

UNIT (III)

Polymeric materials

Definition – Classification of polymers with examples – Types of polymerizations –

addition and condensation polymerization with examples – Nylon 6:6, Terylene **Plastics:** Definition and characteristics- thermoplastic and thermosetting plastics, Preparation, Properties and engineering applications of PVC, Bakelite and Teflon.

Rubbers: Natural rubber and its vulcanization.

Synthetic Rubbers- Characteristics –preparation – properties and applications of Buna-S, Butyl and Thiokol rubber.

Conducting polymers: Characteristics and Classification with examples-mechanism of conduction in trans-polyacetylene and applications of conducting polymers.

Biodegradable polymers: Concept and advantages – Poly lactic acid and poly vinyl alcohol and their applications.

Polymer:

A polymer is a large molecule formed by repeating units of small molecules through covalent bonds.

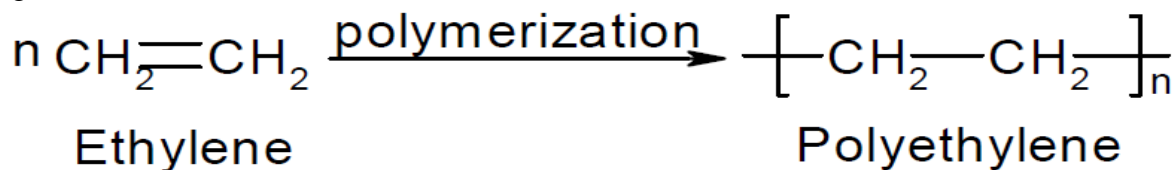
Monomer:

The simple molecule from which the polymer is formed is called monomer.

Degree of polymerization:

The number of monomeric units available in the polymer is known as degree of polymerization.

Eg:



Degree of polymerization = n

Polymerisation:

“The process in which the simpler molecules combine together to form very large molecule having high molecular weight is known as polymerization”. The molecule is known as polymer.

Classification of Polymers:

1. Classification based on **source of origin**
2. Classification based on **structure of monomer chain**
3. Classification based on **variety of monomers**
4. Classification based on **molecular forces**
5. Classification based on **polymerization**

1. Classification of Polymers based on source of origin

- a. **Natural polymers:** These are obtained from nature found in plants and animals. Examples- Natural Rubber, Starch, Cellulose, Protein etc.
- b. **Synthetic polymers:** These have been prepared by humans in laboratories (Man-made polymers). Eg: PVC, Bakelite, Teflon, Nylon-6,6 etc.

2. Classification of Polymers based on structure of monomer

- a. **Linear Polymers:** Monomers join with each other to form long straight chains. Eg: PolyVinyl Chloride, polystyrene and polypropylene.
- b. **Branched Chain Polymers:** In these polymers, monomers are joined to form long chains with side chains or branches of different lengths. They have low melting points and low densities. Eg: Low-density polyethylene (LDPE).
- c. **Cross-linked Polymers/Network Polymers:** These polymers are formed by bi-functional and tri-functional monomers with a strong covalent bond between the various linear polymer chains. Eg: Bakelite and melamine formaldehyde resin.

3. Classification of Polymers based on variety of the monomers

- a. **Homo-polymer:** When the same monomer is repeated throughout the chain of the polymer, it is called homo-polymer.
Eg: Polyvinyl Chloride, Polyethylene and Teflon
- b. **Hetero-polymer or Co-polymer:** When there are at least two different monomers along the entire chain, it is called co-polymer.
Eg: Nylon 6, 6 and Terelene,

4. Classification of Polymers based on molecular forces

- a. **Thermoplastics:** plastics which are softened on heating and harden on cooling are known as thermoplastics Eg: Polystyrene, polyethylene, polypropylene.
- b. **Thermosets:** Thermosets are the polymers that undergo chemical changes and crosslinking on heating and become permanently hard, rigid and infusible. They will not soften on heating, once they are set. Eg: Bakelite, melamine.
- c. **Elastomers:** Polymer chains that are elastic and can be stretched like rubber. They have weak intermolecular forces between the chains and may have cross bonds.
Eg: Vulcanized rubber.

- d. Fibers:** They have strong intermolecular forces hydrogen bonds between their chains. These chains have a high tensile strength and less elasticity, and high melting points.

Eg:Silk, Nylon etc.

5. Classification of Polymers based on polymerization

a. Addition polymers Or Chain growth polymers:

Polymerization in which monomers are added together to form polymer without elimination of simple molecules is called addition polymerization and polymers are called addition polymers.

Eg: Polyvinyl chloride and Teflon

- b. Condensation polymers:** Polymerization in which monomers are added together to form polymers with elimination of simple molecules like water, NH₃, HCl etc. is called condensation polymerization and polymers are called condensation polymers

Eg: Nylon-6,6 and Poly ethylene terephthalate (PET)

Types of polymerization

a. Addition polymers Or Chain growth polymers:

Polymerization in which monomers are added together to form polymer without elimination of simple molecules is called addition polymerization and polymers are called addition polymers.

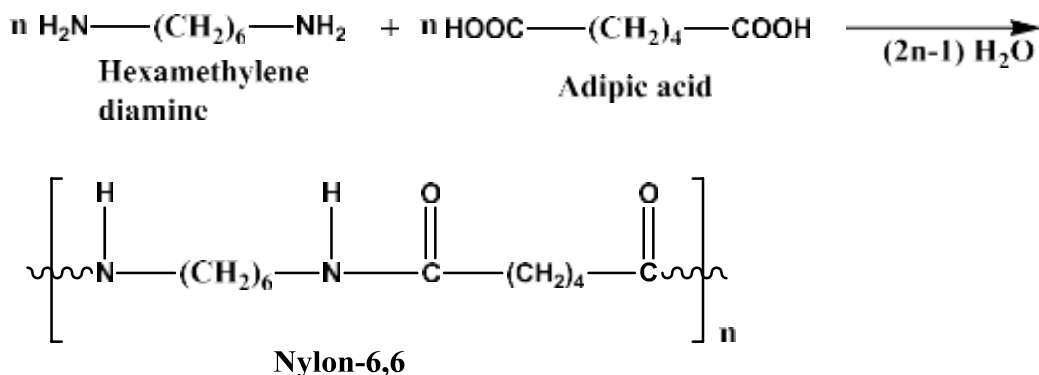
Eg: Polyvinyl chloride (PVC), polystyrene and Teflon



- Monomers must have either a double bond or triple bond (unsaturated compounds)
- Molecular weight of the resulting polymer product is the exact multiple of monomers molecular weight.
- In addition polymerization, no by products will be formed.
- It follows three step mechanism of initiation, propagation, and termination.

- b. Condensation polymers or Step growth polymerization:** Polymerization in which monomers are added together to form polymers with elimination of simple molecules like water, NH₃, HCl etc. is called condensation polymerization and polymers are called condensation polymers.

Eg: Nylon-6,6 and Poly ethylene terephthalate (PET)



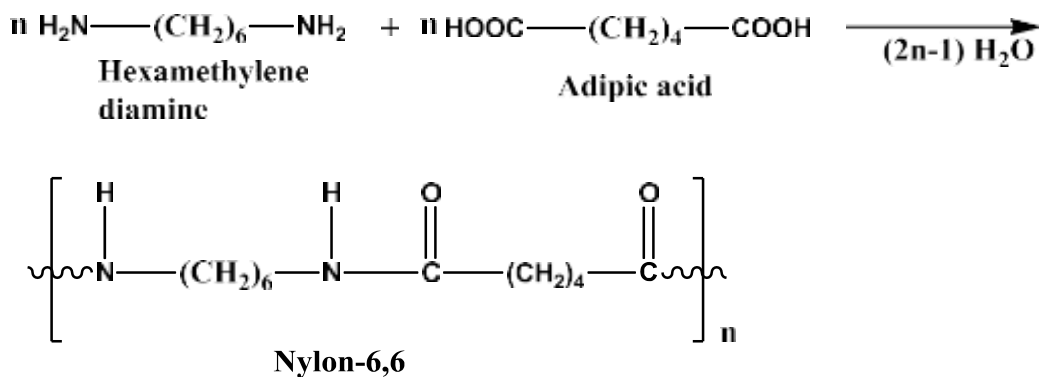
- The monomers contain functional groups like $-\text{COOH}$, $-\text{CHO}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{COOR}$ and halides etc.
- Monomers must have two similar or different functional groups.
- In this polymerization by-products will be formed like H_2O , NH_3 , HCl etc.

Differences between addition and condensation polymerization:

S. No.	Addition polymerization	Condensation polymerization
1	It is also called as Chain growth polymerization	It is also called as step growth polymerization
2	monomers are added together to form polymer without elimination of simple molecules	monomers are added together to form polymers with elimination of simple molecules
3	Monomers must have either a double bond or triple bond	Monomers must have two similar or different functional groups
4	Produces no by-products	By-products such as ammonia, water and HCl are produced
5	molecular weight of the polymer is an integral multiple of molecular weight of monomer	molecular weight of the polymers need not be an integral multiple of monomer's
6	It follows three step mechanism of initiation, propagation, and termination.	It not follows three step mechanism
7	Examples Polyethene, polypropene, PVC, Teflon	Examples : Nylon-6,6, Bakelite

1. Nylon 6,6:

Preparation: It is a polyamide. It is prepared by the condensation of hexamethylene diamine and adipic acid.



Properties:

1. They are insoluble in common solvents and dissolve only in phenols and formic acid.
2. They possess high temperature stability and high melting point ($>500^\circ\text{C}$).
3. They absorb moisture.
4. They have good mechanical strength and self-lubricating properties.
5. They are light, flexible and retain their original shape after use.

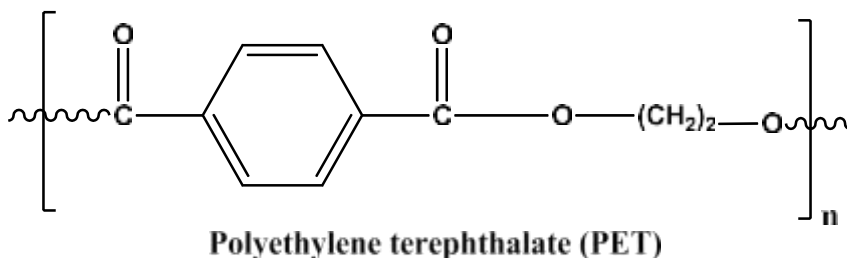
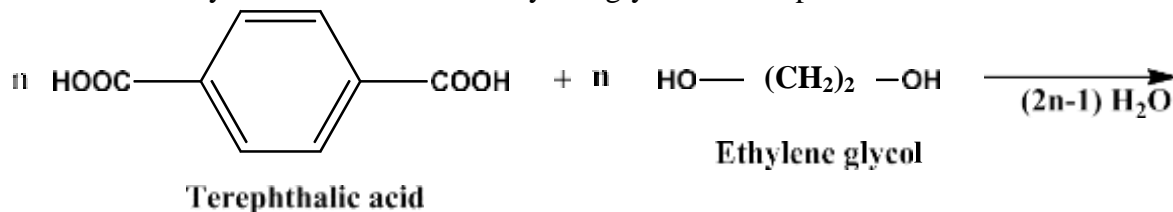
Applications:

1. The major application is in textile industry.
2. They are used in making socks, dresses, nets, carpets and ropes.
3. It can be blended with wool.
4. Because of its high thermal & abrasion resistance nylons are used in automobile industry (gears, bearings, electrical mountings, radiator parts). These bearings and gears work quietly without any lubrication.
5. Nylons are used as electrical insulators.
6. They are also used for making bristles for tooth brushes, films and tyre cords.

2. Poly ethylene terephthalate (PET) or Terylene or Dacron:

Preparation:

It is made by the condensation of ethylene glycol and terephthalic acid.



Properties:

1. They are insoluble in common solvents and resistance to acids.
2. They are high crease and wrinkle resistant's.
3. They are stable at high temperature.
4. They absorb very little moisture.

Uses:

1. They are used in textile industry to make hard ware cloths like sarees, and dress materials.
2. It can be blended with wool and cotton to make more variety of cloths.
3. It is used for ropes, hoses and threads.
4. It is used for making containers (soft drinks, water, food item packing and others purpose).

Plastics

Plastics are high molecular weight organic materials, which can be moulded into any desired form by the application of heat and pressure.

Eg: Polyethylene, Polystyrene, Polyvinyl chloride etc.

Plastics are classified into two types. 1) Thermoplastics 2) thermosetting

Thermoplastic polymers (Thermo plastics): 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.

Eg: Polyethylene, polystyrene, PVC, Polypropylene

- These are formed by addition polymerization.
- These are linear polymers without any cross linking.
- The plasticity of these plastics is reversible.
- These are weak, soft and less brittle.
- Polymeric chains are held together by weak van der Waals forces.
- These are soluble in some organic solvents.
- These can be reclaimed from waste.

Thermosetting polymers (Thermosets): Thermosets are the polymers that undergo chemical changes and crosslinking on heating and become permanently hard and rigid. They will not soften on heating, once they are set.

Eg: Phenol formaldehyde resin (Bakelite), urea formaldehyde resin, melamine formaldehyde resin.

- These are formed by condensation Polymerization.
- These are three dimensional cross linked polymers.
- The plasticity of these plastics is irreversible.
- These are strong, hard and more brittle.
- Polymeric chains are held together by strong covalent bonds in the form of cross links.
- These cannot be reclaimed from waste.
- These are insoluble in almost all organic solvents.

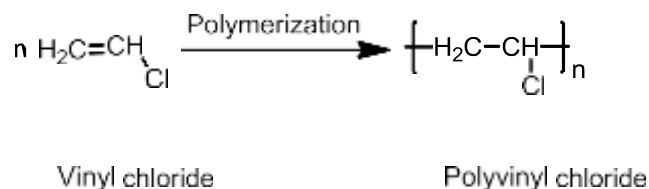
Distinguish between thermoplastics and thermosetting plastics

	<i>Thermoplastic polymers</i>	<i>Thermosetting polymers</i>
1	On heating they become <i>soft and on</i> cooling become hard.	Plastics which are hardened on heating and cannot be softened by any means
2	They are formed by <i>addition Polymerization</i> .	They are formed by <i>condensation Polymerization</i> .
3	They can be reclaimed from wastage.	They can't be reclaimed from wastage.
4	These are linear polymers without any cross linking.	These are three dimensional cross linked polymers.
5	The plasticity of these plastics is reversible.	The plasticity of these plastics is irreversible
6	By heating to a suitable temperature, <i>they can be softened, reshaped</i> and thus <i>reused</i> .	They retain their shape and structure, even on heating. Hence, they cannot be <i>reshaped</i> and <i>reused</i> .
7	Polymeric chains are held together by weak van der waals forces	Polymeric chains are held together by strong covalent bonds in the form of cross links.
8	These are weak, soft and less brittle.	They are, usually <i>hard, strong</i> and <i>more brittle</i> .
9	They are, <i>soluble</i> in some organic solvents.	Due to strong bonds and cross-linking, they are <i>insoluble</i> in almost all organic solvents.
10	Examples polythene, PVC, Polystyrene etc.	Ex: Nylon-6,6, Bakelite etc.

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

1. Polyvinyl chloride (PVC):

Preparation: Polyvinyl chloride is prepared by the addition polymerization of vinyl chloride in presence of benzoyl peroxide or hydrogen peroxide as catalyst and under pressure.



Properties:

1. PVC is a colorless and odourless powder.
2. It is chemically inert and non-inflammable and exhibits high resistance to atmospheric conditions.
3. It is having high density.
4. It is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons.
5. It has melting point 148 °C.

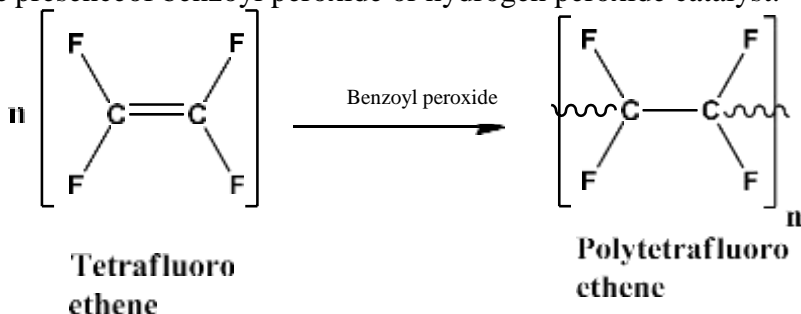
Applications:

It is used for

- a) Electrical insulations like covering of electrical cables.
- b) The production of pipes, Making sheets, window frames,
- c) Tank- linings, light-fittings, safety helmets, refrigerator components.
- d) tyres, cycle and motor cycle mudguards and chemical containers.
- e) Plasticized PVC is used for making packing rain coats, table-cloths and curtains, jackets and bags.

2. Poly tetrafluoro ethylene (PTFE) or Teflon**Preparation:**

Polytetra fluoro ethylene is prepared by the addition polymerization of tetrafluoro ethylene gas under pressure in the presence of benzoyl peroxide or hydrogen peroxide catalyst.

**Properties:**

1. Teflon also known as fluon. Due to the presence of high electronegative fluorine atoms. There are strong attractive force is responsible for high chemical resistance towards all chemicals except hot alkali metal and hot fluorine.
2. It shows nonstick property.

Applications: It is used for making

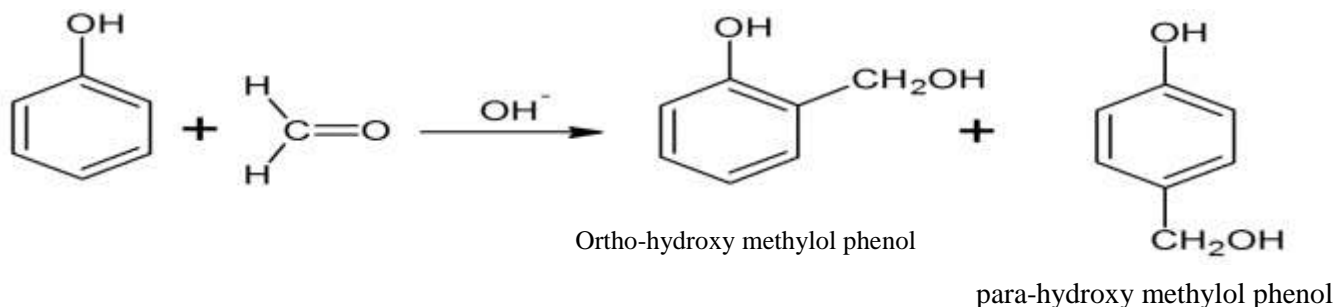
1. Oil seals and gaskets.
2. Stopcock for burettes.
3. Insulating of electrical items like cables.

4. Chemical carrying pipes and tank linings.
5. Non-stick surface coated utensils.

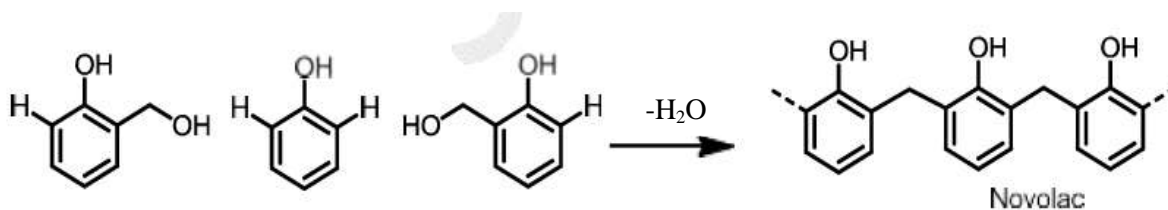
3. Bakelite or phenol-formaldehyde resin:

Preparation: Bakelite is prepared by the condensation polymerization of phenol and formaldehyde in the presence of acidic or alkali catalyst.

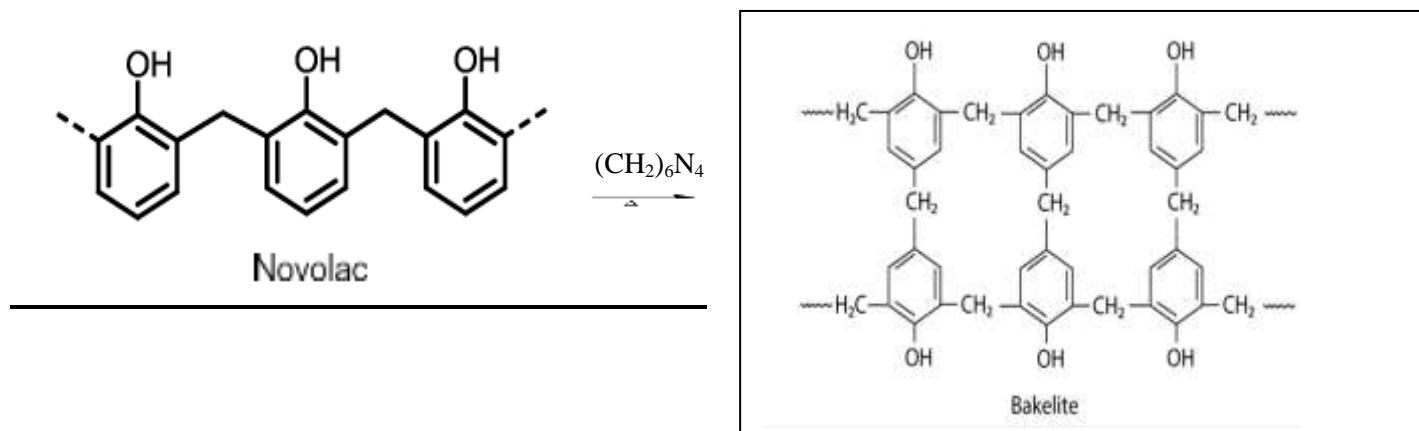
The initial reaction results in the formation of ortho-hydroxy methylol phenol.



Methylol phenols react with each other to form intermediate compound called novolac.



Heating of novolac with hexamethylene tetramine gives bakelite.



Properties:

1. Bakelites are very hard, strong and rigid materials.
2. These are scratch and water-resistant infusible and insoluble solids.
3. These are resistant to non-oxidizing acids, salts and many organic solvents, but are attacked by alkalis, because of the presence of free hydroxyl group in their structures.
4. They possess excellent electrical insulating character.

Applications:

1. Bakelite is used for non-conducting parts of telephones, radios and other electrical devices, including switches, plugs, switch-boards, heater-handles, bases and sockets for light bulbs and electron tubes, supports for any type of electrical components, automobile distributor caps and other insulators.
2. As adhesives (binder) for grinding wheels.
3. In paints and varnishes.
4. For impregnating fabrics, wood and paper.
5. It is also used in jewelry, kitchenware, pipe stems, children's toys, and firearms

Rubbers:

Rubber is an elastomer—that is, a polymer that has the ability to regain its original shape after being deformed. Rubber is made by the polymerization of Isoprene (2-methyl-1,3-butadiene). Ex: Buna-S, Neoprene etc.

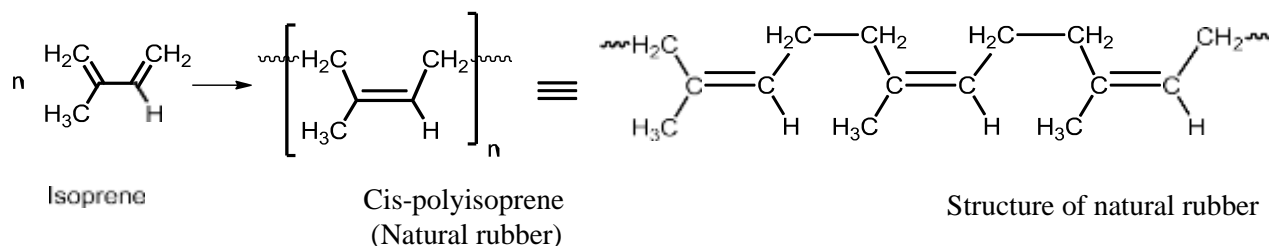
Types of rubber

There are two primary types of rubber, namely

1. Natural rubber and
2. Synthetic rubber.

Natural rubber:

The main source of natural rubber is the species of tree known as *Hevea brasiliensis* and *guayule*. Natural rubber is a polymer of isoprene (2-methyl-1,3-butadiene). Isoprene units undergo addition polymerization and give polyisoprene called natural rubber.



Drawbacks of raw rubber:

Raw rubber has the following drawbacks:

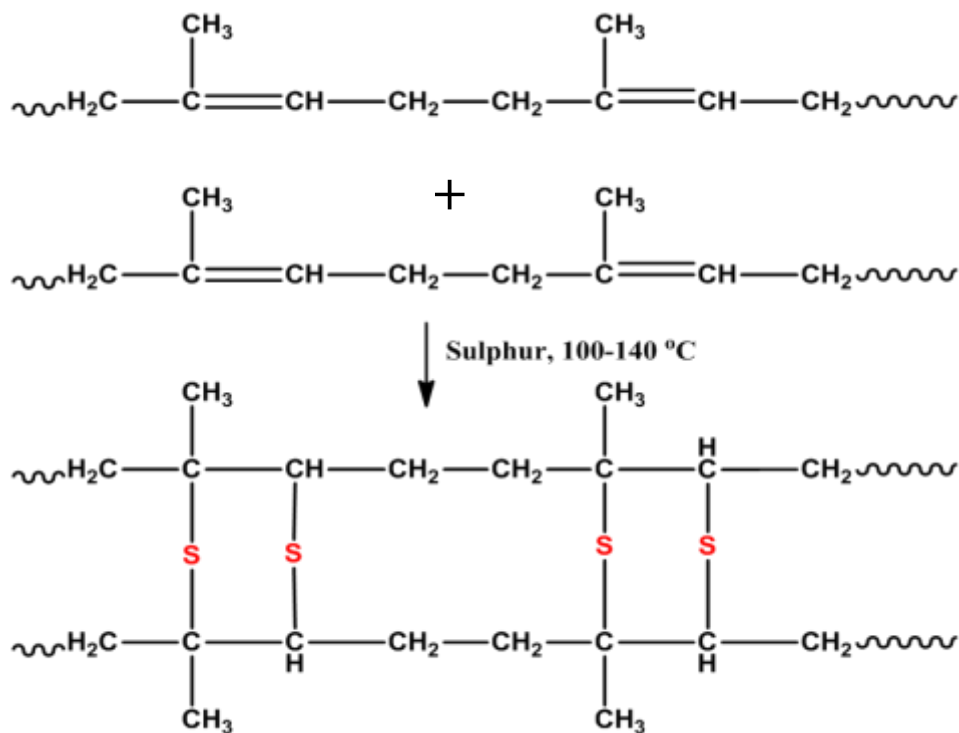
1. It is hard and brittle at low temperature and soft and sticky at high temperature.
2. It is soft and soluble in many hydrocarbon solvents and carbon disulphide (CS₂).
3. It has high water absorption power.
4. It is a sticky substance, rather difficult to handle.
5. It is readily attacked by acids and alkalis.
6. It has low tensile strength (200 kg/cm²).
7. It has poor abrasion resistance.

Vulcanization:

Vulcanization is a process of heating the raw rubber with sulphur at 100-140°C. The sulphur combines chemically at the double bonds of different rubber molecules and provides cross-linking between the chains. The degree of vulcanization depends on the amount of sulphur used.

Advantages of vulcanization:

1. The tensile strength of vulcanized rubber is very good (2,000 kg/cm²).
2. It has excellent resilience i.e., articles made from it returns to the original shape when the deforming load is removed.
3. It has better resistance to moisture, oxidation and abrasion.
4. It has broader useful temperature range (-40 to 100°C) compared to raw rubber's useful temperature range (10-60°C).
5. It is resistant to i) organic solvents like petrol, benzene, CCl₄, ii) fats and oils, but it swells in them.
6. It has only slight tackiness.
7. It has low elasticity. Their property depends on the extent of vulcanization.
8. It is very easy to manipulate the vulcanized rubber to produce the desired shapes.



Vulcanised rubber

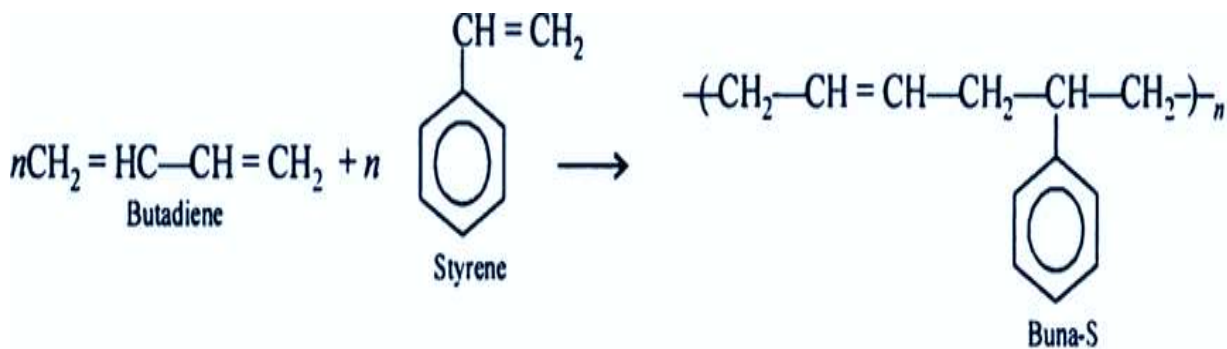
Synthetic Rubber:

It is any vulcanisable man-made rubber like polymer, which can be stretched to at least twice its length, but it returns to its original shape and dimension as soon as stretching force is released. Ex: Buna-S, Neoprene and butyl rubber etc.

Styrene rubber (Buna-S):

Preparation:

It is prepared by the co-polymerization of emulsion of butadiene (about 75% by weight) and styrene (about 25% by weight) in the presence of peroxide or Na.



BUNA-S stands for the composition of the monomers and catalyst.

“Bu” stands for the Butadiene – monomer

“Na” Stands for the sodium – Catalyst.

“S” stands for the Styrene – monomer.

Properties:

1. It possesses high abrasion resistance, high load bearing capacity and resilience.
2. It gets readily oxidized especially in presence of traces of ozone present in the atmosphere.
3. It swells in the oils and solvents.
4. It is a good electrical insulator.

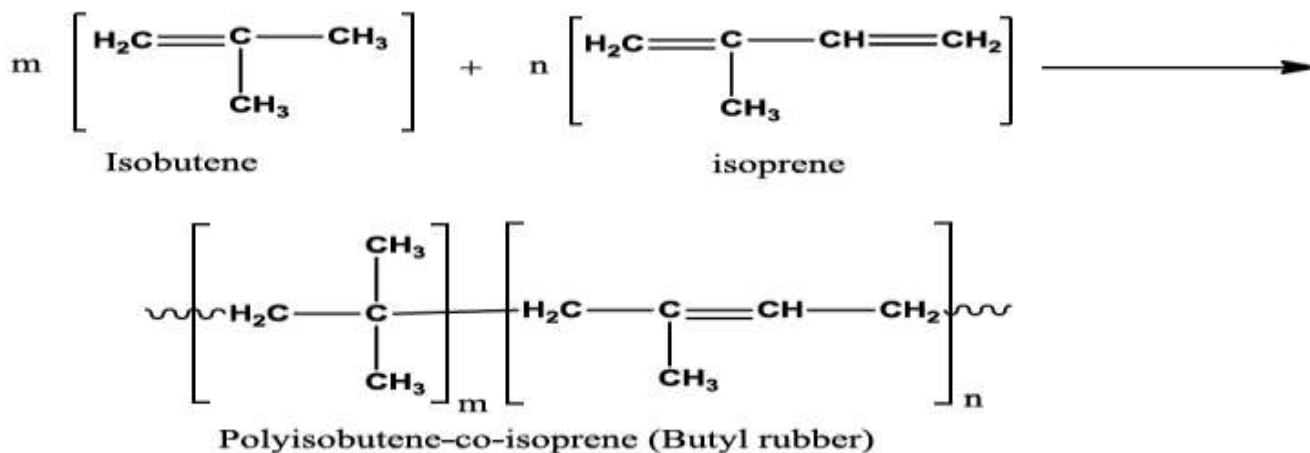
Uses:

1. It is used for the manufacture of car, bike and cycle tyres.
2. Other uses of this elastomer are floor tiles, shoe soles, foot wear components, gaskets, wire and cable insulations, adhesives, tank-lining, carpet backing, conveyor belts, hose, and brake and clutch pads.

Butyl rubber:

Preparation:

It is made by copolymerization of isobutene with small amount (1-5%) of isoprene.



Properties:

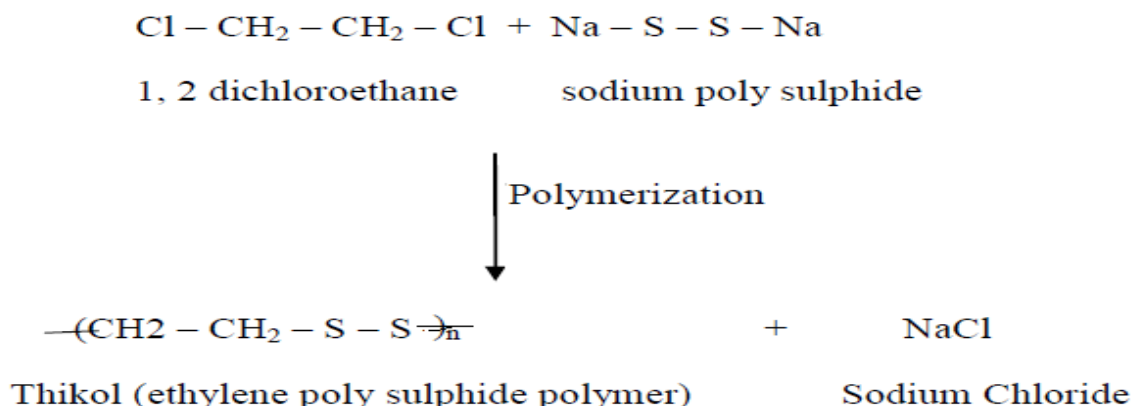
1. It is a strong and tough synthetic rubber.
2. It has excellent resistance to heat, abrasion, ageing and chemicals.
3. It is highly resistant to atmospheric gases and to ozone.
4. It is a good electrical insulator.

Uses:

1. It is used for insulation for high voltages wires and cables.
2. It is used for making cycle and other automobile tubes (Inner tubes).
3. It is also used for making hoses, gloves, gas masks, tank linings, conveyor belts and chewing gums.

Thiokol rubber:

Thiokol rubber can be prepared by the condensation of 1, 2-dichloroethane with sodium polysulphide.



Properties

- Thiokol rubber is resistant to the action of oxygen, ozone and also to the action of petrol, lubricants and solvents.
- Thiokols outstanding resistance to swelling by organic solvents but benzene and its derivatives cause some swelling.
- This rubber cannot be vulcanized because its structure is not similar to natural rubber and it cannot form hard rubber.
- Thiokol films are impermeable to gases to a large extent
- The odour of Thiokol is very bad.

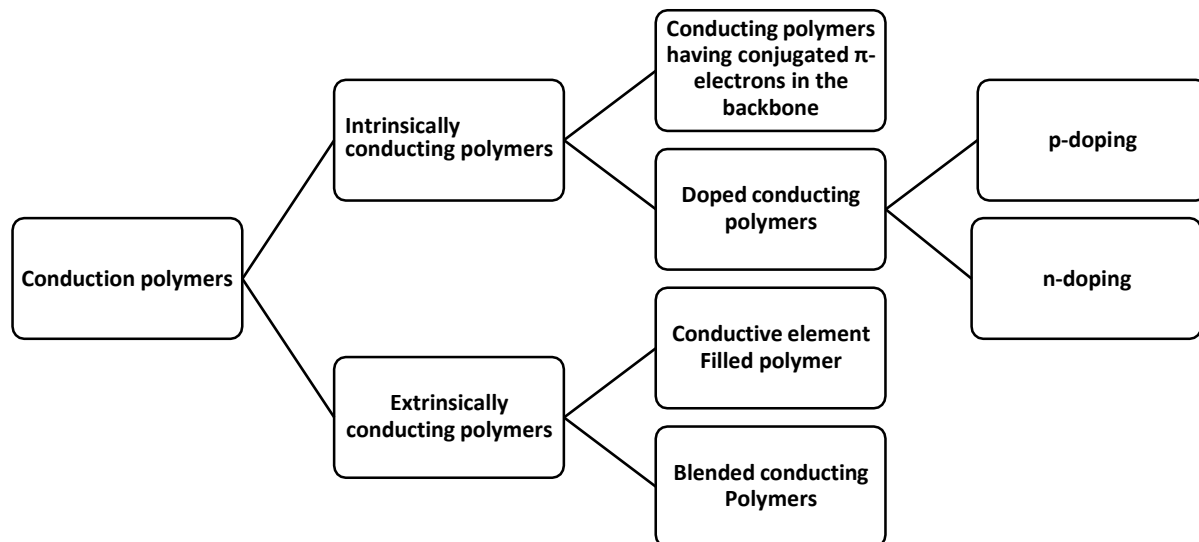
Uses

1. It is used in making engine gaskets, hoses and tank linings for the handling and storage of oils and solvents.
2. It is used in lining of vessels used in the manufacture of chemicals.
3. Thiokol mixed with oxidizing agents is used as a solid propellant fuel in rocket engine.
4. It is also used for printing rolls.

Conducting polymers:

A polymer that can conduct electricity is known as *conducting polymer*.

Classification: Conducting polymers can be classified as follows.



Intrinsically conducting polymers:

The polymers have extensive conjugation in the backbone which is responsible for conductance.

These polymers are classified into two types.

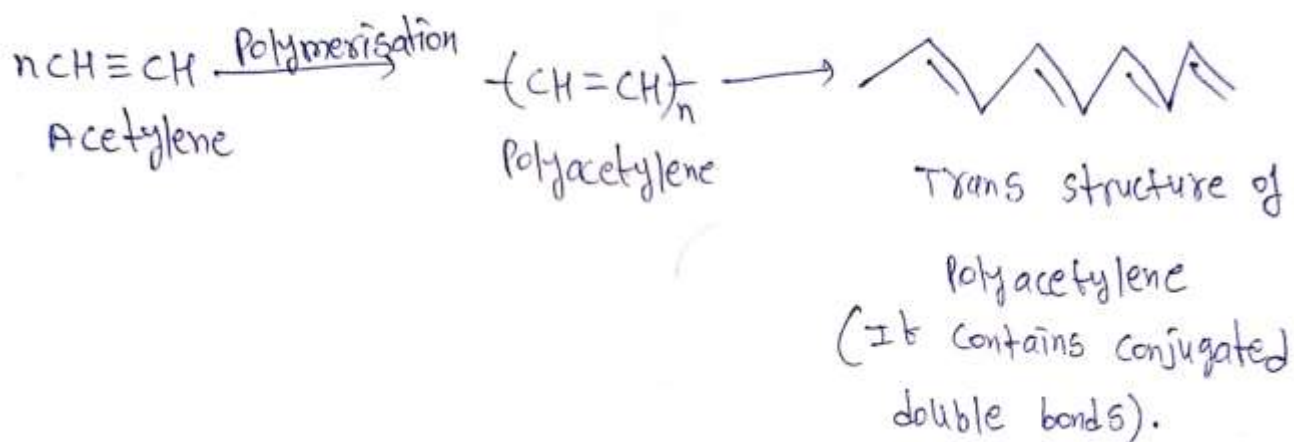
Conducting polymers having conjugated π -electrons in the backbone:

Such polymers contain conjugated π -electrons in the backbone which increases their conductivity to a large extent.

Explanation: Overlapping of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands that extends over the entire polymer molecule. The valence band and the conduction bands are separated by a significant band gap. Thus, electrical conduction occurs 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.

Examples of polymers in this category are polyacetylene, polyaniline, polypyrrole and polybutadienylene. Conductivity of such polymers is of the order of $10^{-10} \text{ Scm}^{-1}$.

Ex: polyacetylene



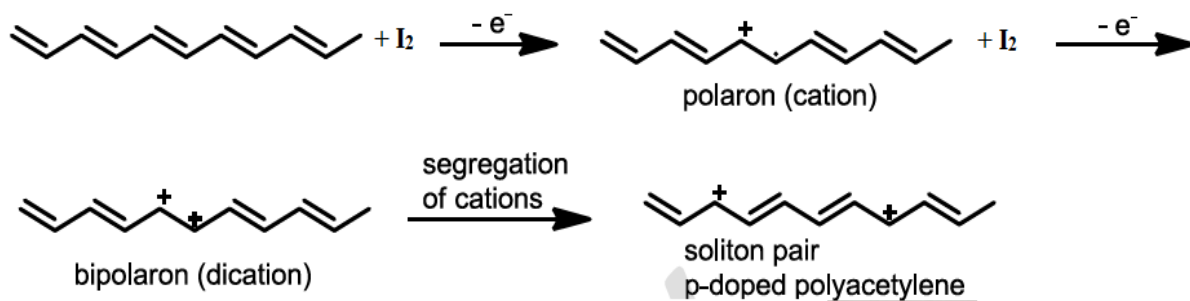
Doped conducting polymers:

The conducting polymers having conjugated π -electrons in their backbone structure can be easily oxidized or reduced. Hence the conductance can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. It is referred to as doping.

This is of two types.

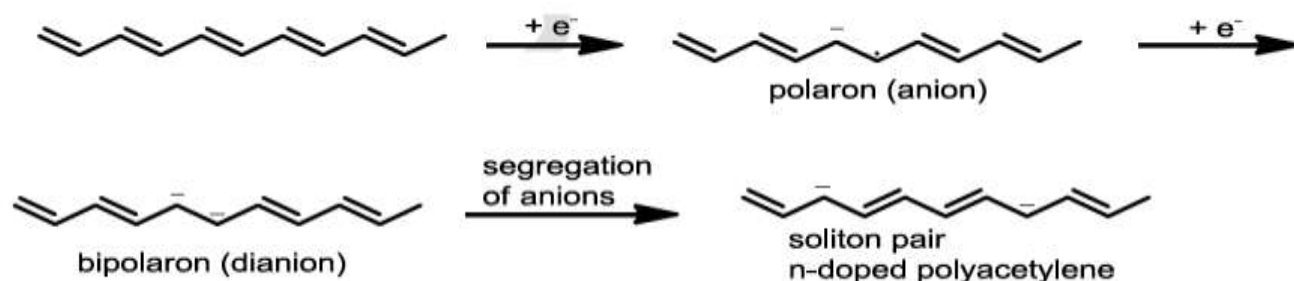
- a) p-doping or oxidative doping
- b) n-doping or reductive doping

p-doping: It is done by oxidation of conducting polymer with a Lewis acid or I_2 vapour or I_2 in CCl_4 . This is called p-doping or oxidative doping. During the oxidation process the removal of π electron from polymer backbone leads to the formation of delocalized radical cation called 'Polaron'. These delocalized positive charges are current carriers for conduction. The common p-dopants used are I_2 , Br_2 , AsF_5 , PF_6 .



The second oxidation of the polaron results in two positive charges in each chain called bipolaron.

n-doping: n-doping is done by reduction process. N-doping involves the treatment of an intrinsically conducting polymer with a Lewis base like Na, Li, sodium naphthalide. n-doping leads to the formation of polaron and bipolaron in two steps. This followed by recombination of radicals yields two negative charge carriers on each chain of polyacetylene which are responsible for conduction.



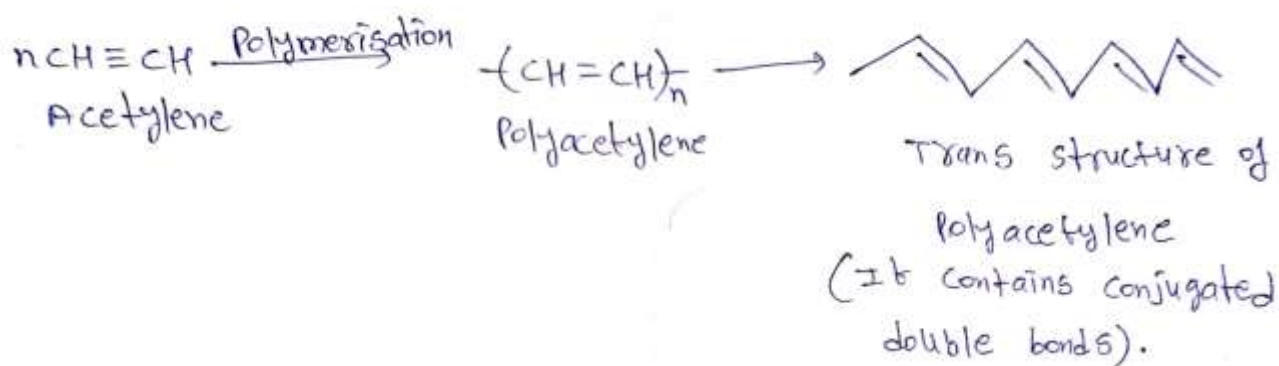
Extrinsically conducting polymers:

These are the polymers whose conductivities due to the presence of externally added ingredients in them. These are of two types.

Conductive element filled polymer: In this type, the polymer acts as the binder to hold the conducting element such as carbon black, metallic fibers.

Minimum concentration of conductive filler which should be added so that the polymer starts conducting is known as 'percolation threshold'. These polymers possess reasonably good bulk conductivity. They are generally low in cost, light in weight, mechanically durable and strong and are easily process able in different forms, shapes and sizes.

Ex: Polyacetylene



Blended conducting polymers: These polymers are obtained by blending a conventional polymer with a conducting polymer to improve physical, chemical, electrical and mechanical properties.

Applications of Conducting Polymers:

1. In rechargeable batteries: These are about 10 times lighter than conventional lead storage batteries. These can produce current density up to 50 mA/cm^2 .
2. In electrochromic displays and optical filters: ICP's can absorb visible light to give coloured products so can be useful for electrochromic displays and optical filters. Thus the conducting polymers can be used as electrochromic materials i.e., the materials that change colour reversibly during the electrochemical processes of charge and discharge.
3. In wiring in aircrafts and aerospace components.
4. In analytical sensors: for making sensors for pH, O_2 , NO_x , SO_2 , NH_3 and glucose.
5. In telecommunication systems.
6. In electromagnetic screening materials.
7. In electronic devices such as transistors and diodes.
8. In solar cells, drug delivery system for human body etc.,
9. In photovoltaic devices.
10. Membranes made up of conducting polymers can show boundary layer effects with selective permeability for ions, gases etc., Hence they are useful for ion exchangers and controlled release of drugs.

Biodegradable polymers:

Biodegradable polymers are defined as the degradable polymers in which degradation is caused by the action of naturally occurring microorganisms such as algae, fungi and bacteria. They are easily compostable. During composting, they yield CO₂, N₂, H₂O, inorganic compounds and biomass at a rate consistent with other compostable materials without leaving toxic residues.

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

Naturally occurring biodegradable polymers:

Ex: starch, cellulose, silk and wool.

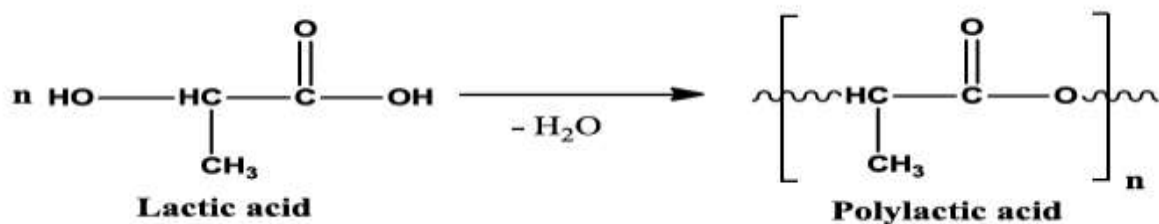
Synthesized biodegradable polymers:

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

Polylactic acid or polylactide (PLA)

Preparation:

Poly lactic acid is a biodegradable thermoplastic polymer. It is synthesized by the polycondensation reaction of lactic acid.



Properties:

1. It is a thermoplastic, meaning it will turn into a liquid in its melting point of 150-160 °C.
2. It is insoluble in water. But it is soluble in solvents, hot benzene, tetrahydrofuran, and dioxane.
3. PLA is a hydrophobic polymer due to the presence of –CH₃ side groups.

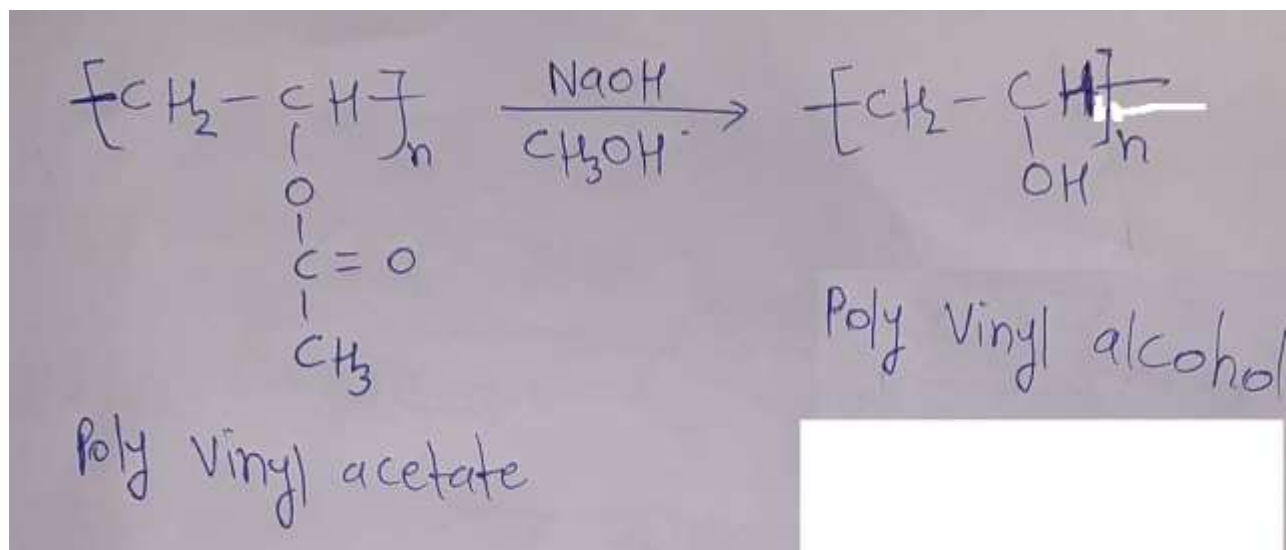
Applications:

1. It is used in a number of biomedical applications such as sutures, stents, drug delivery devices and dialysis media.
2. It is used as medical implants in the form of anchors, screws, plates, pins, rods, and as a mesh.
3. It can be in the form of fibers and nonwoven textiles; potential uses: upholstery, disposable garments and diapers.
4. It is used in the preparation of bio-plastics for packing food and disposable tableware.

poly vinyl alcohol (PVOH, PVA)

Preparation:

PVA prepared from polyvinyl acetate by acid or base, hydrolysis process with methanol or ethanol, as shown below.



Vinyl alcohol does not exist in its free state because it is unstable; it forms a stable tautomer, acetaldehyde. As a result, polyvinyl acetate is used as the starting material for the manufacture of polyvinyl alcohol.

Properties:

1. It is a Water-soluble synthetic polymer and is odorless.
2. dissolution in water is slow while faster in hot water
3. is easily degradable by biological organisms

Applications:

1. Polyvinyl Alcohol is a water soluble polymer used widely in adhesives, paints, sealants, coatings, textiles, plastics, etc.
2. It is used in papermaking, textile warp sizing, as a thickener and emulsion stabilizer in polyvinyl acetate (PVAc) adhesive formulations, in a variety of coatings, and 3D printing.
3. PVA is used in a variety of medical applications because of its biocompatibility, low tendency for protein adhesion, and low toxicity. Specific uses include cartilage replacements, contact lenses, and eye drops.