

Polymer chemistry

(* Polymers :- These are the compounds of very high molecular masses formed by the combination of a large number of simple molecules

Ex:- PVC (Polyvinyl chloride), Nylon 6.6

Polymerisation :- It is the process by which the simple molecules (monomers) are converted into polymer.

Classification of polymers :-

a) On the basis of Origin (Source) :-

1) Natural polymers :- These are the polymers obtained from nature

Eg:- Starch, cellulose

2) Synthetic polymers :- These are the polymers prepared in the laboratories.

Eg:- PVC, Nylon 6.6

b) On the basis of structure :-

1) Linear chain polymers :- In these polymers, monomers units are connected together to form linear chains.

Eg:- Nylons

2) Branched chain polymers :- In these polymers, monomers are joined to form long chains with side chains (or) branches of different lengths.

Eg:- Starch.

3) Cross-linked polymers :- These are the polymers in which monomers are cross-linked together to form a three dimensional network.

Eg:- Bakelite

c) On the basis of mode of synthesis :-

1) Addition polymers :- These polymers are formed by direct addition of repeated monomers without the elimination of any byproducts.

Eg:- Polyethene

2) Condensation polymers :- These polymers are formed by condensation of two or more than two monomers with the final elimination of simple molecules like water, ammonia, HCl etc.

Eg:- Nylon-6.6

d) On the basis of molecular forces :-

1) Elastomers :- The polymers that have elastic character and in which the polymer chains are joined by weakest inter-molecular forces are called "Elastomers".

Eg: Natural rubber

2) Fibres :- The polymers which have strong intermolecular forces between the chains are called "Fibres".

Eg: Silk

3) Thermo-plastics :- These polymers can be easily softened when heated and hardened when cooled with little change in their properties

Eg: polythene

4) Thermo-setting polymers :- These polymers undergo permanent change on heating

Eg:- Bakelite.)

Types of polymerisation :-

These are two types

- 1) Addition polymerisation (or) chain polymerisation
- 2) Condensation polymerisation (or) Step ^{with} polymerisation.

1) Addition polymerisation :- (chain polymerisation)

* Addition polymerisation is the process of repeated addition of monomers that posses double (or) triple bonds to form polymers.

* Molecular weight of the resulting polymer product is the exact multiple of monomer's molecular weight.

* In this polymerisation, the monomers used are mainly the unsaturated compounds.

* In addition polymerisation, no by products will be formed. i.e addition polymer is formed by without eliminating the byproducts.

* It follows three step mechanism of chain initiation, chain-propagation and chain termination.

Ex:- Thermoplastics \rightarrow PVC, polythene, polystyrene.



2. Condensation polymerisation :- (step-growth polymerisation)

- * step polymerisation takes place by condensation reaction of the functional groups of the monomers. Hence, known as a condensation polymerisation.
- + The monomers contain functional groups like $-COOH$, $-OH$, $-ClO$, $-COOR$, $-NH_2$ and halides etc.
- * The functionality of the monomers must be two (or) more than two.
- * In this polymerisation, by products will be formed like - H_2O , NH_3 etc.
- * It is not a three step-mechanism of initiation, propagation and termination.

Eg:- Nylon 6.6 , Dacron)

(Differences between Addⁿ & condensation polymerization:-

S.No	ADDITION POLYMERIZATION/CHAIN GROWTH POLYMERISATION	CONDENSATION POLYMERIZATION/STEP GROWTH POLYMERISATION
1	It is also called as chain growth polymerization.	It is also called as step growth polymerization.
2	Monomers add on to give polymer without elimination of simple molecule.	Monomers condense among themselves to form the Polymer with elimination of simple molecules (H ₂ O, NH ₃ , CH ₃ OH).
3	Molecular weight of the polymer is an integral multiple of that of monomer.	Molecular weight of the polymer need not be an integral multiple of monomers.
4	Monomer must have at least one multiple bond. Eg. Alkene, amines, aldehydes, etc.,	Monomer must have at least two identical or different functional group. E.g. Glycol, Dicarboxylic acid, Acetic Acid, etc.,
5	Products obtained are thermoplastic.	Product obtained may be thermosetting /thermoplastic.
6	It follows three step mechanisms of Initiation, Propagation and Termination.	It not follows three step mechanisms.
7	E.g., Polyethene, Polystyrene, Polypropene, PVC, etc.	E.g Bakelite, Nylon 6.6.

Plastics:

Plastics are the materials that show the property of plasticity and can be moulded into any desired shape and dimensions by the application of heat and pressure. Plastics having variety of properties are in use in present applications.

Plastic are classified into two types: 1) Thermoplastics
2) Thermosetting

Thermoplastics:

Thermo plastics are the polymers that become soft on heating and hard on cooling and the process can be repeated for a number of times. They undergo reversible changes on heating.

Ex: Polythene (PE), polypropylene (PP), polyvinyl-chloride (PVC), polytetrafluoroethylene (PTFE or Teflon),

- These are formed by addition polymerization.
- Consists of linear polymer chains with negligible cross-linking.
- These are soft and less brittle.
- These are soluble in organic solvents.
- Soften on heating and hence are amenable for moulding into any shape in the hot condition on cooling, the resin becomes hard and rigid and retains the moulded shape.

- They can be reheated and moulded into any other shape reversibly any number of times without any change in the chemical nature.
- These can be reclaimed from wastes.

Thermosetting polymers (or) Thermosets:

Thermosets are the polymers that undergo chemical changes and cross-linking on heating and become permanently hard, rigid. They will not soften on heating, once they are set.

Ex: Phenol-formaldehyde resin (Bakelite), urea-formaldehyde resin.

- These are mostly formed by condensation polymerization.
- These are mostly branched polymer chains.
- Thermosets become hard and rigid on heating during moulding process.
- These are not soluble in common organic solvents.
- Thermosets cannot be softened, reformed, reshaped once they are set.
- These cannot be reclaimed from wastes.

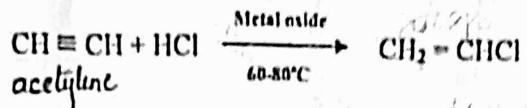
Differences between thermo-plastics and thermo-set plastics:

S.No	THERMO PLASTICS	THERMOSETTING PLASTICS
1	These are produced by addition polymerization.	These are produced by condensation polymerization.
2	On heating they become soft and on cooling become hard.	On heating they become hard. No change on cooling. Chemical nature changes.
3	They can be remoulded.	They can't be remoulded because they are permanently set.
4	They can be reclaimed from wastage	They can't be reclaimed from wastage.
5	Soluble in organic solvent.	Insoluble in any solvent.
6	Adjacent polymer chains are held together by weak Vander Waals forces.	Adjacent polymer chains are held together by strong covalent bond.
7	Soft, weak and less brittle.	Hard, strong and more brittle.
8	E.g: PE, PVC, PTFE	E.g: Bakelite, Thiokol etc.,

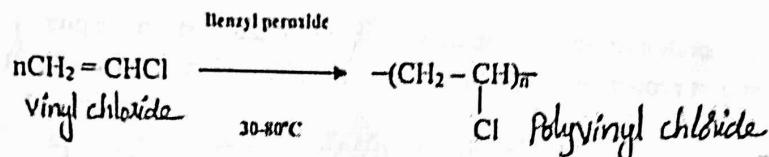
Preparation, properties and engineering applications of PVC, Teflon and Bakelite:

PVC: (Poly Vinyl Chloride):

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



Poly vinyl chloride is produced by heating vinyl chloride in presence of benzoyl peroxide or H_2O_2 .



Properties:

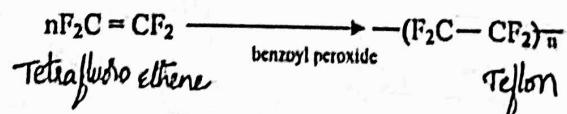
- PVC is colorless, durable, and chemically inert powder.
- It has melting point 148°C.
- Resistant to atmospheric conditions.
- It is having high density.
- It is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons.
- It undergoes degradation in presence of heat.

Uses:

- It is used for making sheets, tank-linings, light-fittings, safety helmets, refrigerator components.
- It is used for injection moulding of articles like toys, tool-handles, radio-components.
- It is used in the production of pipes, cable insulators, table covers and rain-coats etc.

Teflon : (Poly Tetra Fluoro Ethylene):

Teflon is obtained by polymerization of tetrafluoroethylene in presence of benzoyl peroxide as catalyst.



Properties of Teflon :-

Teflon is also known as Fluon. Due to the presence of highly electronegative fluorine atoms. There are strong attractive force is responsible for high toughness & high chemical resistance towards all chemicals except hot alkali metal & hot fluorine.

Uses of Teflon :-

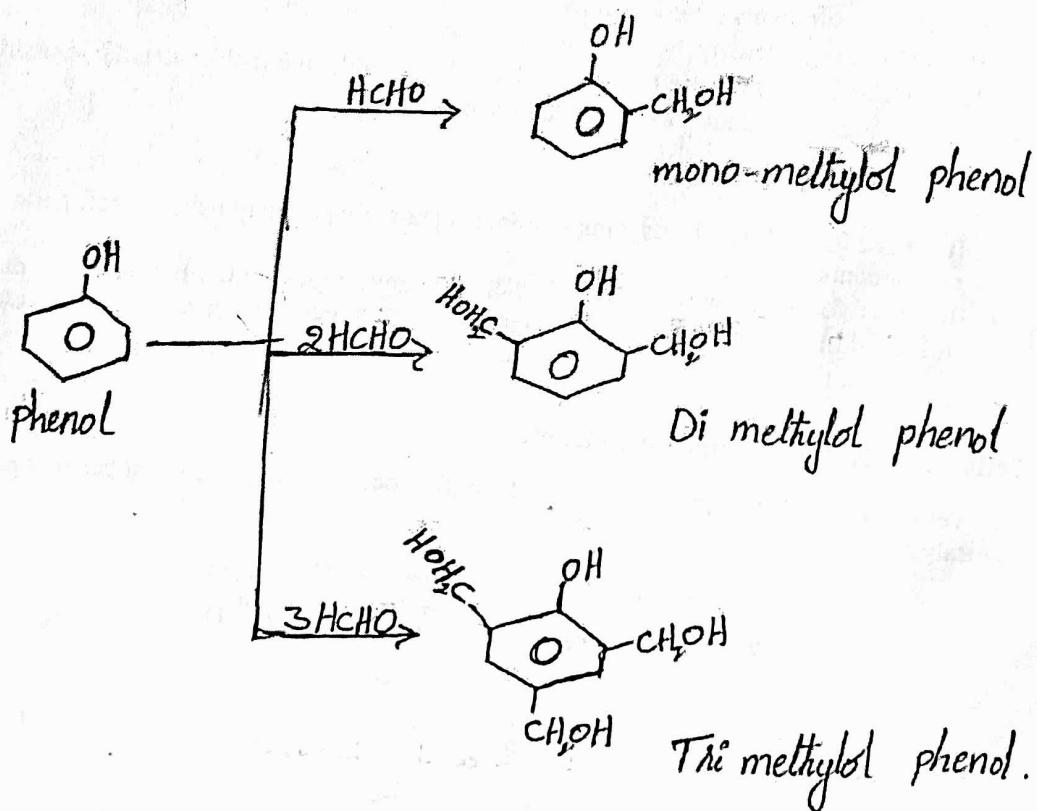
- It is used in making seals & gaskets.
- It is also used for insulation of electrical items and for making non-sticky surface coating, particularly for cooking utensils.
- Teflon used as insulating material for motors, transformers, cables, wires, fitting etc.

(Bakelite (or) phenol formaldehyde Resin:

The condensation reaction of phenol & formaldehyde in the presence of acid or alkali catalyst and at proper temperature produces the phenol formaldehyde resin or Bakelite resin.

Stage I :

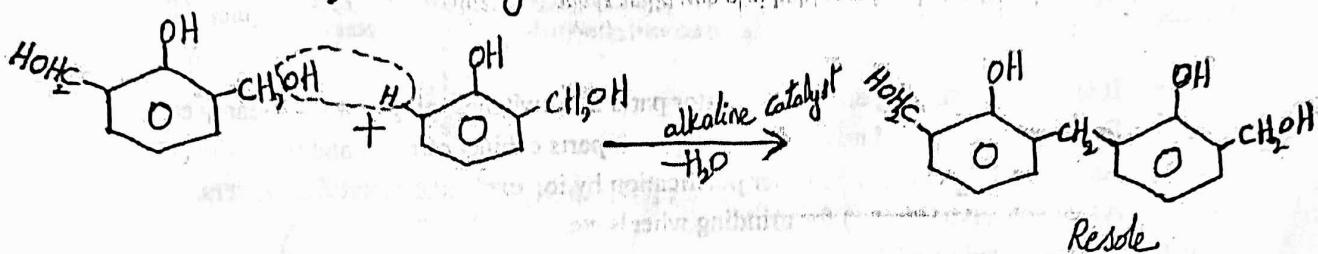
The initial reactions of phenol & formaldehyde in presence of acid or alkali produces mono, di, tri methylol phenols depending on the phenol formaldehyde ratio (P/F ratio)



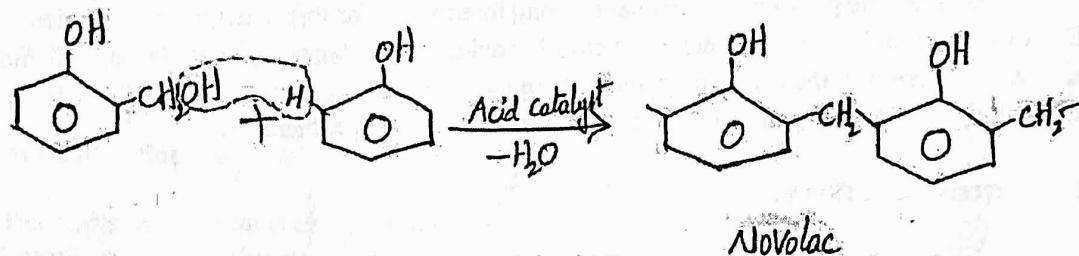
Stage II:

The mono, di, tri methyl phenols are heated to produce two types of straight chain resin by condensation of methylol group with hydrogen atom of benzene ring or another methylol group.

i) Formation of A-stage resin (Resole)

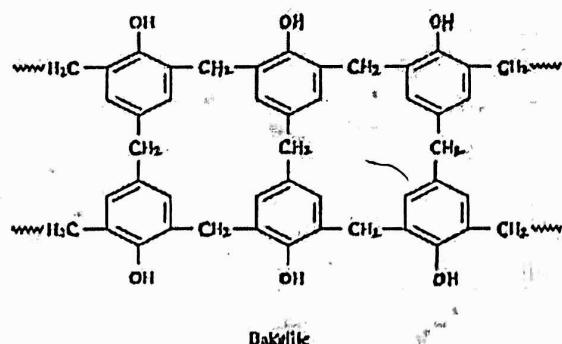


ii) Formation of B-stage resin (Novolac)



Stage III: Production of Bakelite

Resole or novolac or both heated in presence of hexamethylene tetramine produces hard and cross linked polymer called Bakelite.



Properties:

- Bakelite plastic resins are hard, rigid and strong materials.
- They have excellent heat and moisture resistance.
- They have good chemical resistance.
- They have good abrasion resistance.
- They have electrical insulation characteristics.
- They are usually dark coloured.

Uses:

- It is used for making electric insulator parts like switches, plugs, switch boards etc.
- For making moulded articles like telephone parts cabinet of radio and television.
- As an anion exchanger in water purification by ion exchange method in boilers.
- As an adhesive (binder) for grinding wheels etc.
- In paints and varnishes.
- In paper industry and rolling mills

Fibers:

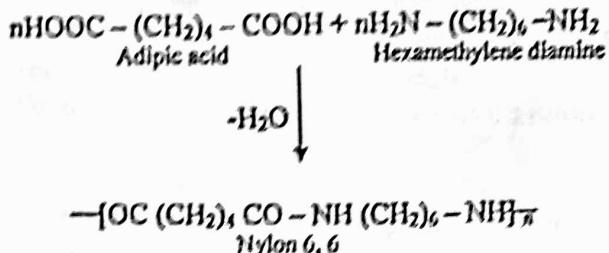
Fibres are the polymers which have strong intermolecular forces between the chains. Because of strong forces, the chains are closely packed giving them high tensile strength and less elasticity. Therefore, these polymers have sharp melting points. These Polymers are long, thin filament of any macromolecular substances.

Characteristics of fibers:

- The fibers must be strong and tough.
- A good fiber must be an insulator.
- The fibers must absorb color easily and washable.
- The fibers must be resistant to corrosion.
- The fibers must be resistant to chemicals.
- Fibers must be wrinkle free and should not develop wrinkles after using for a long time.

Nylon 6.6:

Nylon 6.6 is prepared by the polymerization of adipic acid with hexamethylene diamine.



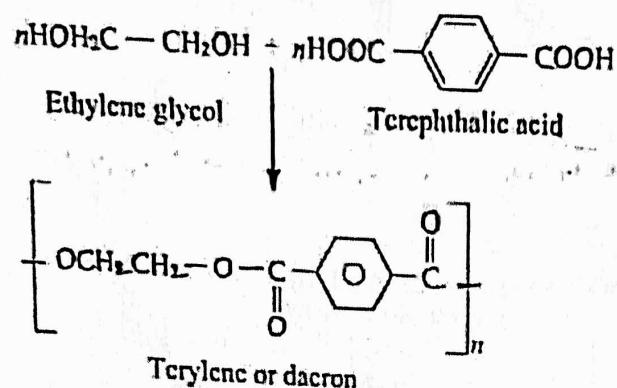
Properties:

- Nylon 6.6 possesses high melting point ($>500^\circ\text{C}$)
- It is soluble in phenol and formic acid and insoluble in common organic solvents.
- This fiber has good strength.
- These are light and tough.
- These fibers are highly resistant to abrasion.
- These fibers are flexible and retain original shape after use.

Applications of Nylon 6.6:

- The major application is in textile industry.
- Because of its high thermal & abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there.
- Nylons are used as electrical insulators.
- Nylon 6 is used for making tire cords.
- Nylons are used in automobile industry and telecommunication industry for making radiator parts.

Dacron (or) Terylene:



Properties:

- It is very easy to dye.
- The fiber does not hold water.
- The fibers are strong with good abrasion resistance.
- The fibers are highly resistant to mineral acids but less resistant to alkalis.

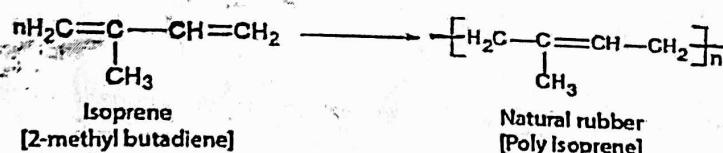
Applications of Dacron:

- Polyester (Dacron) is used for both as domestic fiber and industrial fiber.
- It is also used as glass reinforcing material in safety helmet, battery boxes, etc.
- It is blended with wool and cotton to provide better finish, wrinkle resistance, enhanced life.

Elastomers: Rubbers also known as elastomers. An elastomer is any vulcanisable man made rubber like polymer, which is superior to natural rubber in certain properties.

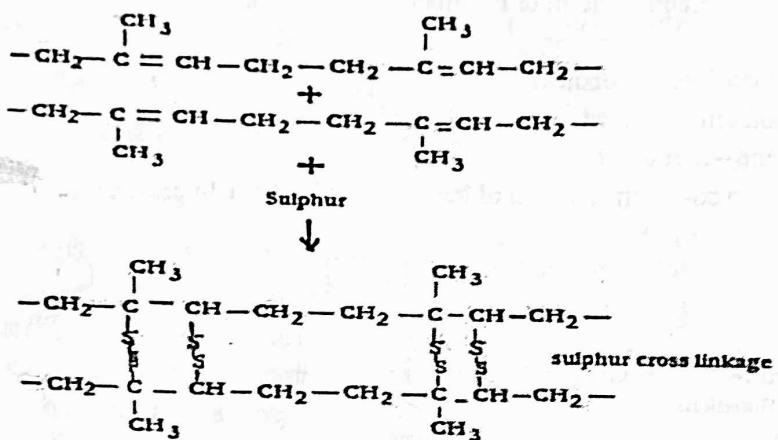
Ex: BUNA-S

Natural Rubber: it is obtained from a milk emulsion called latex by tapping the bark of the tree, "Hevea brasiliensis". It is a polymer of isoprene units.



Vulcanization:

- Vulcanization process discovered by Charles good year in 1839.
- The most important vulcaniser is 'Sulphur'
- The raw rubber is heated at 100-140C with sulphur.
- During the vulcanization process, rubber molecules are cross-linked with each other by heating the liquid rubber with sulphur, which combines chemically at the double bonds of different rubber chains and producing sulphur cross-linkings, imparting strength increases, the brittleness also increases.
- The amount of sulphur added determines the extent of stiffness of vulcanized rubber.



Advantages of vulcanization:

- The tensile strength increase.
- It has better resistance to moisture, oxidation and abrasion.
- It is resistance to organic solvents like CCl₄, Benzene petrol etc.
- It has only slight thickness.
- It has low elasticity.

Applications:

- The major application of natural rubber is in the manufacture of tyres.
- The tank linings in chemical plants where corrosive chemicals are stored are prepared from rubber.
- To reduce machine vibrations, rubber is used for sandwiching between two metal surfaces.
- Foam rubber is used for making cushions', matrices, etc. toys and sports items are manufactured from natural rubber.

Synthetic rubbers:

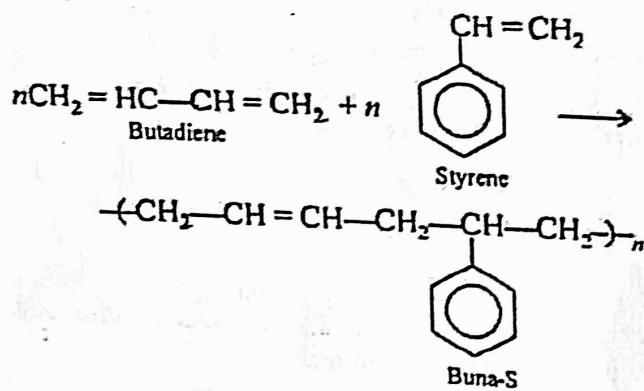
Synthetic rubber is an artificial elastomer mostly created from petroleum byproducts.

Approximately 70% of rubber is synthetic rubber.

Ex: Buna-S and Butyl rubber

BUNA - S:

- It is also called styrene rubber.
 - BUNA-S stands for the composition of the monomers and catalyst.
- 'Bu' stands for Butadiene – monomer
'Na' stands for sodium – catalyst
S stands for styrene – monomer
- It is produced by the co-polymerization of butadiene and styrene in presence of sodium.



Properties of Buna - S:

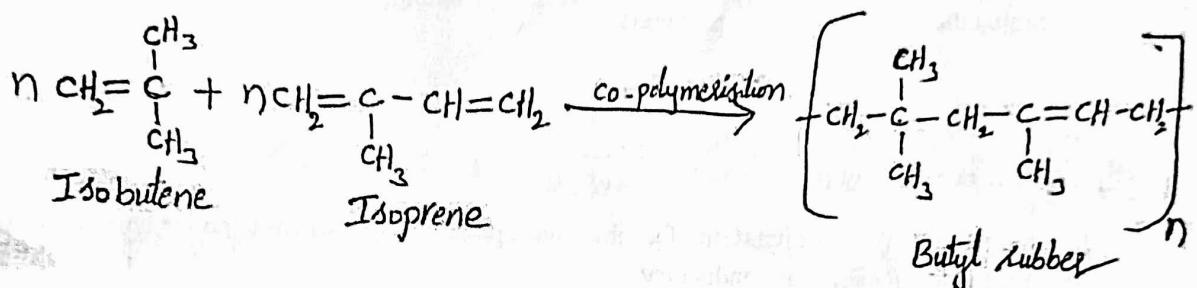
- It possesses high load-bearing capacity.
- It gets readily oxidized, especially in presence of traces of ozone present in the atmosphere.
- It swells in oils and solvents.
- It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride (S_2Cl_2).
- It requires less sulphur for vulcanization.
- It is a good electrical insulator.

Uses of Buna- S:

- It is mainly used for the manufacture of motor tyres.
 - It is used for floor tiles, shoe soles, gaskets, foot-wear components, wire-cable insulations, carpet backing, adhesives, and tank-linings.

Butyl rubber:

It is produced by co-polymerization of isobutene and isoprene.



Properties of Butyl rubber: Butyl rubber has following characteristics:

- It is a strong and tough synthetic rubber.
 - It has excellent resistance to heat.
 - It is a good electrical insulator.
 - High resistance to atmospheric gases.
 - It is soluble in hydrocarbon solvent.

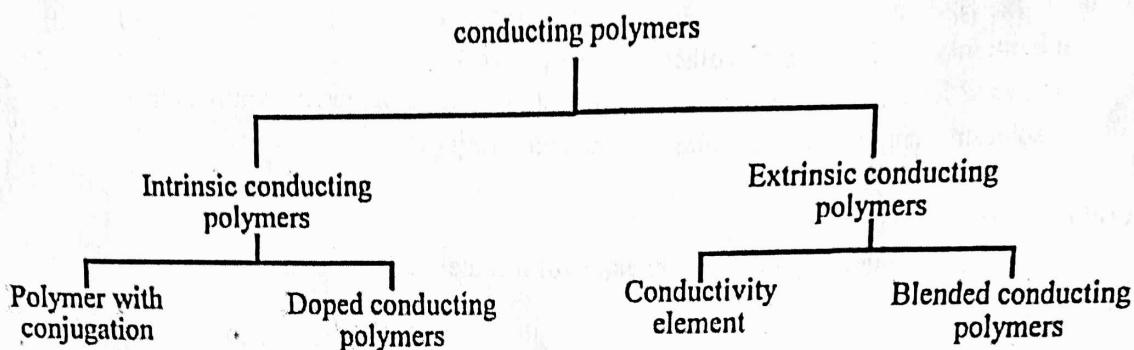
Applications of Butyl rubber: Butyl rubber used for

- Insulation of high voltage wires and cables.
 - Inner tubes of automobile tyres.
 - Conveyor belts for food and other materials.
 - Lining of tanks.

Conducting polymers:

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

Classification of conducting polymers:



I. Intrinsic conducting polymers:

In these polymers the conjugation of double bonds present in the structure (i.e the back bone the polymer) is responsible for conductance.

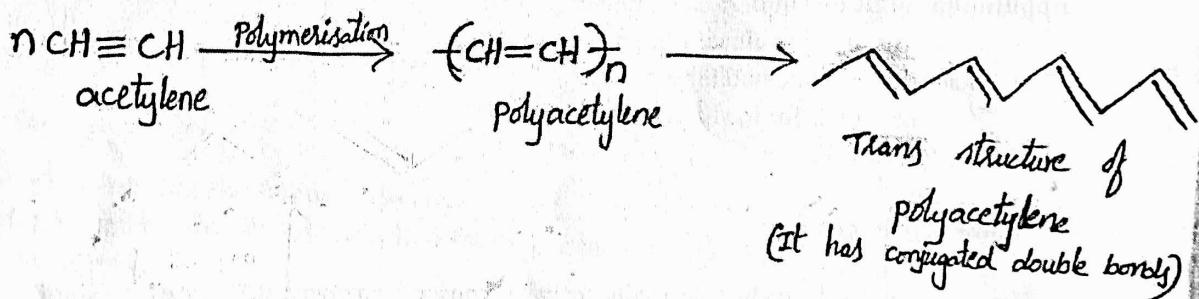
Intrinsic conducting polymers again classified into two types :-

(a) Conducting polymers with conjugation (b) Doped conducting polymers

a) Conducting polymers with conjugation:

Conductance is due to the π electrons present in the back bone of the polymer chain.

Ex: polyacetylene



b) Doped conducting polymers:

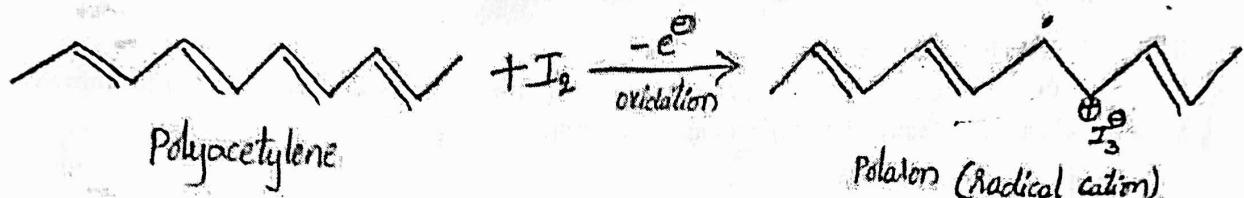
The conducting polymers having π electrons in their back bone structure can be easily oxidized or reduced. Hence the conductance can be increased by introducing a positive charge or negative charge on polymer back bone by oxidation or reduction is called doping.

i) p-doping (Creating a positive site on polymer back bone)

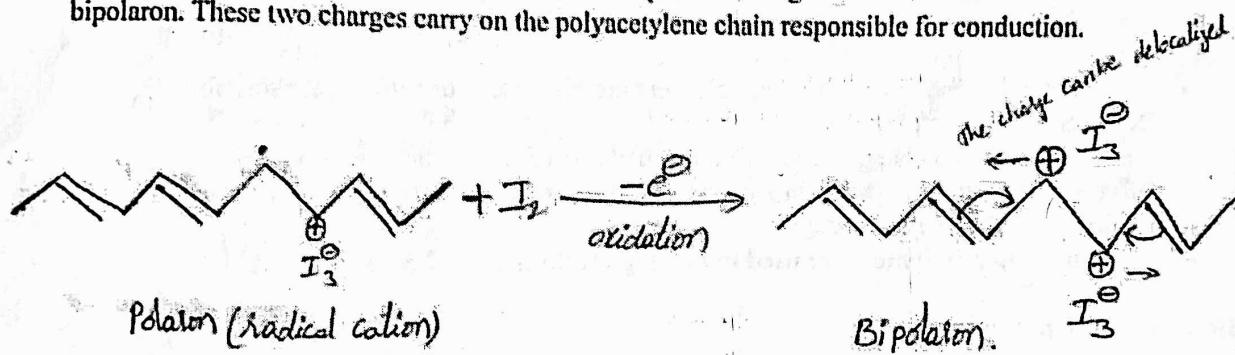
ii) n-doping (Creating a negative site on polymer back bone)

i) p-doping: it is done by oxidation of a conducting polymer with iodine vapour or a Lewis acid. This is called p-doping or oxidative doping.

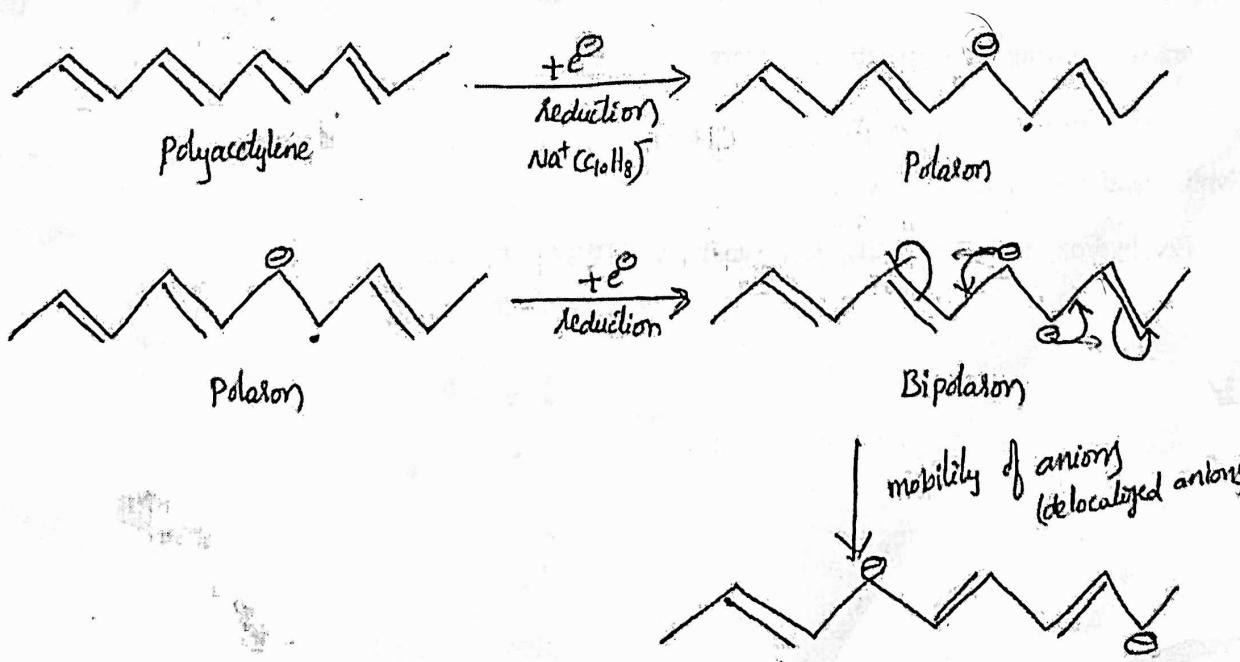
During the oxidation process the removal of π electron from polymer back bone lead to the formation of a delocalized radical cation called polaron.



The second oxidation of the polaron results in two positive charges in each chain called bipolaron. These two charges carry on the polyacetylene chain responsible for conduction.



ii) n-doping: it is done by reduction process by the addition of an electron to polymer back bone by using reducing agent like sodium naphthalide. Formation of polaron, bipolaron takes place in two steps. These two charges carry on the polyacetylene chain responsible for conduction.



Extrinsic conducting polymers:

The conductivity of these polymers is due to the presence of externally added ingredients in them.

Extrinsic conducting polymers again two types.

i) Conducting element filled polymer:

The polymer acting as a binder to hold the conducting element such as carbon black, metallic fibers.

These polymers possess reasonably good bulk conductivity and are low in cost light in weight mechanically durable and strong and easily processable in different forms shapes and size.

ii) Blended conducting polymers:

It is obtained by blending a conventional polymer with conducting polymer to improve physical, chemical, electrical and mechanical properties.

Applications of conducting polymers:

- In rechargeable batteries: These batteries are small in size, longer lasting and can produce current density up to 50mA/cm^2 .
- In analytical sensors: Conducting polymers are also used for making sensors for pH, O₂, NO_x, SO₂, NH₃ and glucose.
- For making Ion-exchangers: Membranes made up of them can show boundary layer effects with selective permeability for ions, gases, etc. They are useful for ion-exchangers and controlled release of drugs.
- The conducting polymers are used in making electronic displays and optical fibers.

Biodegradable polymers:

Those polymers which degrade by the enzymatic action of naturally occurring micro-organisms such as bacteria, fungi and algae are called biodegradable polymers.

The biodegradable polymers are classified as naturally occurring and synthesized polymers.

* Naturally occurring biodegradable polymers:

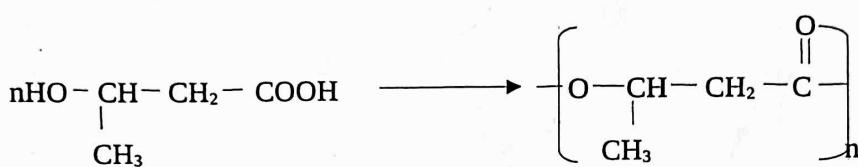
Ex: Starch, cellulose, silk and wool

* Synthesized biodegradable polymers:

Ex: Polyhydroxy butyrate (PHB), Polyglycolic acid (PGA), Polylactic acid (PLA).

Polyhydroxy butyrate (PHB):

3-Hydroxy butanoic acid monomers undergo polymerization and form polyhydroxy butyrate.

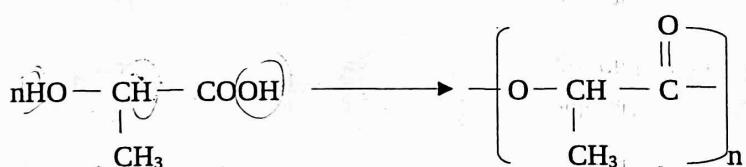


Properties of PHB:

- Its melting temperature is 180 °C.
- It is brittle and hard.
- Water insoluble but soluble in chloroform and other chlorinated hydrocarbons.
- Good ultra-violet resistance.

Poly lactic acid (PLA):

Poly lactic acid is a biodegradable aliphatic thermoplastic polymer. Lactic acid monomers undergo polymerization in the presence of stannous octate catalyst to give poly lactic acid.

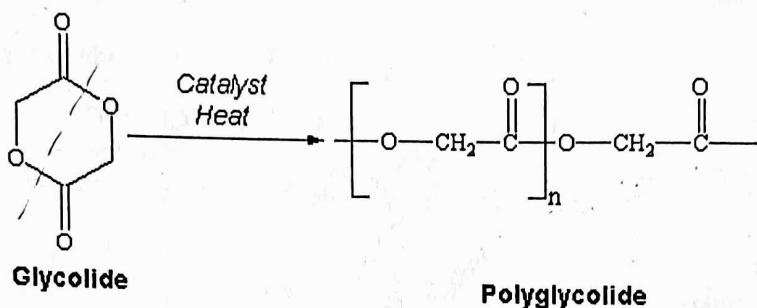


Properties of PLA:

- PLA is a hydrophobic polymer due to the presence of $-\text{CH}_3$ side groups.
- It is more resistant to hydrolysis than PGA.
- PLA has disadvantages of brittleness and poor thermal stability.
- It shows much lower tensile strength.

Polyglycolic acid or Polyglycolide (PGA):

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



Properties of PGA:

- PGA is the simplest linear aliphatic polyester.
- It is not soluble in most organic solvents.
- It has a high melting point.
- PGA has excellent mechanical properties.

D₄, E₄, F₄, H₄

Applications of Biodegradable polymers:

- It is used in the preparation of bioplastics like packing for food and disposable materials.
- It is mainly used in biomedical applications like sutures, stents, drug delivery devices and dialysis media.
- It is used in controlled release of drugs, medical implants and repairs, orthopedic devices and manufacturing bottles for consumer goods.
- Biodegradable polymers are used commercially in both the tissue engineering and drug delivery field of biomedicine.
- Biodegradable drug system for therapeutic agents such as anti tumor, antipsychotic agent, anti-inflammatory agent.
- Polymeric materials are used in and on soil to improve aeration, and promote plant growth and health.