

UNIT- IV POLYMER TECHNOLOGY

Introduction:

Polymer: Polymers are large molecules made up of many smaller molecules. 'Poly' means many or number of, and 'mer' means unit or part.

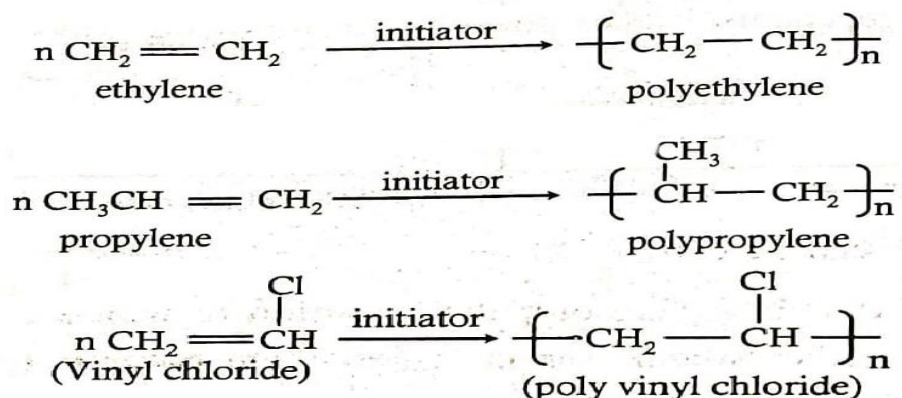
Monomers: Small molecules of low molecular weight, which combines to give a polymer, are called monomers. (Mono = one, mer = unit) monomers are joined together through polymerization to form polymers. A polymer contains, hundreds of thousands of monomers.

Degree of polymerization: The number of repeating units (or) monomer units available in the polymer is known as degree of polymerization. Polymers with a high degree of polymerization are called High polymers. Polymers with low degree of polymerization are called Oligo polymers.

Classification of polymers:

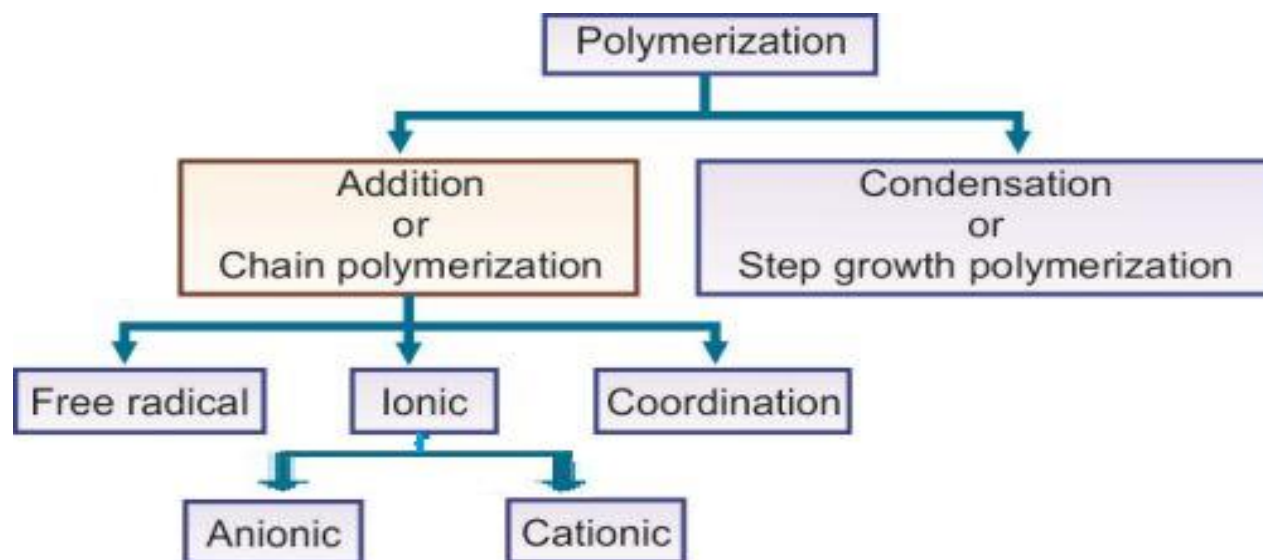
- 1. Natural polymers:** These are obtained from natural sources such as plants & animals, are called natural polymers. Ex: *Cotton, Wool, Cellulose, Natural rubber etc.*
- 2. Synthetic polymers:** These are synthesized with the help of chemicals in industries E.g.: *Polythene, PVC, Polystyrene, Teflon, Bakelite, Nylon-6,6, synthetic rubber etc.*
- 3. Homo polymer:** a polymer, in which a single type of monomer is used, is called homo polymer. Examples: *Polythene, polystyrene, PVC, Teflon etc.*
- 4 Hetero polymer or Copolymer:** A polymer in which the monomers are more than one type is called copolymer (hetero polymer). Ex: *Buna-S, buna-N, Etc.*
- 5 Organic & inorganic polymers, Thermo plastics & Thermo Setting plastics, etc.**

POLYMERIZATION: The process of formation of polymers from respective monomers is termed as Polymerization.



MECHANISM OF POLYMERIZATION:

Polymerization mechanism takes place by the following ways.



ADDITION POLYMERIZATION:

During the polymerization process, if the polymer is formed *without loss* of small molecules like H_2O , NH_3 , HCl etc; then this type of polymerization is called *Addition polymerization*. It is also known as *Chain growth polymerization*.

Ex: Polyethylene(PE), Polystyrene(PS), Polyvinylchloride (PVC), Neoprene, Teflon and etc.

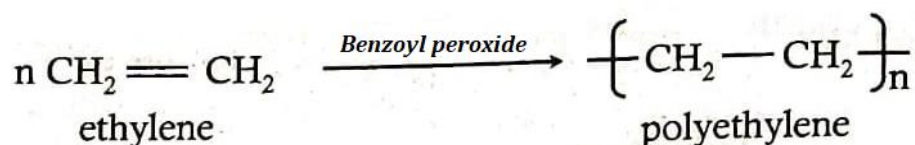
In Addition polymerization mechanism, takes place three steps. They are

- i) Chain Initiation
- ii) Chain propagation
- iii) Chain termination.

Free radical polymerization mechanism:

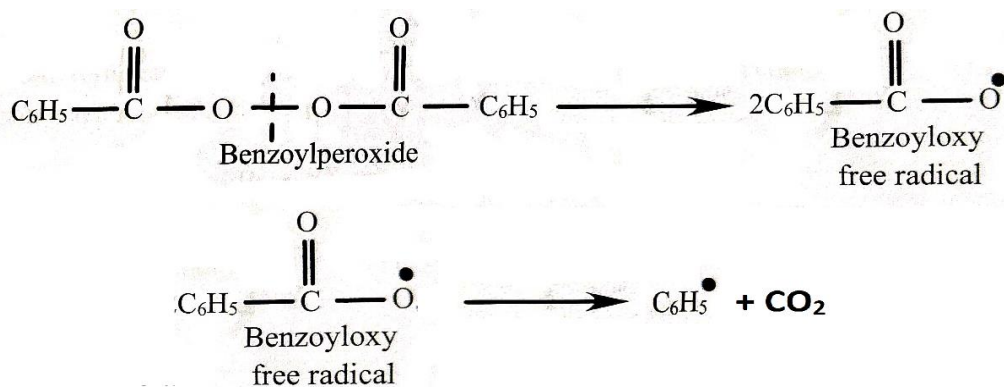
In free radical polymerization mechanism, *Peroxides* (Hydrogen Peroxide, Alkyl Peroxides-Benzoyl peroxides) are used as catalyst.

Preparation of polyethylene in free radical mechanism



The polymerization reaction is initiated by initiators which undergo homolytic fission in presence of light or heat.

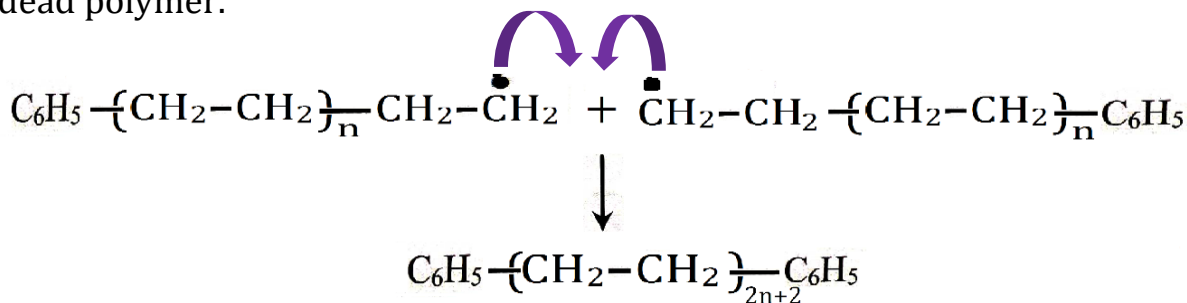
i) **Chain initiation**: In initiation process, the benzoyl peroxides go through hemolytic fission to give benzoyloxy *free radicals*. The benzoyloxy free radicals are combining to monomer (Ethene) and produce monomer free radical.



ii) **Chain propagation**: The monomer free radical/initiator reacts with number of monomers rapidly resulting the chain growth and producing polymer free radical.

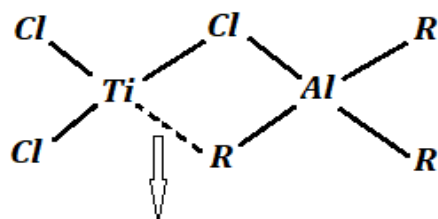


iii) **Chain Termination**: Termination (to stop chain growth) of the growing polymer chain carried by coupling (collision of two growing chains), resulting in the formation of dead polymer.



CO-ORDINATION POLYMERIZATION (OR) ZEIGLER-NATTA POLYMERIZATION:

The combination of metal halides (TiCl_4 , ZnBr , etc.) and organo metallic compounds (Aluminium tri alkyl) are called as zeigler-Natta catalyst. In this polymerization, stereospecific polymers are prepared.

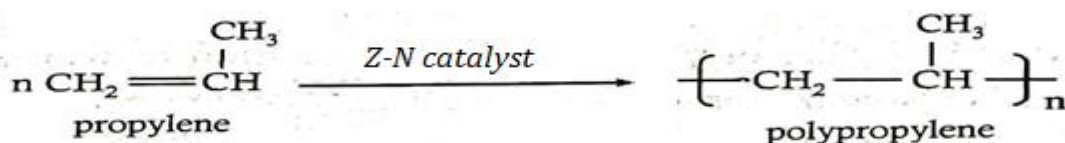


Where:

$\text{R} = -\text{CH}_3, -\text{C}_2\text{H}_5, -\text{C}_3\text{H}_7, -\text{C}_6\text{H}_5$, etc.

Co-ordination bond

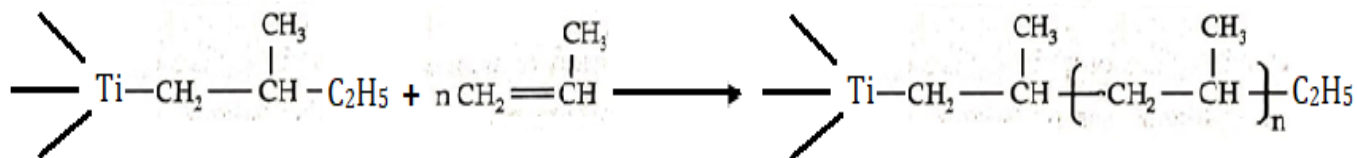
Preparation of Polypropylene by using *Zeigler-Natta catalyst*:



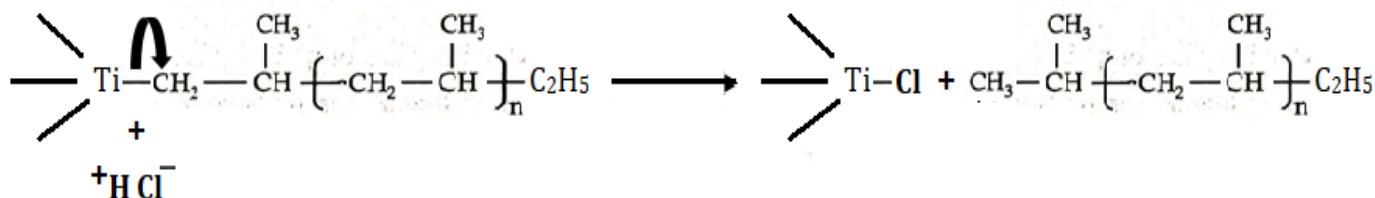
Chain initiation: in initiation process the monomer reacts with Z-N catalyst.



Chain propagation: in propagation process no. of monomers join the coordination bond and develops chain.

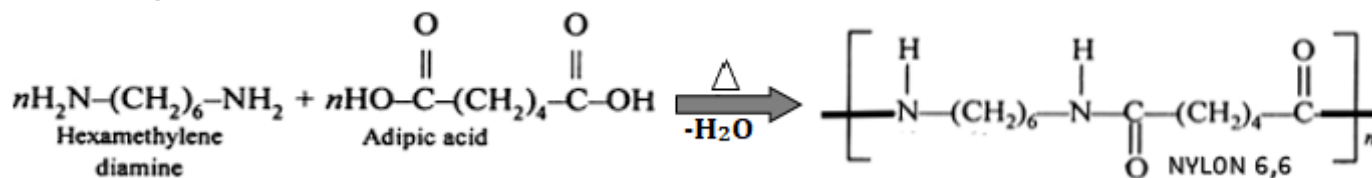


Chain termination: Termination is carried out with an active halogen compound (HCl).

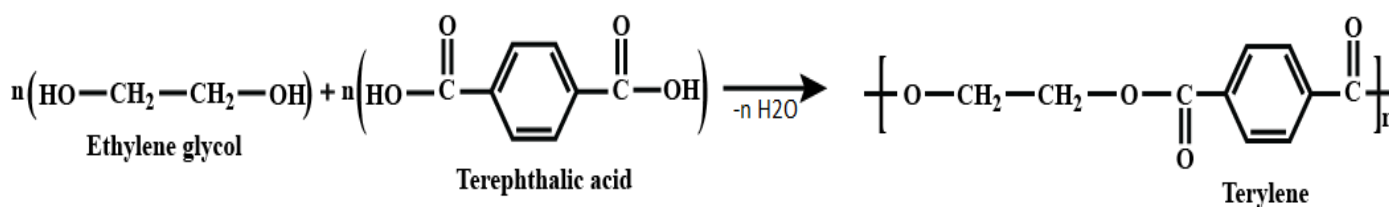


CONDENSATION POLYMERIZATION: During the polymerization process, if the polymer is formed *with loss* of small molecules like H₂O, NH₃, HCl etc; then this type of polymerization is called *condensation polymerization*. It is also known as *Step polymerization*. **Ex:** Nylon-6,6, Terylene, Urea-Formaldehyde resin, Bakelite etc.

NYLON6,6:



TERYLENE:



Difference between Addition polymerization & Condensation polymerization:

S.No.	Addition polymerization	Condensation polymerization
1	Polymer formation takes place without losing simple molecules like H ₂ O, HCl, NH ₃ , etc.,	Polymer formation takes place losing simple molecules like H ₂ O, HCl, NH ₃ , etc.,
2	Monomers must have unsaturation (double bonds or triple bonds)	Monomers must having active functional groups.(-OH, -NH ₂ , -COOH, etc.)
3	The molecular weight of polymer is the sum of molecular weights of monomers.	The molecular weight of polymer is not the sum of molecular weights of monomers.
4	Thermo plastics are formed	Thermosets are formed
5	The mechanism of polymerization carried out in three steps- initiation, propagation and termination.	The mechanism of polymerization carried out by slow step-wise condensation.
6	Ex: PE, PVC, Teflon, Poly styrene, etc.	Ex: Bakelite, nylons, U-F resin, etc.

Co-Polymerization: Combination of *two or more different monomers* to produce a polymer. Those polymers are called *co-polymers or hetero polymers*, and the process is called as Co-Polymerization. **Ex:** BUNA-S, BUNA-N, etc.,

PLASTICS

The word plastic itself comes from the Greek word *plasticos*, which means to be able to be shaped or moulded by applying heat and pressure.

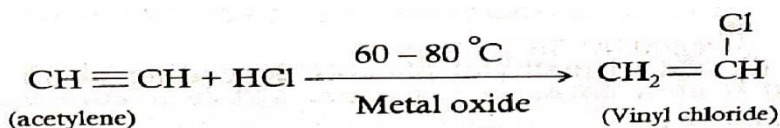
All plastics are polymers, but all polymers are not plastics. Plastics are broadly classified into two categories, *thermoplastics* and *thermo setting plastics*.

Difference between Thermo Plastics & Thermo setting plastics

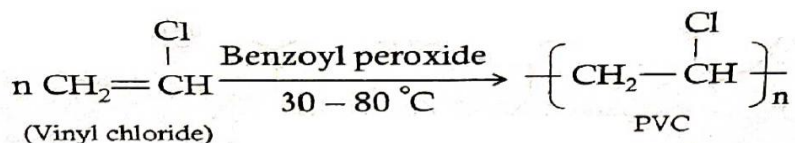
	<i>Thermo Plastics</i>	<i>Thermo setting plastics</i>
1	These are become soft on heating and hard on cooling.	These plastics, once they are solidified they cannot be softened.
2	Thermoplastic resins are formed by chain/addition polymerization.	Thermosetting resins are formed by condensation/step Polymerization.
3	They can be remould, reshaped reused and reclaimed from waste.	They cannot be remould, reshaped, reused and they cannot be reclaimed from waste.
4	They consists of long chain linear polymers.	They have cross-link or three dimensional structures.
5	These are soft, weak and less brittle.	These are hard, strong and more brittle.
6	These resins are usually soluble in organic solvents. <i>Eg: PE, PVC, Teflon, Polystyrene, etc.</i>	Due to strong bonds and cross links, they are insoluble in almost all organic solvents. <i>Eg: Bakelite, U-F resins, Nylons, etc.</i>

i) Preparation, properties and applications PVC (Poly Vinyl Chloride):

Vinyl chloride is prepared by treating acetylene with HCl at 60-80°C, presence of metal oxide catalyst.



Poly vinyl Chloride(PVC) is produced from vinyl chloride by free radical chain polymerization of vinyl chloride in presence of benzoyl peroxide.



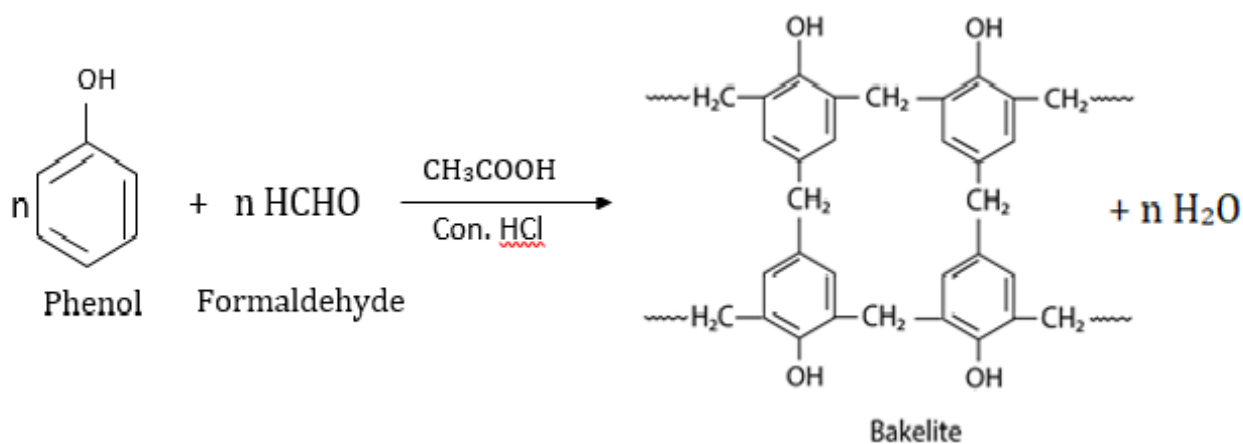
Properties:

- PVC is strong and brittle in nature. It is colourless, odorless, non-inflammable and chemically inert powder.
- It acts as insulator.
- PVC is not stable to heat and UV radiation. And Resist to atmospheric conditions.
- It has outstanding strength, lightness and chemical resistance.

Applications of PVC:

- i) P.V.C is mainly used as an electrical insulating material.
- ii) It is used in making cycle and automobile parts.
- iii) It is used for making pipes, chemical containers; It is used for making helmets, radio, telephone, refrigerator components, etc.
- iv) It is used for making table clothes, toys, tool handles, radio components, etc.

ii) Bakelite (or) Phenol-Formaldehyde Resin: Bakelite is a *condensation polymer*. It is a *thermosetting plastic*. It is prepared in step polymerization of phenol and formaldehyde in presence of Con. HCl as heat producing agent and glacial acetic acid as a catalyst.



Properties:

- i) Bakelite plastic resin is hard, rigid, and strong. It is a scratch resistant and water resistant polymer.
- ii) Bakelite has got good chemical resistance, resistant to acids, salts and any organic solvents.
- iii) It is a good anion exchanging resin, exchanges - OH group with any other anion. It is an excellent electrical insulator.
- iv) It is a very good adhesive. It has very good corrosion resistance, resistant to atmospheric conditions like O₂, CO₂, moisture, light, U.V. radiation etc.

Applications:

- i.) Bakelite is used widely. For making electrical insulator parts like switches, switch boards, heater and cooker handles etc.
- ii.) For making moulded articles like telephone parts, cabinets for radio and television. For making wood laminates and glass laminates.
- iii.) Used as an ion-exchanger in water purification methods. And also used as an adhesive (binder) for grinding wheels etc. In paints and varnishes.
- iv.) For making bearings used in propeller shafts, paper industry and rolling mills.

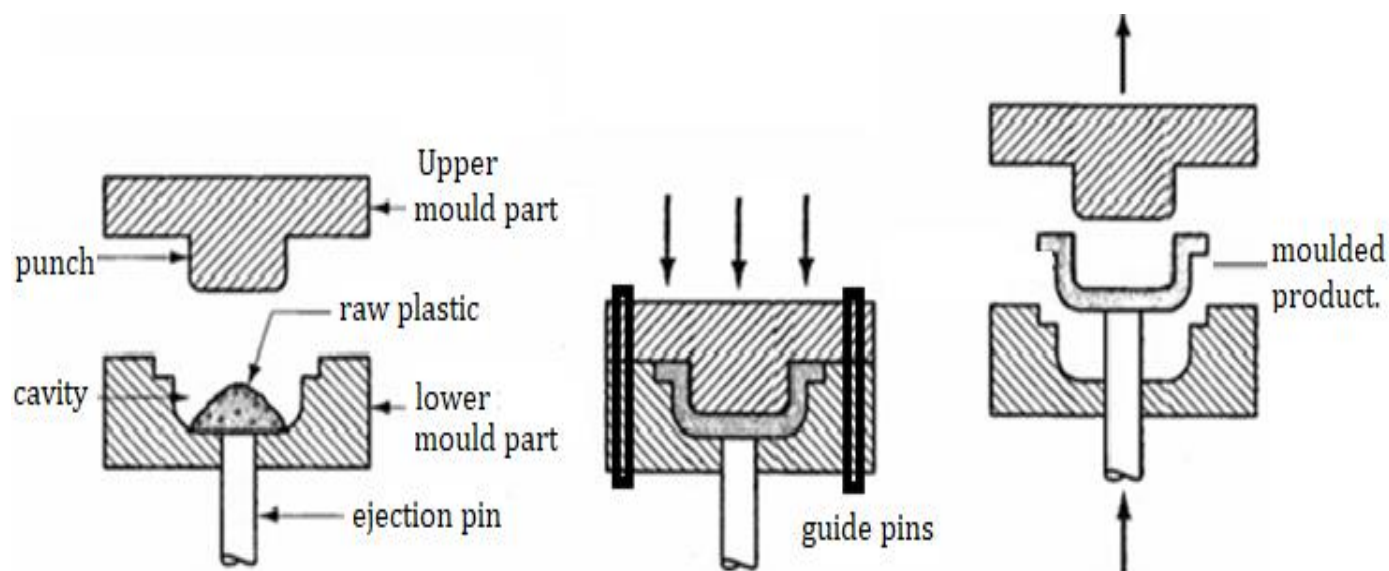
Moulding of Plastics: [Or] Fabrication Techniques:

The process of converting the given polymeric material into suitable designs is called moulding. The different moulding methods used are,

Compression moulding, Injection moulding, Extrusion moulding, transfer moulding, thermoforming, blow film, etc.

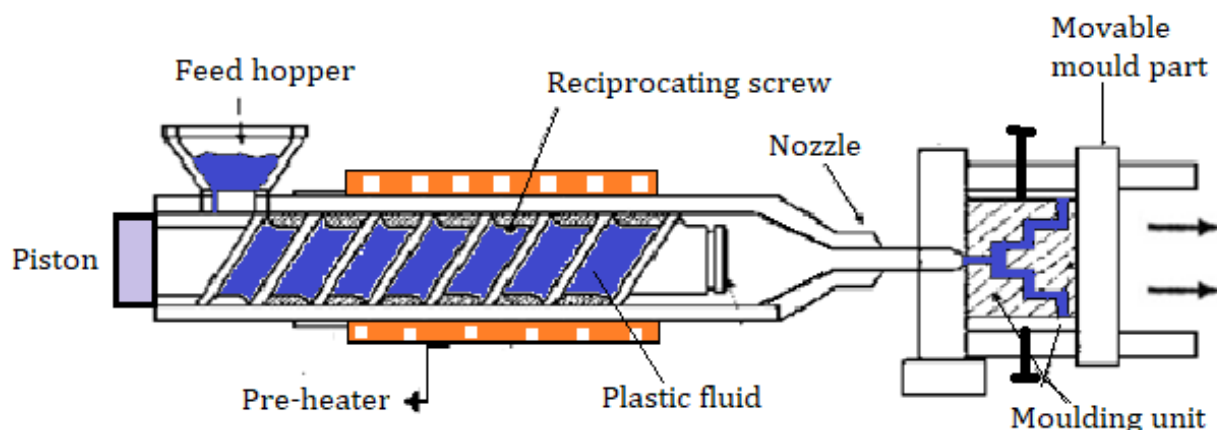
1. Compression Moulding:

- Compression moulding is applicable for both thermoplastics and thermosetting plastics. This method involves application of heat and pressure.
- The mould consists of two halves, the upper and the lower halves. The required amount of moulding compound (raw plastic) is placed in a cavity of bottom moulding part and is closed under pressure.
- The moulding temperature up to 200°C and 70kg/cm pressure can have applied.
- The mould is subjected to simultaneous heating and cooling. When heated after closing, the material goes through a chemical change that causes harden in to desired shape.
- After some time, the mould can be opened to release the moulded article.



2. Injection Moulding:

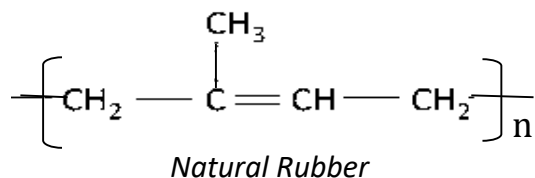
- i. Injection moulding method is used for only thermoplastic resins. This process is one of the most common of all plastics manufacturing processes.
- ii. The raw plastic is fed to hopper, which moves to heated injection unit, here the raw plastic is softened to a fluid state by pre heaters, where it is pushed by piston through a long chamber with reciprocating screw.



- iii. The fluid plastic moves in to cold moulding unit through a nozzle.
- iv. Fluid plastic changes into hard desirable shape in the cool moulding unit and is ejected from the moulding unit.

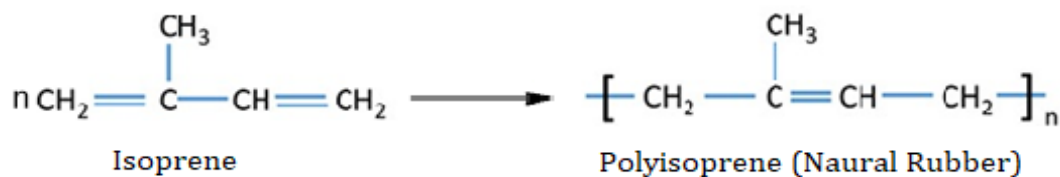
ELASTOMERS

Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on released of stress. Those rubbers are therefore referred to as elastomers. The property of elastomers is known as elasticity. All rubbers are polymers, but polymers are not rubbers.



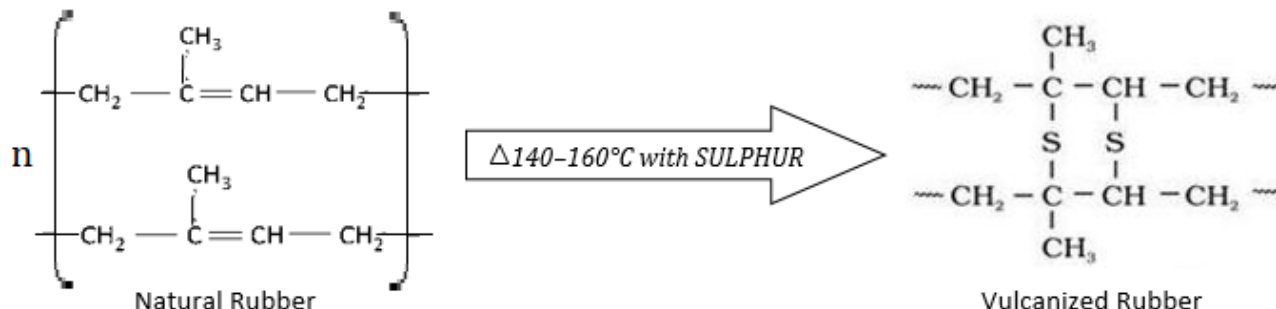
Natural rubber:

Natural rubber is found in several species of rubber trees grown in tropical countries. Hevea brasiliensis is the most important source of natural rubber. Rubber is stored in the form of white fluid called '**latex**' behind the bark of the rubber tree.



Natural rubber is a high polymer of isoprene (2-methyl 1,3 butadiene). Polyisoprene exists in two geometric isomers *cis* and *trans* forms.

The natural rubber has some disadvantages like strength properties. To overcome these disadvantages, natural rubber undergoes vulcanization process in presence of Sulphur. Addition of *Sulphur* to natural rubber is called as *Vulcanization* process.

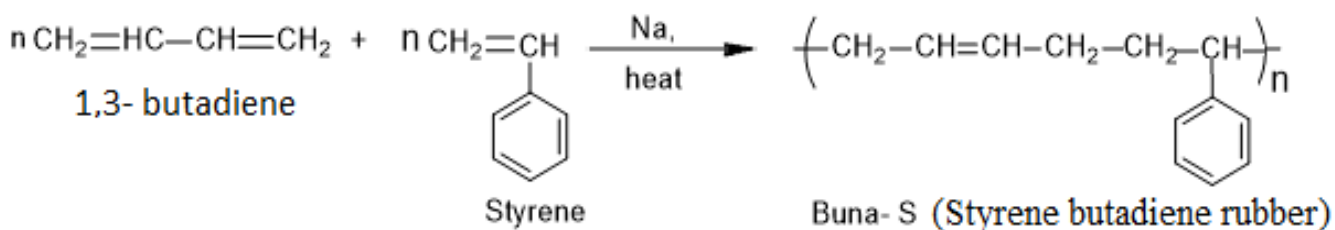


BUNA-S (Styrene- Butadiene Rubber):

Buna-S is a *synthetic rubber and Copolymer*. Which is also called as *SBR* (Styrene Butadiene Rubber) or *GR-S* (Government Rubber Styrene) or *Ameripol*. BUNA-S stands for the composition of the monomers and the catalyst.

BU- butadiene (monomer), Na- Sodium (catalyst), S- styrene (monomer).

BUNA-S is produced by the **Copolymerization** of 1,3 butadiene (75%) and styrene (25%) in presence of Sodium (Na) as a catalyst.



Properties:

1. Buna-S is a strong and tough rubber.
2. It is vulcanized by Sulphur.
3. It is a good electrical insulator.
4. Which possess high load bearing capacity.
5. It is resistant to chemicals but swell in oils and attacked by even traces of ozone present in atmosphere.

Applications:

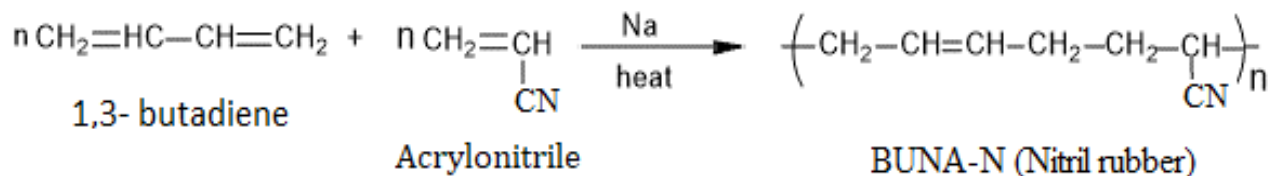
1. It is used for manufacturing of tyres.
2. Used in footwear industry for making shoe soles and footwear components.
3. Used for making wires and cable insulators.
4. Used for the production of floor tiles, and linings in chemical industries.
5. Used as gaskets, etc.

BUNA-N (Nitrile Butadiene Rubber):

Buna-N is a *synthetic rubber and Copolymer*. Which is also called as *NBR* (Nitrile Butadiene Rubber) or *GR-A* (Government Rubber Acrylonitrile). BUNA-N stands for the composition of the monomers and the catalyst.

BU- butadiene (monomer), Na- Sodium (catalyst), N- Acrylonitrile (monomer).

BUNA-N is produced by the **Copolymerization** of 1,3 butadiene and Acrylonitrile in presence of Sodium (Na) as a catalyst.



Properties:

1. It is vulcanized by Sulphur.
2. It is a good electrical insulator.
3. Buna-N is a strong, tough & light weight.
4. Less resistance to alkalis than natural rubber.
5. It is resistant to heat, sunlight, oils, acids and salts.

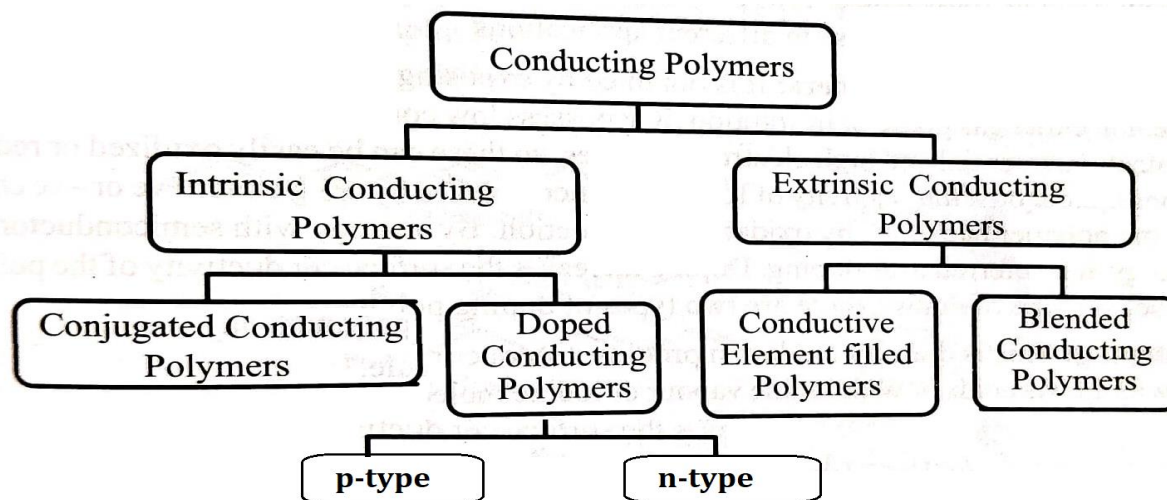
Applications:

1. It is used for making conveyor belts.
2. Used as gaskets, oil resistant foams and printing roller.
3. Used for making tank linings and pipes in chemical industries.
4. Used in high altitude aircraft components and automobile parts because of its strength and light weight.

CONDUCTING POLYMERS

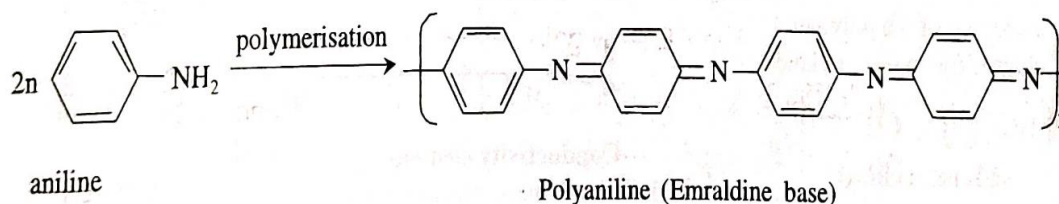
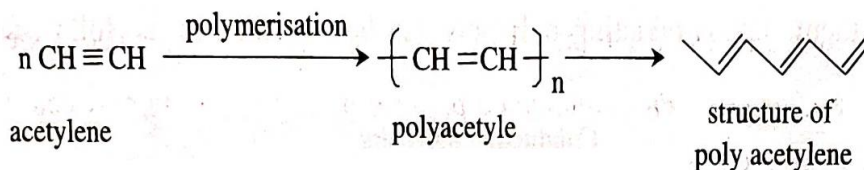
A polymer which *conducts electricity* is called *conducting polymer*. The conduction of the polymers may be due to unsaturation or due to presence of externally added ingredients in them. Eg :- Polyaniline, polyacetylene, polypyrrole, polyfuron, etc.

The conducting polymers can be classified in the following way.



1. Intrinsic conducting polymers: These have extensive *conjugation* in the backbone which is responsible for conductance. These polymers can be divided into...

a. Conjugated Conducting polymers: These polymers contain conjugated π -electrons in backbone chain, which increases their conductivity to a large extent. This is because, overlapping of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands, which extends over the entire polymer molecule. The valence band and the conduction bands are separated by a significant band gap (fermi energy gap). Thus, electrical conduction could occur only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band.

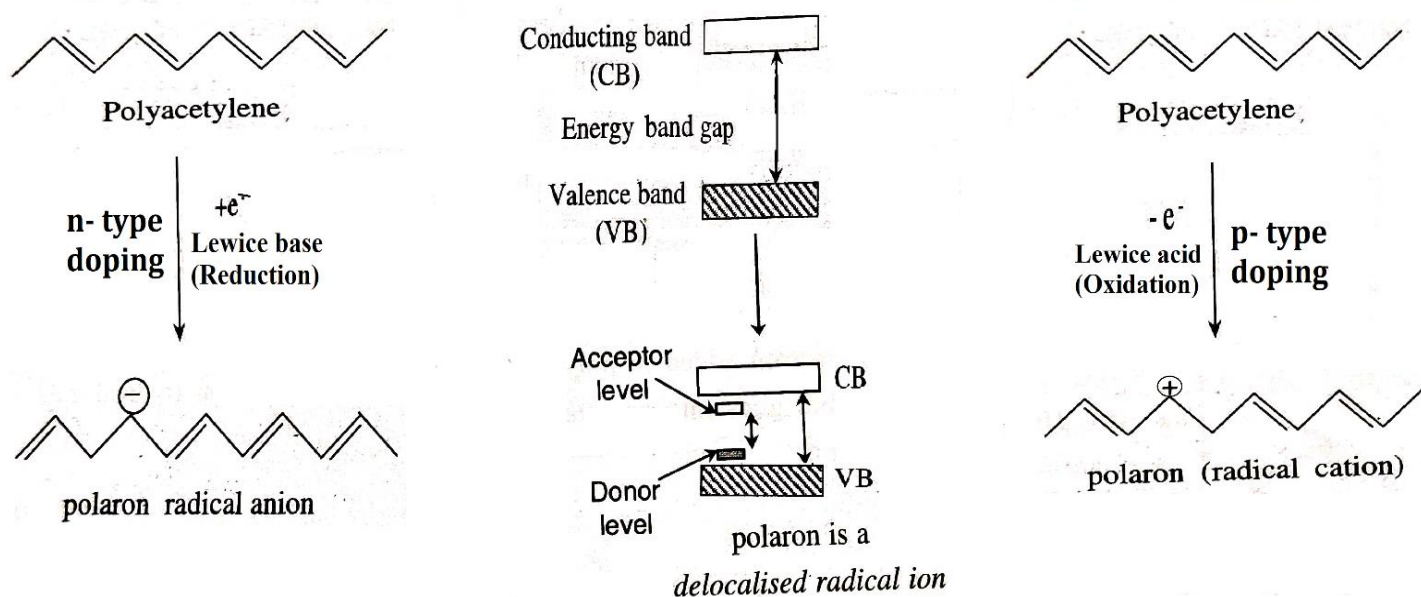


b. Doped conducting polymers: Conductivities of polymers having conjugated π -electrons in the backbone can be increased by creating either *+ve* or *-ve* charges on the polymer backbone by oxidation or reduction. This process is called *doping*. It can be done in two ways.

i) p- type doping (Oxidative doping): It involves treating the conjugated polymer (Ex: Polyacetylene) with a Lewis acid or iodine vapour or etc., thereby oxidation takes place and +ve charges are created on the back bone chain of polymer.

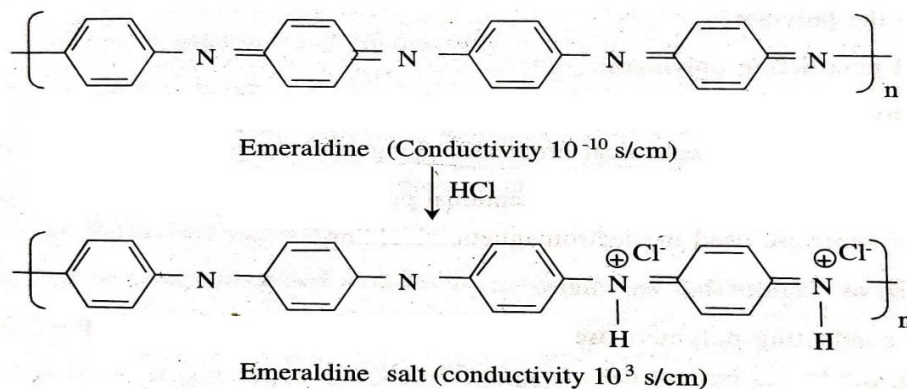
ii) n- type doping (Reductive doping): It involves treating the conjugated polymer (Ex: Polyacetylene) with a Lewis base like RNH_2 there by reduction takes place and -ve charges are created on the back bone chain of polymer.

Ex: Conducting properties of Polyacetylene:



Ex: Conducting Properties of Polyanilines:

Polyaniline is a famous conductive polymer; Polyanilines exist in several oxidation states as far as electrical conductivities are concerned varying from 10^{-11} S/cm to $> 10^5$ S/cm only one form called emeraldine salt is electrically conducting.



The flexible dark blue thin films of conducting polyaniline is made by protonic doping i.e. protonation of imine nitrogen atoms in the backbone. Doping is a reversible process, deprotonation can also be done by treatment with alkali Emeraldine salt also known as synthetic metal because it possess metallic conductivity, metallic lusturous.

2. Extrinsically conducting polymers: Some of the polymers conduct electricity due to externally added ingredients to them. They are of two types.

a) Conductive elements filled Polymers.

b) Blended conducting polymers.

a) Conductive elements filled polymers: In these polymers, the polymer acts as a 'binder' and holds the conducting element added so that the polymer becomes a conductor. Examples of conductive elements are carbon black, metallic fibers, metallic oxides etc.

b) Blended conducting polymers: These polymers are obtained by blending a conventional polymer with a conducting polymer. The polymer thus obtained has good chemical, physical, electrical properties and mechanical strength.

Ex; 40% pyrrole when blended with a conventional polymer, the combination gives conducting polymer with good impact strength.

Applications of conducting polymers:

1. They are used in rechargeable batteries, chemical and analytical sensors and etc.
2. Used in the manufacturing of electro-magnetic shielding, corrosion inhibitors, etc.
3. Used in telecommunication systems, solar cells.
4. Used in making electronic display, optical fibers, ion exchangers, etc.
5. Used in molecular wires and molecular switches.
6. Used in electronic devices such as transistors and diodes.

BIODEGRADABLE POLYMERS

A polymer that can be *decomposed by enzymatic action of naturally occurring microorganisms and bacteria* is called a *biodegradable polymer*. Biodegradation is the chemical breakdown of materials by physiological environment.

Some polymers undergo degradation when exposed to moisture, heat, oxygen, ozone and microorganism. Generally materials obtained from plants, animals and other living organism and synthetic materials similar to plant and animal material undergo degradation by microorganism.

These organic materials can be degraded either aerobically or anaerobically. Like Hydro-biodegradable polymers and Oxo-biodegradable polymers. The biodegradable polymers are classified as.,

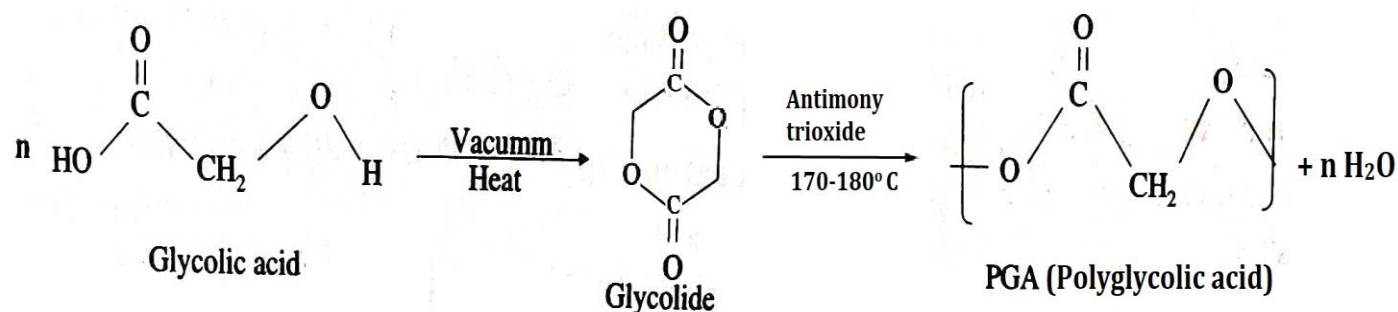
Naturally occurring biodegradable polymers: which is also called as *Biopolymers*. Polysaccharides (starch and cellulose), Proteins (Gelatin, silk, wool), Polyesters (poly hydroxyl alkanates), others (Ligin, natural rubber) etc

Synthetic biodegradable polymers: Poly glycolic acid(PGA), poly lactic acid (PLA), Polyhydroxy alkanates (PHA), Polyvinyl acetate(PVA), PHV, PHBV and etc.

Polyglycolic acid (PGA):

Polyglycolic acid (PGA) is a *biodegradable and thermoplastic polymer*. PGA is the simplest linear and aliphatic ester.

Preparation: PGA was prepared by polycondensation or ring-opening polymerization of glycolic acid.



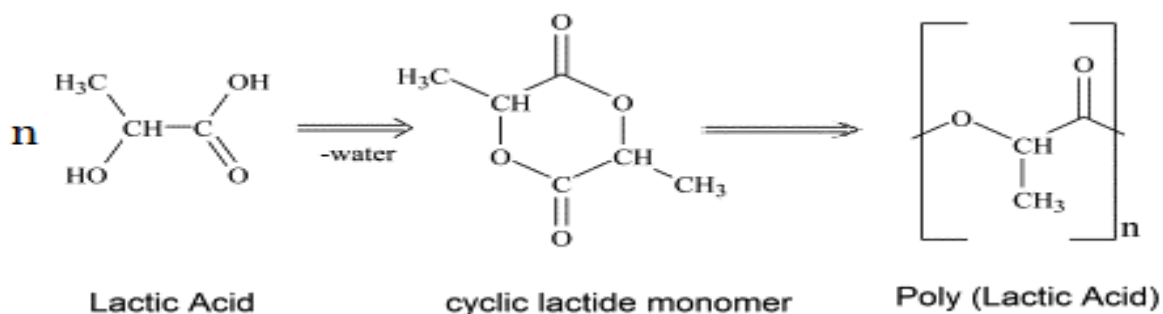
Properties: PGA is non-toxic and thermoplastic. These are unstable to water, good elasticity. These are high heat distortion temperature. High stiffness & tensile strength.

Applications: PGA used in surgical suture is indicated for use in General surgery, Plastic surgery, Gynecology, Urology, Orthopedics general closure cuticular.

Polylactic acid:

Polylactic acid is a biodegradable and thermoplastic polymer. Which belongs to polyhydroxy alkananoates.

Preparation: Lactic acid is derived from renewable sources like corn, starch, sugarcane, etc. Lactic acid undergo polymerization then produce, Polylactic acid.



Properties:

1. The glass transition temperature of PLA is 60-65 °C.
2. Its melting point is 179- 178 °C.
3. PLA is a thermoplastic nature.
4. PLA is good biocompatibility, processability and high strength.

Applications:

1. It is used in a no. of biomedical applications such as sutures, stents, drug delivery devices and dialysis media.
2. It is used in the preparation of bioplastics for packing food and disposal tableware.

