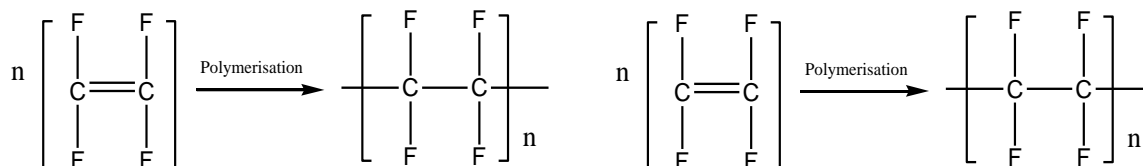
- It is used for making sheets, which are employed for water carrying pipes, chairs/tables, window frames, light-fittings, safety helmets.
- Refrigerator components.
- Cycle and motor cycle mud guards

Plasticized PVC applications:

- Used for making continuous sheets Ex: packing rain coats, table cloths & curtains; rain proof foot wear
- Electrical insulation like covering of electrical cables.
- Chemical containers, conveyor belts etc.

TEFLON (or) FLUON (or) Poly tetra fluoro ethylene (PTFE) polymer

Preparation: It is obtained by polymerization of water- emulsion of tetra fluoro ethylene, under pressure in presence of benzyl peroxide as catalyst.

**Properties:**

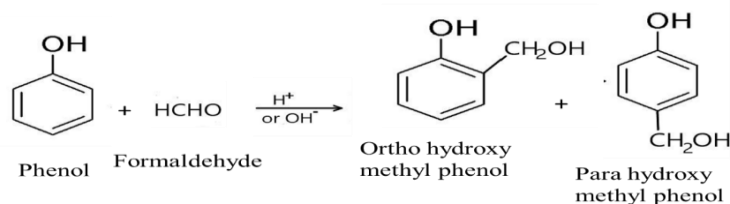
1. Due to high electro negative fluorine atoms and regular configuration of the molecule results in very strong attractive forces between the chains.
2. It possess extreme tough ness
3. High softening point (about 350°C)
4. Chemical resistance is more
5. In hot alkali metal and hot fluorine, the Teflon resistance is low.
6. High density
7. Very low coefficient of friction
8. Good electrical and mechanical properties.

Applications:

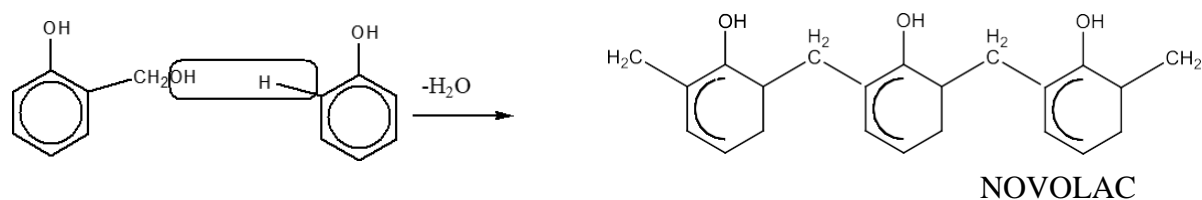
1. Insulating material (Floor tiles, transformers cables, wires etc.)
2. Making gaskets
3. Tank linings
4. Chemical carrying pipes
5. Making non sticking stop corks (For burette)

Bakelite or Phenol-formaldehyde resin:

Preparation: It is prepared by the condensing phenol with formaldehyde in presence of acid or alkali as catalyst. Phenol and formaldehyde react to form methylol derivatives which act as monomers for subsequent polymerization.

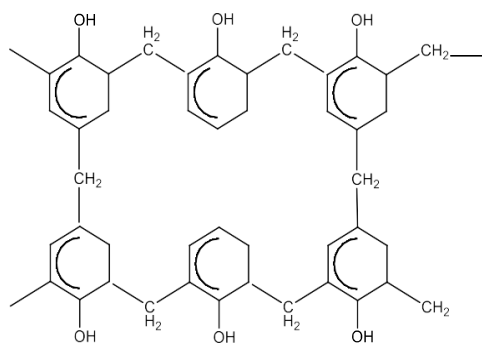


The orthohydroxy methyl phenol reacts with phenol to form linear NOVALAC polymer. The formed novalac polymer is fusible and soluble in organic solvents.

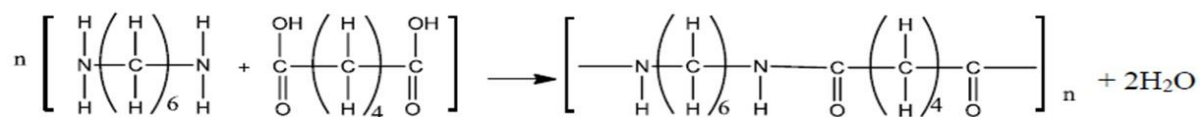


When NOVOLAC is treated with hexa methylene tetra amine (HMTA), the soluble and fusible novalac gets converted into pink coloured, hard, infusible and insoluble solid cross-linked polymer (Bakelite) with the following structure.

BAKELITE

**Nylon 6, 6**

Preparation: Nylon-6,6 is prepared by condensation polymerization of hexamethylene diamine and adipic acid in 1:1 ratio at high temperature and pressure.



Hexamethyle diamine

adipic acid

Nyloln 6, 6

Properties

- (i) It has high crystallinity (due to hydrogen bonds)
- (ii) It has high tensile strength & melting point ($>500^\circ\text{C}$)

- (iii) These are light, tough & abrasion resistant
- (iv) It has heat resistance (sterilizable) & low coefficient of friction
- (v) They absorb little moisture and are thus drip dry in nature

Applications:

- Used as fibres in making socks, under garments, dresses (swim wear & Jackets)
- Used in ropes, parachutes, fishing nets
- Tooth brushes, bristles & carpets, luggage & conveyer belts
- Gears, Nylon coated ball bearings/roller bearings & Bushes
- Electrical ware (as insulator) & reinforcing fibre in FRP
- These fibres easily blend with wool to increase the strength and abrasion resistance of wool

Properties:

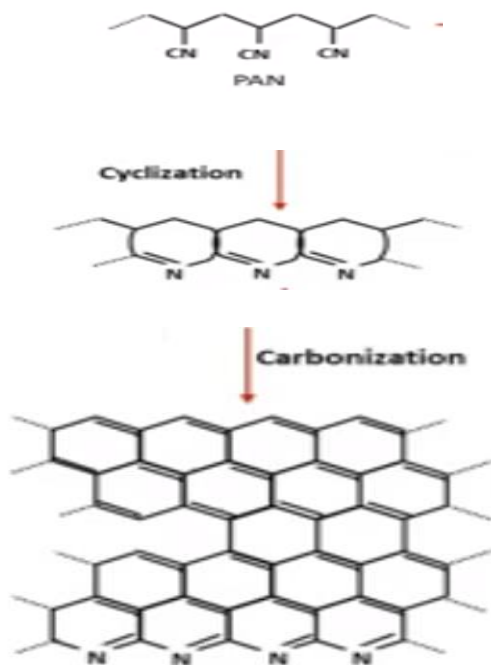
- (i) Phenolic resins are hard, rigid and strong materials
- (ii) Excellent chemical, heat and moisture resistance
- (iii) It is attacked by alkalis, because of free hydroxyl groups present in the structure.

Applications:

- Making electrical insulator parts like domestic plugs and switches.
- Making moulding articles like Radio and T.V. Cabinets
- In paints and varnishes (scratch resistant) & as an anion exchanger (water purification).

Carbon Fibers

Preparation: About 90 percent of carbon fibres are made by using the polyacrylonitrile (PAN) process. The remaining 10 percent are made using either the rayon or petroleum pitch process.



Properties:

1. Carbon fibers have high stiffness
2. They are rigid
3. They have high abrasion resistance
4. Carbon fibers have high tensile strength
5. Carbon fibers are fire proof
6. They can withstand even at high heat
7. They do not react with chemicals

Applications:

1. These are used to prepare aerospace components like wings, panels, engine blades etc.
2. These are used to prepare car body parts, wheel rims and disc brakes
3. Used to prepare bicycle frames, surfing boards golf clubs
4. Used in X-ray and MRI scanning equipment's
5. Used in making wind mill rotor blades and solar panels
6. Used in concrete reinforcement.

ELASTOMERS

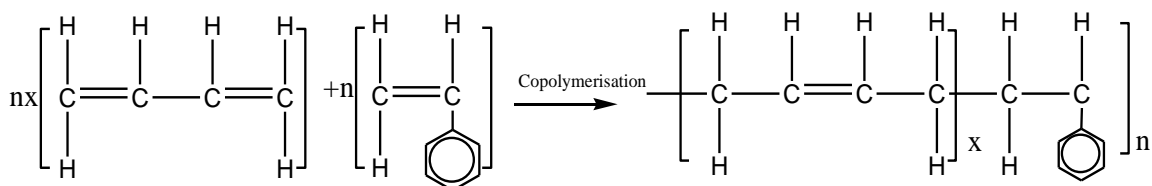
Any vulcanizable man-made rubber like polymer which can be stretched to at least twice its length, but returns to its original shape as soon as the stretching force is removed is called elastomer or synthetic rubber.

It should be called as 'Artificial rubber' rather than 'Synthetic rubber', because structurally it is not the same as natural rubber. Buna –S and Buna – N are two common synthetic rubbers.

Buna-S

Preparation:

It is produced by copolymerization of butadiene (about 75 % by weight) and styrene (25 % by weight) in an emulsion system at 50 °C in the presence of cumene hydro peroxide as catalyst.



Properties:

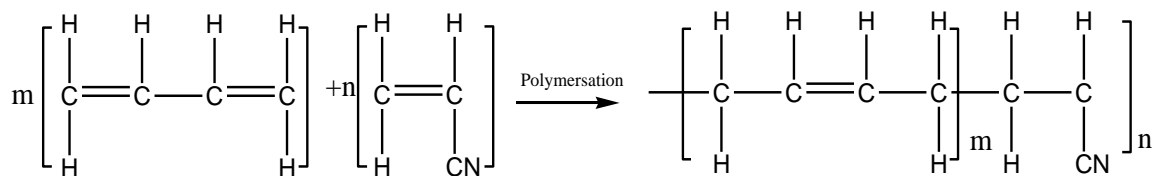
1. It possesses high abrasion resistance
2. High load bearing capacity
3. But it readily gets oxidized, especially in presence of traces of ozone present in the atmosphere.
4. It swells in oils and solvents
5. It can be vulcanized by using Sulphur

Applications:

1. Manufacture of motor tyres
2. Floor tiles, shoe soles, gaskets, foot wear components.
3. Wire and cable insulation
4. Tank lining etc.

Buna-N rubber or Nitrile Rubber or GR-A

Preparation: It is a copolymer of butadiene and acrylonitrile

**Properties:**

1. Excellent resistance to heat, sunlight, oils, acids and salts
2. Less resistant to alkalis, because of the presence of cyano groups
3. Vulcanized nitrile rubber is more resistant to heat

Applications:

For making

- (i) Conveyor belt
- (ii) Tank linings
- (iii) Printing rollers
- (iv) Gasket
- (v) Auto mobile parts etc.

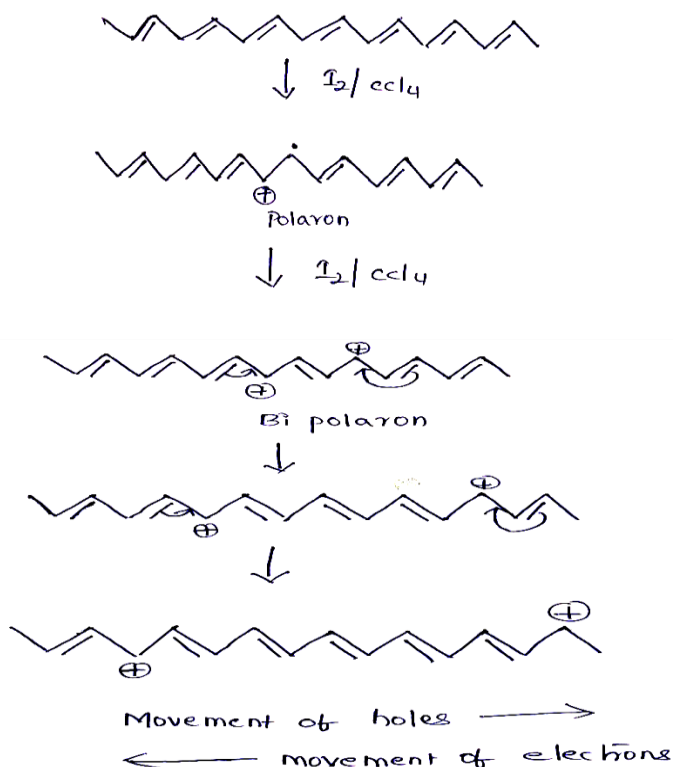
CONDUCTING POLYMERS

In general many organic polymers are used as electric insulators (Ex. PVC, PE, Teflon, Bakelite and Nylon 6,6'). The main reason for non-conducting nature of organic polymers is due to the absence of conjugation. In saturated chemicals, all the valence electrons are strongly localized. These electrons do not contribute electrical conductivity of the material.

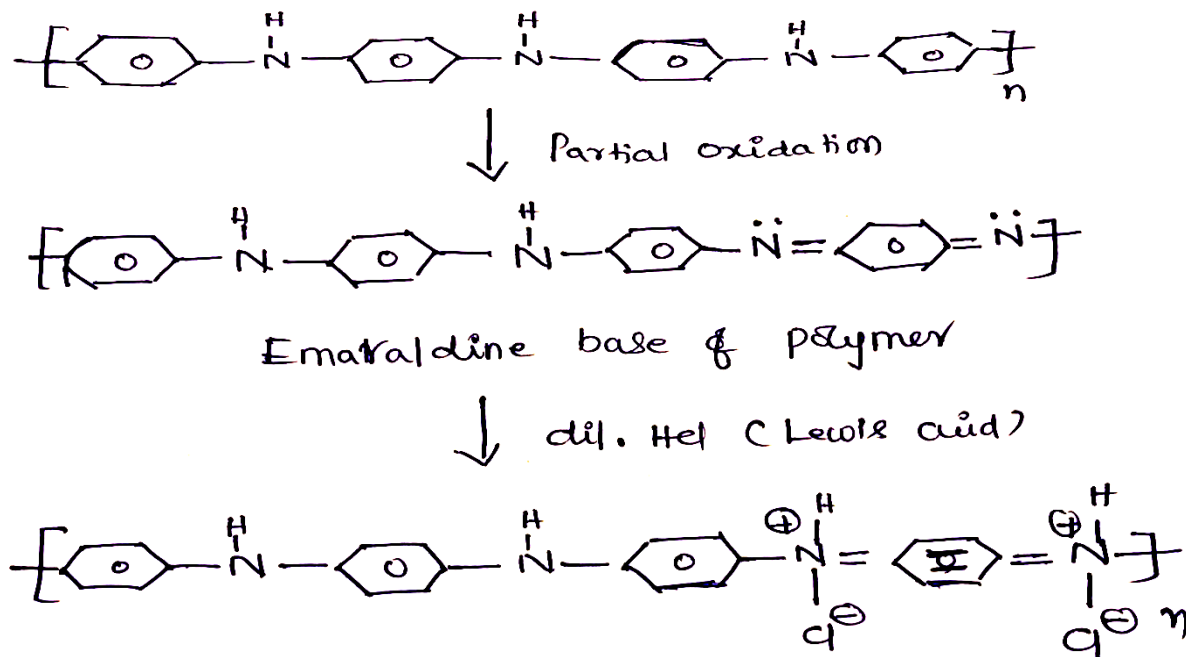
Conducting polymers are classified into two types

- (i) *Intrinsically conducting polymers*: The conduction of electricity is due to the extensive conjugation in the backbone of a polymer. These are further classified into two types i) Conjugated conducting polymers ii) Doped conducting polymers
- (ii) *Extrinsically conducting polymers*: These are basically blended polymers. The blends are responsible for conduction. These are further classified into two types i) Polymers with conducting element ii) polymers with conducting blends.

Polyacetylene: Polyacetylene has conjugation in the backbone when treated with lewis acid like I_2 in CCl_4 , oxidation occurs and a positive charge is created. Removal of one electron from pi-backbone of a conjugated polymer forms a radical cation (Polaron), which on losing another electron forms bipolaron. The delocalization of positive charges causes electrical conduction.

Mechanism of Conduction in Polyacetylene:

Polyaniline: The mechanism of formation of is shown in scheme below. Polymerization of aniline involves oxidation of aniline monomer to form dimeric species as the oxidation potential of aniline is higher than those of dimers, subsequently formed oligomers and polymers. Upon creation, the dimers are immediately oxidized and then react with an aniline monomer via an electrophilic aromatic substitution, followed by further oxidation and deprotonation to afford the trimers. This process is repeated, eventually leads to the formation of Polyaniline.



Applications of Conducting Polymers:

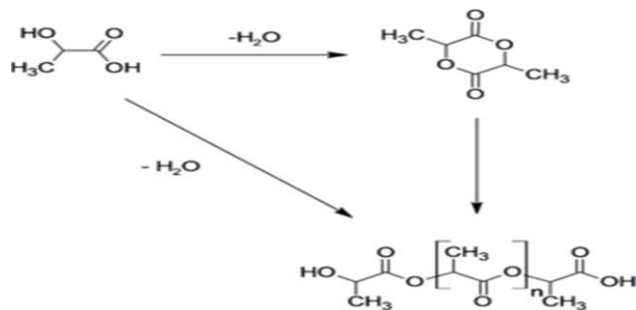
These are used in

- Solar cells and rechargeable batteries
- In printed circuit boards
- In fuel cells and transistors
- In printed circuit boards
- In bio-sensors
- In chemical sensors
- In fabrication of carbon Nano tubes
- In anti-corrosion coatings
- In auto mobiles
- In pollution control

- In conductive textiles
- In cancer therapy

BIO-DEGRADABLE POLYMERS

Polylactic acid (PLA): Preparation: Polylactic acid (PLA) is biodegradable as well as recyclable polyester made from renewable feedstock. The monomer lactic acid (LA) of PLA is derived from natural sources. LA is produced using bacterial fermentation of corn, sugarcane, potatoes, and other biomass. Polylactic acid is prepared from poly condensation of lactic acid or by ring-open polymerization of lactide.



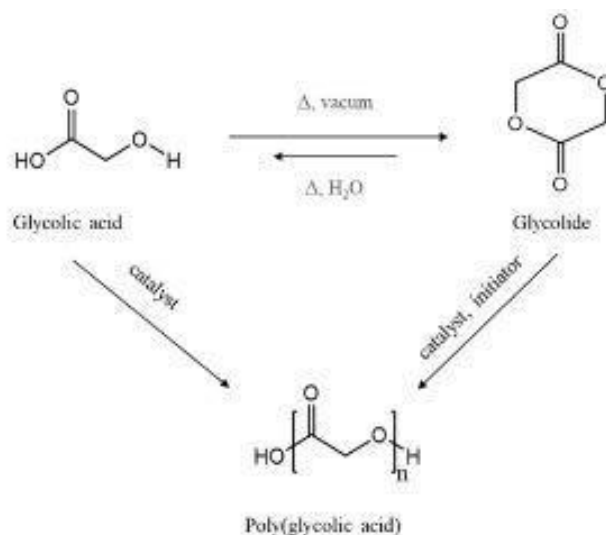
Properties:

- It is a biodegradable polymer
- It is bio-active polymer
- Its glass transition temperature is 60°C
- Its melting point is 130°C
- It is soluble in chlorinated solvents, hot benzene and Tetra hedra furan
- It has high surface area
- It is soluble in range of organic solvents

Applications:

- PLA is used in a large variety of consumer products such as disposable tableware, cutlery, and housings for kitchen appliances.
- It is used for compost bags, food packaging
- It is used for sandbags, planting pots, binding tape and ropes
- It is used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh
- It is used as water cups
- It is used as tea bags

Polyglycolic acid (PGA): Preparation: Polyglycolic acid, is a biodegradable, thermoplastic polymer and the simplest linear, aliphatic polyester. It can be prepared starting from glycolic acid by means of poly condensation or ring-opening polymerization.

**Properties:**

- It is a bio-degradable polymer
- It is a bio active polymer
- Polyglycolide has a glass transition temperature between 35 and 40°C
- Its melting point is reported to be in the range of 225 to 230°C
- It is insoluble in almost all common organic solvents
- Polyglycolide is soluble in highly fluorinated solvents

Applications:

- It is used to make sutures
- It is used to make Implantable medical devices such as rings, pins, rods, plates and screws
- It is used in food packaging
- It is used in making capsules