

UNIT - IV

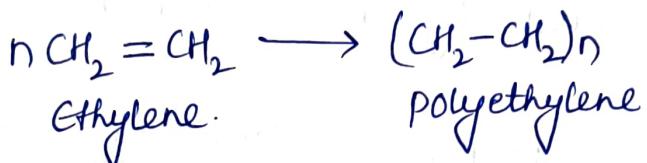
POLYMERS & MATERIALS

Define polymers explain the degree of polymerisation (3min)

POLYMERS:

The word polymer is derived from Greek word

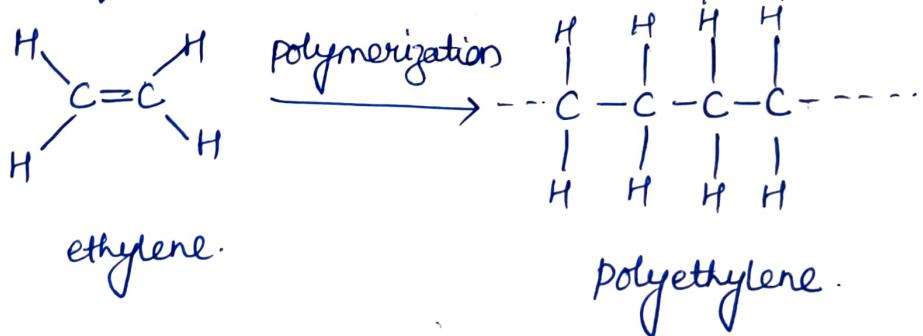
Polys - many, mers - parts. Polymers are large molecules composed of repeated chemical units. The smallest repeating units ~~are~~ called monomer. mono single, mer - part. It is described in terms of single repeated units such as.



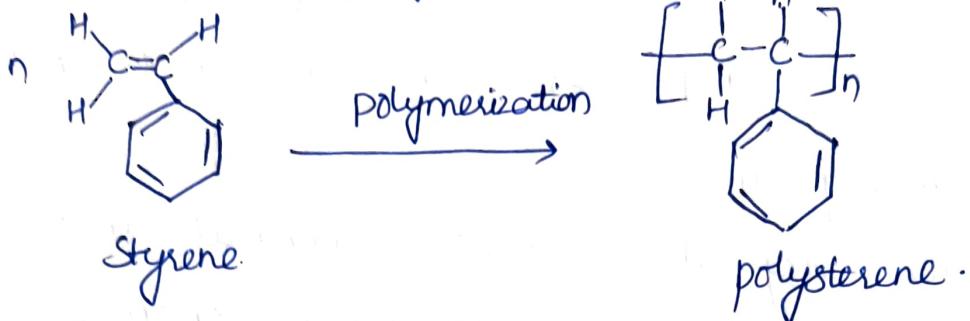
DEFINITION:

Polymers is a macromolecule built up by linking together of a large number of smaller molecule called monomers.

Eg: polyethylene is a polymer formed by linking together of a large number of ethylene molecule



The process by which the simple molecules (monomers) are converted into polymers is called polymerization.



Degree of polymerisation:

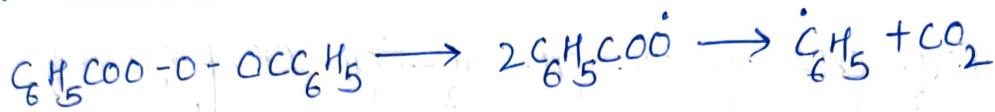
The number of repeating units (n) in a polymer chain is known as degree of polymerisation. It is represented by the relationship.

$$\text{Degree of polymerisation} = \frac{\text{Molecular weight of polymeric network}}{\text{Molecular weight of repeating unit.}}$$

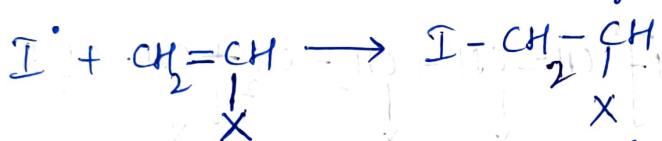
Example: Let the number of repeating units (n). If 100 molecules of ethylene polymerize to give polymer chain, the degree of polymerisation of ethylene is 100.

Free Radical chain Polymerisation:

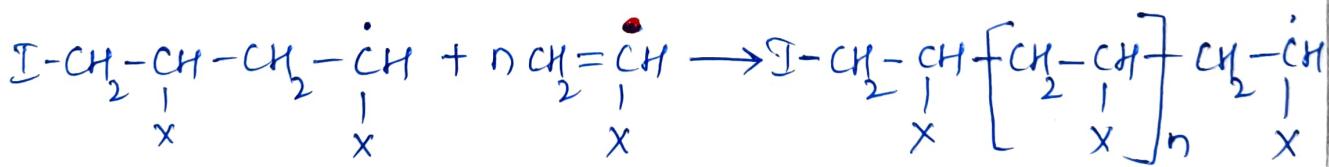
The initiator undergoes homolytic fission to produce free radicals. Benzoyl peroxide, hydrogen peroxide are good initiators.



a) Initiation: Initiators are unstable compounds and undergo homolytic fission to produce free radicals.



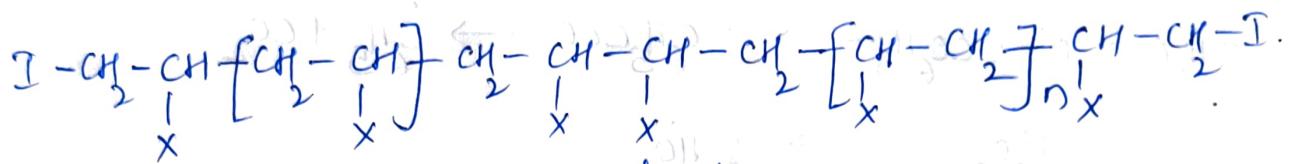
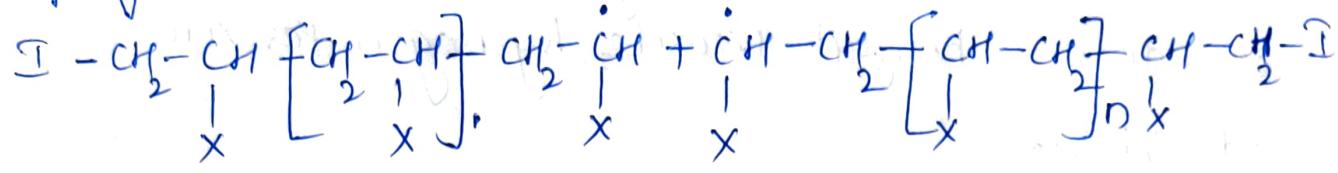
2. Propagation: The monomer free radical reacts with a number of monomers rapidly resulting chain growth at the end chain produces a living polymers.



By adding fresh monomer to living polymer with free radical site, chain growth starts, hence it is known as living polymer.

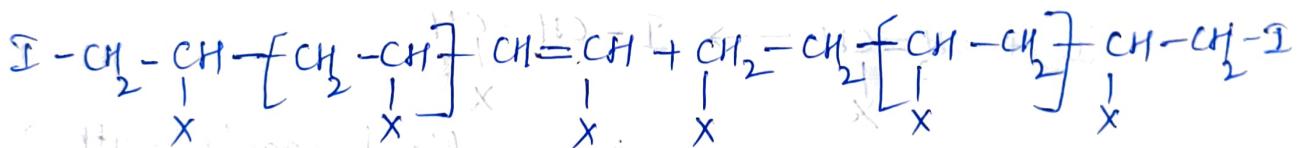
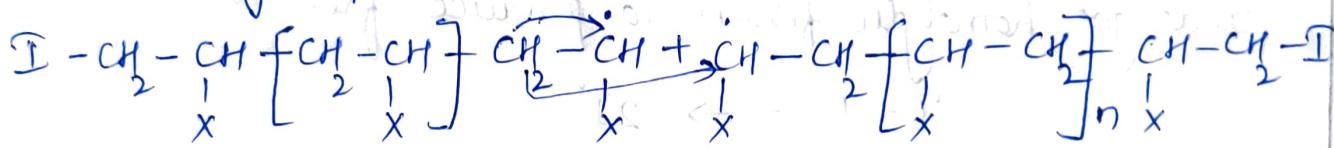
Termination: It is carried out by coupling and disproportionation.

→ Coupling



Dead polymer.

Termination by disproportionation:



Types of Polymerisation :

The conversion of a monomer into a polymer is an exothermic process. If heat is not properly controlled, explosions may take place. The polymerisation reactions are classified into three types.

1. Addition polymerisation (or) chain polymerisation
2. condensation polymerisation (or) step growth polymerisation
3. copolymerisation

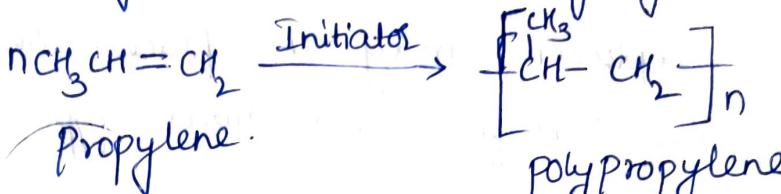
1. Addition or chain polymerisation:

The polymerisation takes place by self addition of the monomer molecules to each other through a chain reaction is called addition polymerisation.

The following are the characteristics.

- The functionality of monomer is a double bond and it is bifunctional.
- No by-products like H_2O , CH_3OH are produced.
- The polymer has the same chemical position as that of monomer.
- The mechanism is carried out in three steps. i.e. initiation, propagation and termination.
- The molecular weight of the polymer is the exact multiple of the monomer. The mechanism is rapid.
- An initiator is required to start the polymerisation.

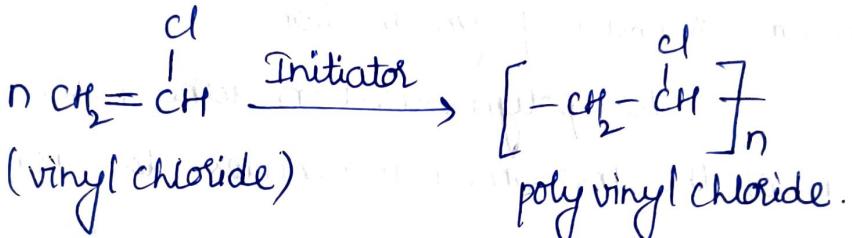
③ Example: Olefins like ethylene, propylene, 1-butene etc.



Vinyl compounds:

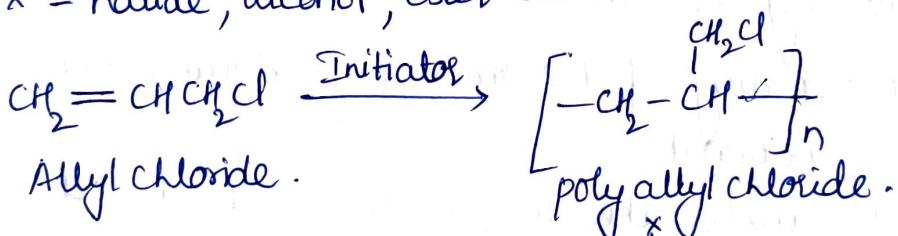
The general representation of vinyl compounds.

$\text{CH}_2=\text{CHX}$, where $X =$ halide, acid, alcohol, amine, phenyl etc.



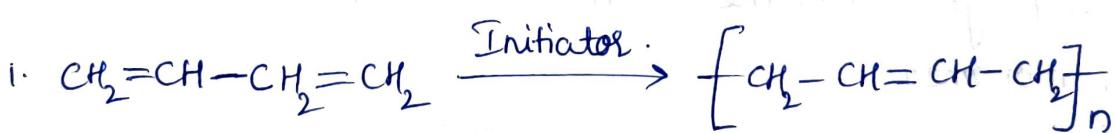
Polyvinyl chloride.

Allyl compounds: General Formula $\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$, where $X =$ halide, alcohol, ester etc.



Polyallyl chloride.

Dienes: General formula $\text{CH}_2=\text{CH}-\overset{\text{C}}{\underset{|}{\text{CH}}}-\text{CH}_2$, where $X =$ halogen.



chain polymerisation is initiated by initiators and carried out in three different types of mechanism.

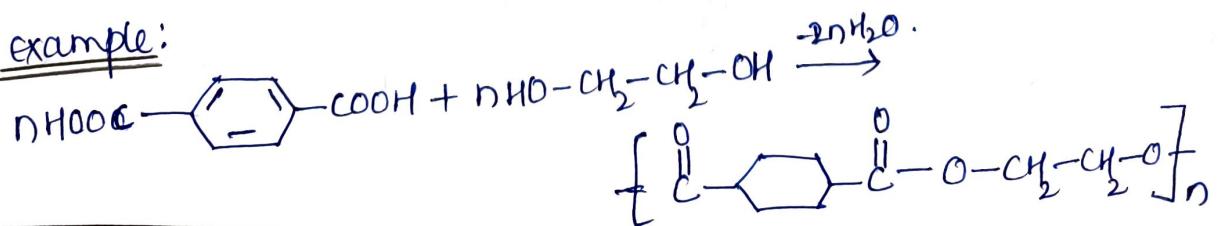
- Free radical mechanism.
- Ionic mechanism.
- Coordination mechanism.

Step polymerisation:

Step polymerisation take place by condensation reaction of the functional groups of the monomers, with the elimination of biproducts like H_2O , HCl etc. The following are the characteristics of step polymerisation.

1. The monomers contain functional groups like. $-OH$, $-COOH$, NH_2 , $RCOOR$, halides etc.
2. The functionality of the monomer must be two or more than two
3. The polymer is built up by a slow step wise condensation reaction of the functional group of the monomer.
4. The polymerisation reaction is accompanied by the elimination of biproducts like HCl , CH_3OH , H_2O etc.
5. The reactions are not exothermic.
6. The molecular weight of the polymer is not the sum of the molecular weight of the monomers.
7. It is not a three step mechanism of initiation, propagation & termination.
8. The reactions are catalysed by catalyst

example:



Difference between Addition and condensation polymerisation

Addition polymerisation	condensation polymerisation.
<ol style="list-style-type: none">1. The functionality of the monomer is double bond which is bifunctional.2. The polymerisation take place by self addition of monomers.3. No byproducts are produced4. The molecular weight of polymer is the sum of molecular weights of monomer5. The mechanism is rapid.6. The mechanism is highly exothermic7. An initiator is required to start the polymerisation8. The polymer has same composition as that of monomer Ex: polyethylene, PVC, polystyrene	<ol style="list-style-type: none">1. The functionality of monomer is bifunctional or tri or polyfunctional.2. The polymerisation take place due to slow stepwise3. Byproducts like H_2O, HCl, CH_3OH etc are produced.4. The molecular weight of polymer is not the sum of molecular weights of monomers.5. The mechanism is slow.6. The mechanism is not exothermic7. A catalyst is required for the reaction.8. The polymer has different composition from the monomer Ex: polyesters, nylon, Silicones etc.

PLASTICS:

Plastics are high molecular weight organic materials, that can be moulded into any desired shape by the application of heat and pressure in the presence of catalyst.

CHARACTERISTICS:

1. They are light in weight, good thermal and electrical insulation
2. They possess very good strength and toughness
3. They can be easily moulded and have excellent finishing
4. Corrosion resistance, chemical inertness, adhesiveness, easy workability, low fabrication cost.

CLASSIFICATION OF PLASTICS:

Based on the structure and type of resin used for the manufacture of plastics, they are classified into two types.

1. Thermoplastics
2. Thermosetting Plastics.

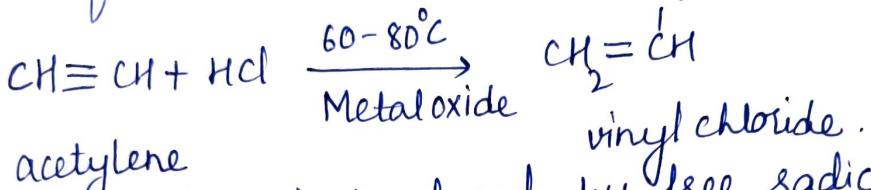
Resin: Resin is a binding material, present in plastics, which undergoes polymerisation reaction during moulding.

Difference between Thermoplastic and thermoset resin

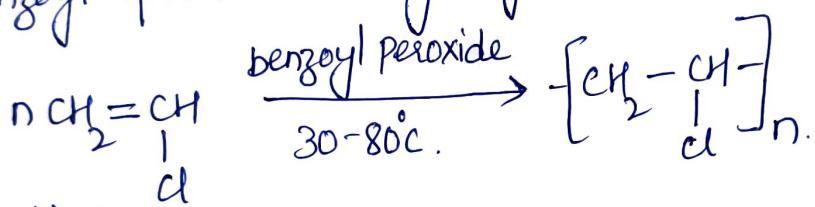
Thermoplastic Resins	Thermoset Resins.
<ul style="list-style-type: none">1. They are formed by addition polymerisation2. They consist of linear long chain polymer3. Polymer chains are held together by weak van der waals force.4. They soften on heating and harden on cooling5. They can be remoulded6. They are weak, soft and less brittle7. They have low molecular weight8. They are soluble in organic solvents9. These plastics can be reclaimed from waste <p>Example: poly ethylene, polyvinyl chloride</p>	<ul style="list-style-type: none">1. They are formed by condensation for polymerisation.2. They consist of three dimensional network structure.3. Polymer chains are linked by strong covalent bonds.4. They do not soften heating5. They cannot be remoulded6. They are strong, hard and more brittle.7. They have high molecular weights.8. They are insoluble in organic solvents.9. They cannot be reclaimed from waste. <p>Example: Bakelite, Nylon.</p>

Poly vinyl chloride:

Vinyl chloride is prepared by treating acetylene with hydrogen chloride at $60-80^{\circ}\text{C}$ in presence of a metal oxide as catalyst.



→ Poly vinyl chloride is produced by free radical chain polymerisation of vinyl chloride in presence of benzoyl peroxide or hydrogen peroxide.



Properties:

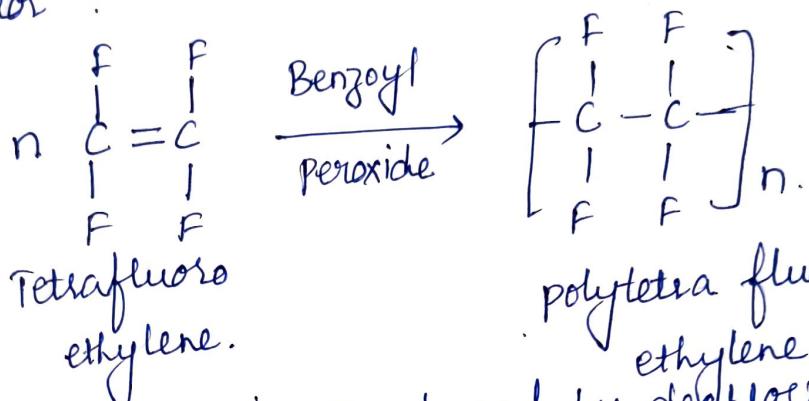
1. PVC is colourless, chemically inert.
2. It has specific gravity ~ 1.33 and melting point 148°C .
3. It is strong, brittle and resistant to atmospheric conditions like CO_2 , O_2 and moisture.
4. PVC is not stable to heat, UV radiation, it undergoes degradation.

Applications:

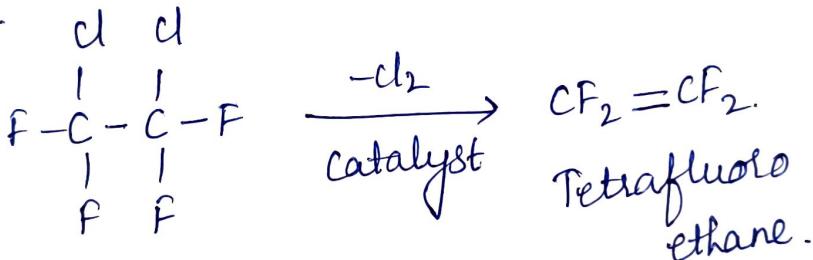
1. It is used in the production of pipes, cable insulations, table covers and rain-coats etc.
2. It is used for making safe helmets, refrigerator components, frames for doors & windows.

TEFLON (Polytetra fluoro ethylene) or Fluon:-

Teflon is obtained by the chain polymerisation of tetrafluoroethylene in presence of benzoyl peroxide as initiator.



Tetrafluoroethylene is produced by dechlorination of syn dichlorotetrafluoroethane in presence of a catalyst.



Properties:

1. It has high melting point ($>350^\circ\text{C}$) and high chemical resistance & high density $2.1 - 2.3 \text{ gm/cc}$.
2. It is very strong, hard polymer that can be machined to drilling, punching etc.
3. It is very good electrical insulator, possess very good abrasion resistance.

Application:

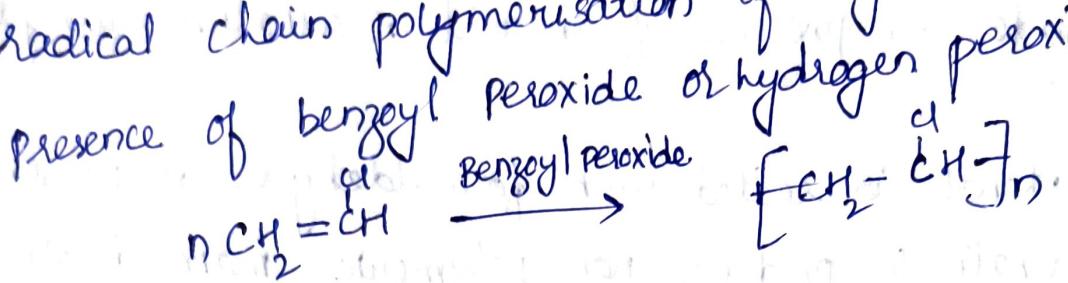
1. Teflon is a very good insulating material for motors, transformers, cables, wires, fitting.

2. It is used for making gaskets, pump parts, tank linings, tubing etc.
3. Due to its chemical resistance, it is used for making chemical carry pipes.

Preparation, Properties & Applications of PVC & Bakelite. X

Polyvinyl chloride:

Polyvinyl chloride is produced by free radical chain polymerisation of vinyl chloride in presence of benzoyl peroxide or hydrogen peroxide.



Properties:

1. PVC is colourless, non-inflammable and chemically inert powder
2. It has specific gravity ~ 1.33 and melting point 148°C
3. PVC is strong, brittle.
4. It is resistant to atmospheric conditions like CO_2, O_2 and moisture.
5. PVC is not stable to heat & U.V radiation, it undergoes degradation.

Applications:

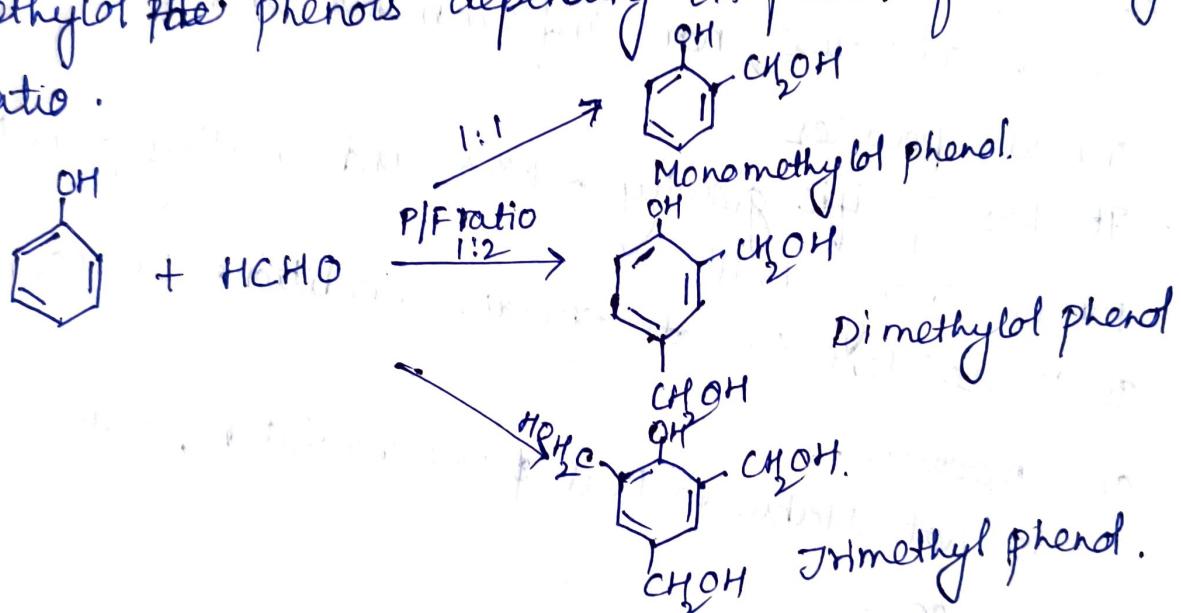
1. It is used for making safe helmets, refrigerator components, bottles for consumable liquids such as edible oil,
2. It has potential in making water carrying pipes, frames for doors & windows.
- 3.

Bakelite/ Phenol-formaldehyde resin:

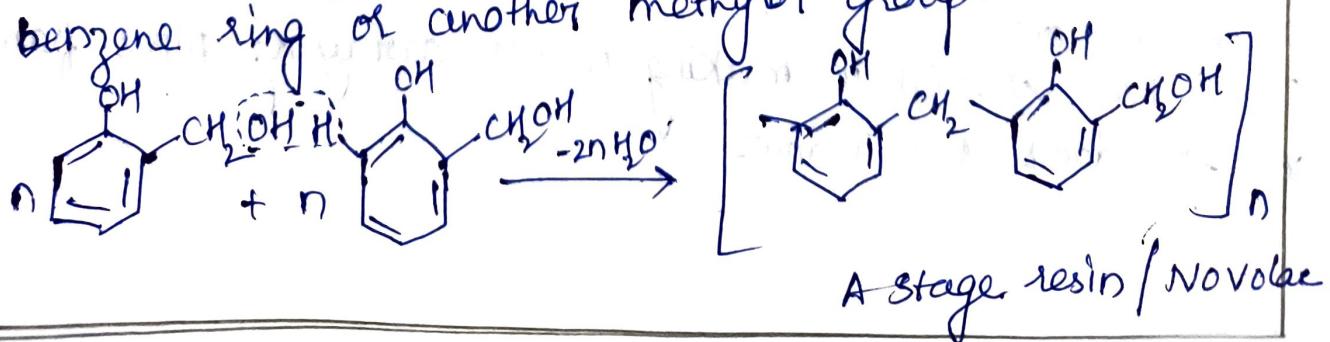
Bakelite is important thermoset resin named after the scientist Bakeland, synthesised in year 1909
 → It is prepared by step polymerisation of phenol with formaldehyde in presence of an acid or alkali as catalyst.

Stage - I :

phenol is reacted with formaldehyde in presence of acid /alkali to produce non-polymeric mono, di, tri, methylol phenols depending on phenol:formaldehyde ratio.



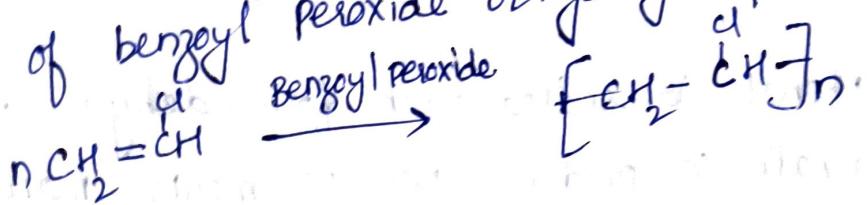
Stage-II: The mono, di, tri methylol phenols are heated to produce two types of straight chain resin by condensation of methylol group with hydrogen atom of benzene ring or another methylol group.



Preparation, Properties & Applications of PVC & Bakelite

Polyvinyl chloride:

Polyvinyl chloride is produced by free radical chain polymerization of vinyl chloride in presence of benzoyl peroxide or hydrogen peroxide.

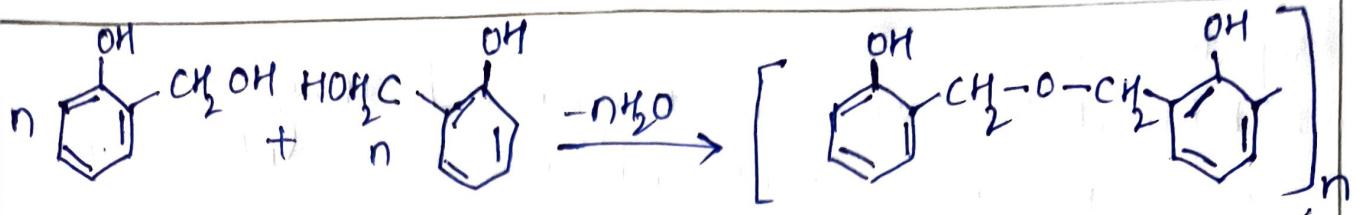


Properties:

1. PVC is colourless, non-inflammable and chemically inert powder
2. It has specific gravity ≈ 1.33 and melting point 148°C
3. PVC is strong, brittle.
4. It is resistant to atmospheric conditions like CO_2, O_2 and moisture.
5. PVC is not stable to heat & UV radiation, it undergoes degradation.

Applications:

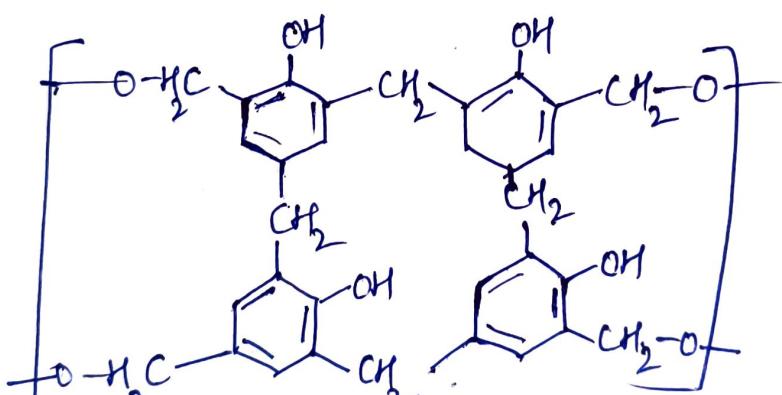
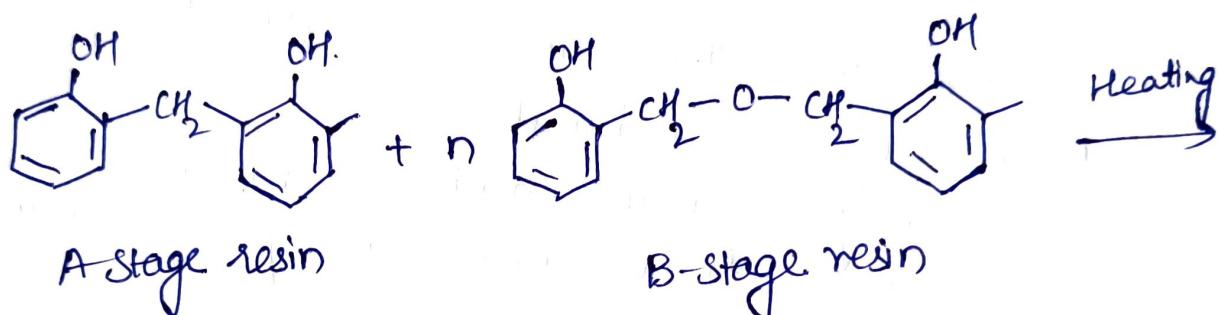
1. It is used for making safe helmets, refrigerator components, bottles for consumable liquids such as edible oil,
2. It has potential in making water carrying pipes, frames for doors & windows.
- 3.



B-Stage resin Resole

III Stage:

Preparation of includes of A stage & B stage resin together, which develops cross linkings and a bakelite plastic resin is produced



Bakelite.

Properties

1. Bakelite plastic resin is hard, rigid and strong
2. It is scratch resistant and water resistant polymer.
3. It is excellent electrical insulator and very good adhesive.
4. It is very good corrosion resistance, resistant to atmospheric conditions like O_2 , CO_2 , moisture, light, UV radiation etc.

Applications:

1. It is used in electrical insulator parts like switches, switch boards, heater handles.
2. It is widely used in paints, varnishes.
3. It is used as adhesive (binder) in plywood laminations & grinding wheels etc.

Fibres:

Polymers which can be drawn in the form of long, thin thread like filaments with high tensile strength.
 → Fibres which do not undergo stretching or deformation.

Fibres are classified into two types.

1. Natural fibres. - wool, silk, cotton, jute etc.
2. synthetic fibres. - Nylon 6,6, Terylene.

Characteristic of Fibres:

1. Fibres are strong, tough and wrinkle resistant.
2. Fibres must be wrinkle free and should possess less shrinkage.
3. It should absorb colour easily and washable.
4. Fibre must be resistant to chemicals, environmental conditions and heat.
5. It should possess low specific gravity.
6. It should possess low water absorbing and (drip-dry) and low water holding capacity.

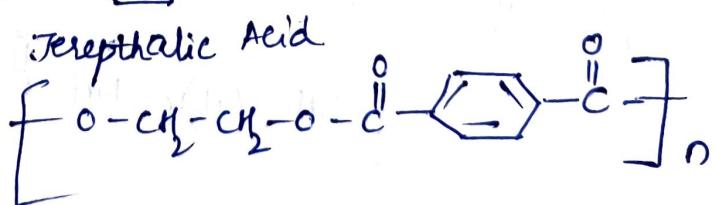
Preparation, properties and Application:

Dacron:

It is a saturated polyester also known as Terene / Terylene. It is formed by condensation polymerisation of ethylene glycol with terephthalic acid.



Ethylene
glycol



Dacron.

Properties:

- Fibres have high resistance, high crease and wrinkle resistance
- It does not hold water, it is very easy to dye.
- It can be blended with wool, silk etc.
- Fibres are strong with good abrasion resistance.

Applications:

- It is used as both domestic and industrial fiber
- It is used to make nylon tyres.
- It is blended with wool and cotton to provide better finish, wrinkle resistance.

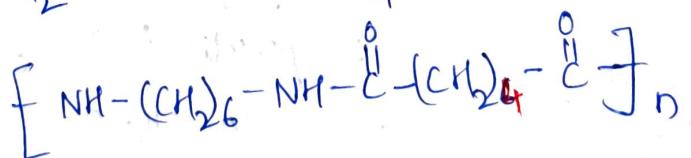
Nylon 6:6

It belongs to polyamide class of synthetic polymers.

The It was synthesised in New York and manufactured

in New York-London.

- The first number stands for the number of carbon atoms in diamine and the second number indicates the number of carbons in diacid.
- It is produced by copolymerisation of Hexamethylene diamine and adipic acid.



Properties:

- It possess high strength, hardness and high Melting point. melting point is due to hydrogen bonding between hydrogen atom of amide group and oxygen of C=O group.
- They possess good chemical resistance, abrasion resistance, to environmental conditions.

Application:

1. It is used in making socks, carpets and engineering applications like gears, bearings, machine parts.
2. It is used for making ropes, bristles for tooth brush.

FR-P. Fibre reinforced Plastic :

Fibre reinforced plastic are produced by bonding a fibre material with a resin matrix and curing them under pressure and heat.

- The reinforcing agents used are glass, graphite, alumina, carbon, boron etc.
- The reinforcing material can be in different form such as short fibres, continuous filaments or woven fabrics.

characteristics:

- It possess high corrosion resistance and heat resistance property.
- low coefficient of thermal expansion, high dimensional stability,
- low cost of production, good tensile strength.

Application:

GFR Glass-FRP - Automobile parts, storage tanks, plastic pipes

Boran-FRP - horizontal & vertical tail in aeroplane.

Carbon-FRP - sports material, antenna disc, solar panels etc.

Aramid-FRP - structural component in aircraft, helicopter parts.

Alumina-FRP - components in engine parts in automobile industry and in turbine engine.

Rubbers:

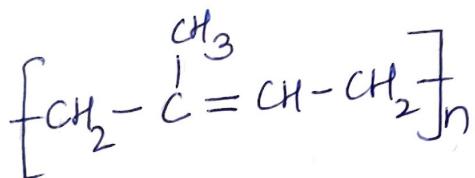
Rubbers (tex) which possess the property of elasticity.
and they are non-crystalline high polymers.

Natural rubber:

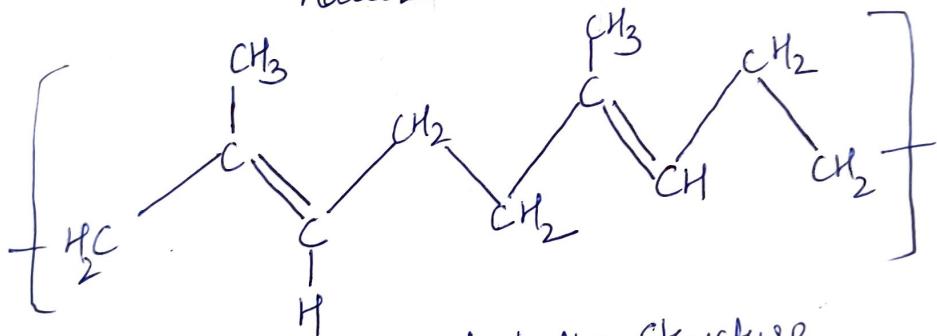
It is obtained from cell sap or latex, which is a dispersion of isoprene, these molecules polymerize to form long-coiled chains of cis-poly isoprene.

→ Natural rubber is processed from the cell sap (latex) of three main types of trees, Hevea Brasiliensis, Guayule, Dichopsis percha, Palagum gutta found in tropical and semi-tropical countries.

→ The main composition of natural rubber is polyisoprene, which is in the form of long coiled chains, responsible for the elasticity of natural rubber.



polyisoprene unit of
natural rubber.



Coiled helix Structure

polyisoprene.

Drawbacks of raw rubber:

1. It becomes soft at high temperature and is too brittle at low temperature.
2. It swells in water and easily attacked by organic solvents, acids, bases and non polar solvents like mineral oils, benzene and vegetable oils.

VULCANISATION:

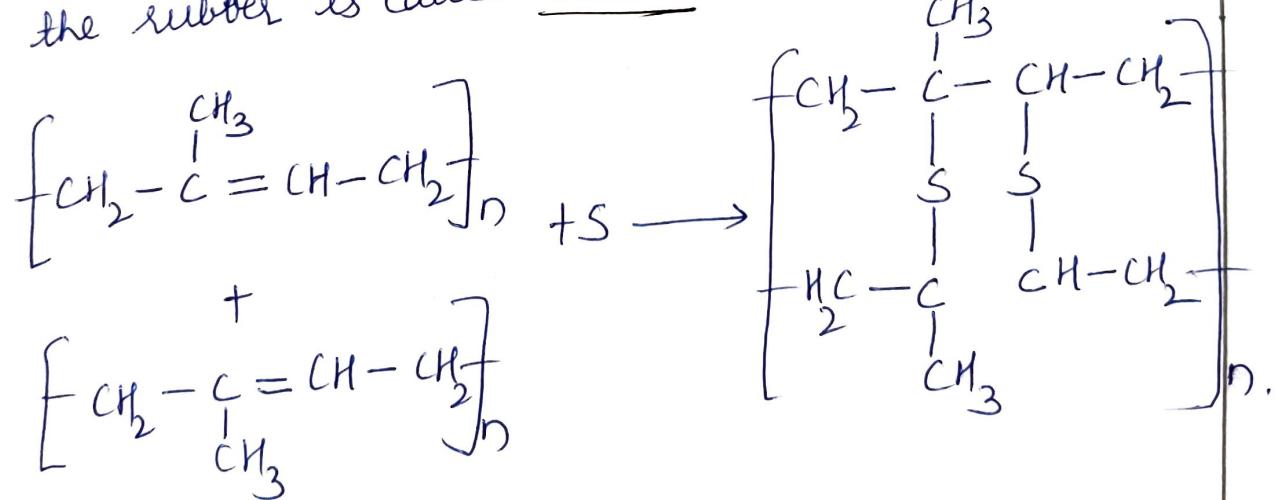
To improve the properties of rubber, Charles Goode in 1839 compounded the raw rubber with some chemicals like sulphur, hydrogen sulphide, benzoyl chloride etc. and heated to $100-140^{\circ}\text{C}$.

- The most important vulcaniser is sulphur which combines chemically at the double bonds of the different chains producing Sulphur cross linkings.
- which helps in increasing in strength, brittleness.
- The percentage of sulphur added is in the range of $0.5 - 35\%$.

Example: 1. Rubber used for making tyre is 3-5% sulphur

2. Battery case rubber contains 30% sulphur.

If the percentage of sulphur is more than 32, the rubber is called ebonite or Vulcanite or hard rubber.



Elastomers :

Elastomers are characterised by the property of elasticity and they can be vulcanised. The following are some important elastomers.

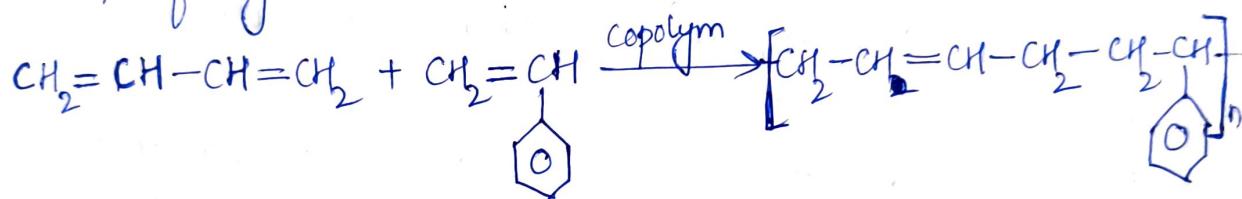
1. BUNA-S / Styrene rubber or GRS: (or) Ameripol.

BV - Butadiene - monomer

Na - Sodium catalyst

S - Styrene monomer.

It is produced by copolymerisation of butadiene 75% and 25% of styrene.



Properties :

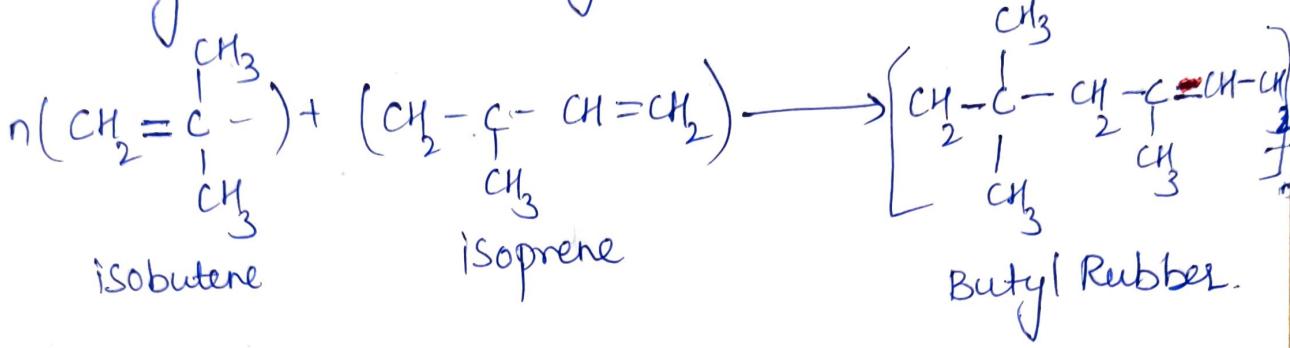
1. Buna-S is resistant to abrasion, and high load bearing capacity
2. It readily oxidized, in presence of traces of ozone present in atmosphere. and it swells in oil and solvents.
3. It can be vulcanised by sulphur monochloride (S_2Cl_2)

Applications :

1. It is used in making shoe soles, gaskets, footwear component, wire and cable insulation.
2. It is used as adhesive, making wires and cable insulator
3. manufacture of tyres.

Butyl rubber : / GR-I

It is produced by copolymerisation of isobutene with isoprene in presence of anhydrous aluminium chloride. In methyl chloride as catalyst.



Properties:

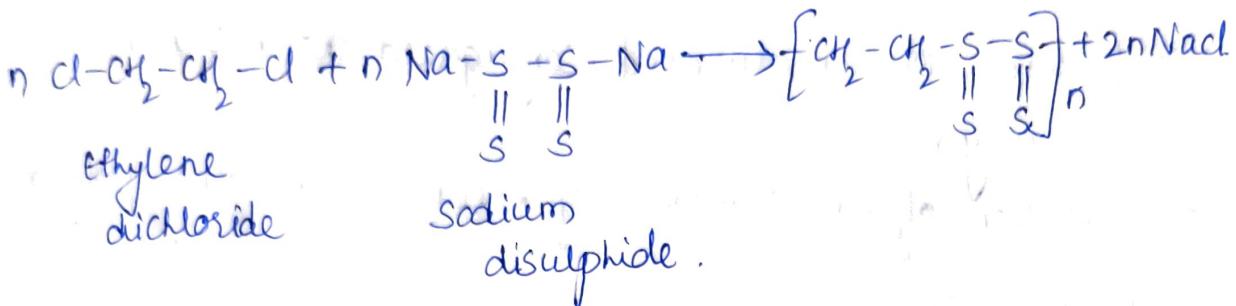
1. It is strong, tough synthetic rubber.
2. Resistant to heat, abrasion, chemicals such as inorganic acids, polar solvents.
3. It is resistant to atmospheric gases, especially to ozone.
4. It can be vulcanised with sulphur.

Applications:

1. Making cycle tyres and automobile tubes.
2. Insulator for high voltage wires and cables.
3. making the linings of tanks where chemicals are stored

Thiokol rubber | GR-P:

It is produced by co-polymerisation of sodium polysulphide (Na_2S_4) and ethylene dichloride produces thiokol rubber.



Properties:

- It possesses good resistance to mineral oils, fuels, solvents etc.
- This cannot be vulcanised and it cannot form hard rubber.
- It possesses low abrasion resistance.

Application:

- It is used for barrage balloons, life rafts and jackets which are inflated by CO_2 .
- It is mixed with oxygen releasing chemicals, used as a solid fuel in rocket engines.
- Conducting

conducting polymer:

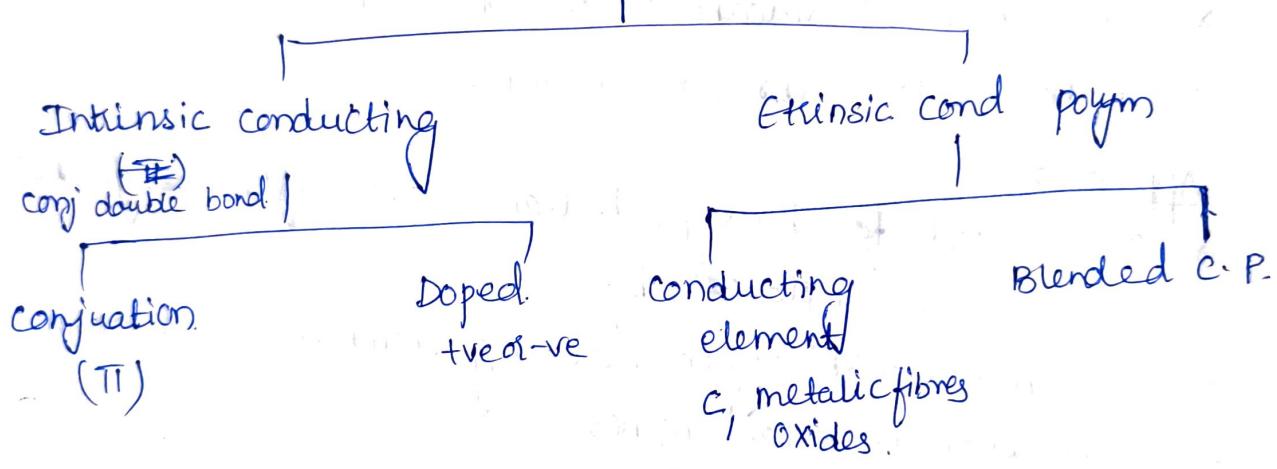
polymer which can conduct electricity is termed as conducting polymer.

Reasons for conduction:

- presence of unsaturated conjugated double bonds in the polymer.
- Addition of (or) removal of electrons into the polymer.

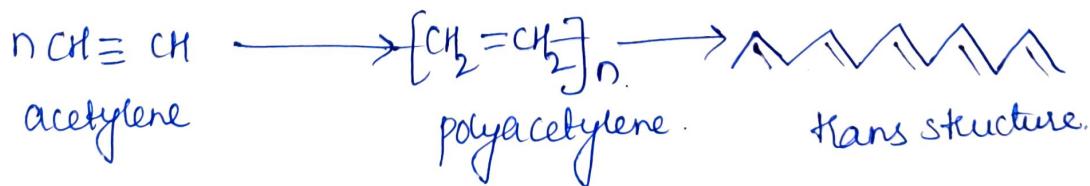
classification:

conducting polymers.

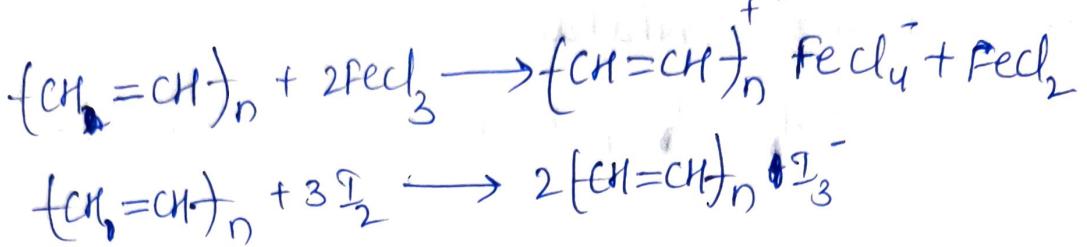


conduction in trans-polyacetylene:

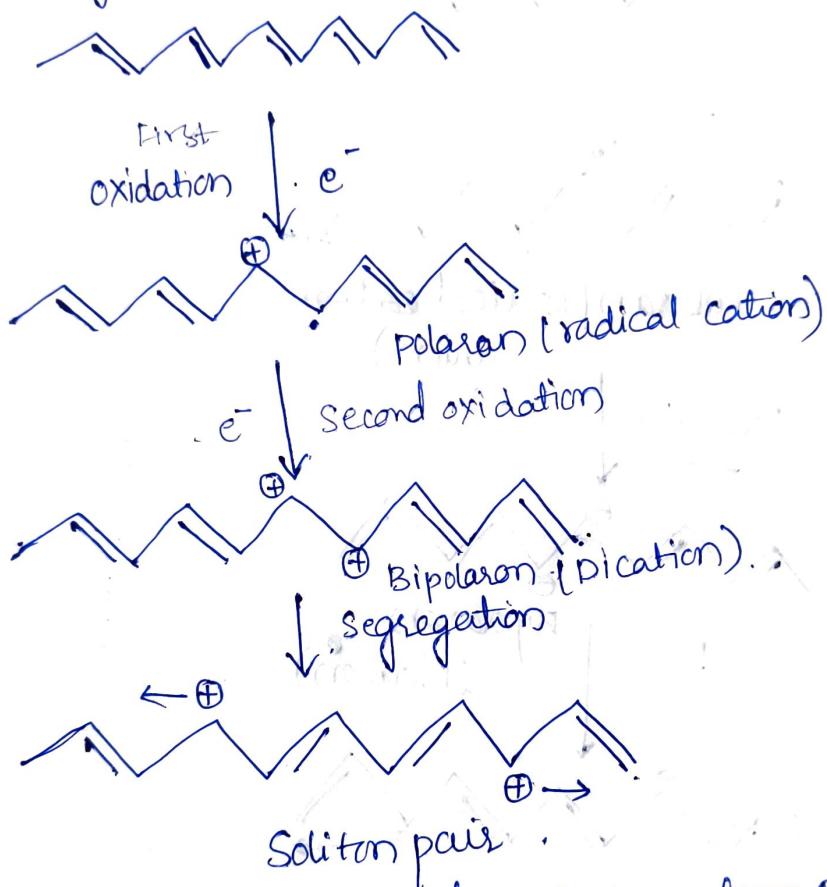
Polyacetylene is prepared by addition polymerisation of acetylene.



P-doping: This is done by oxidation of polymers. They are treated with Lewis acid or with iodine vapour

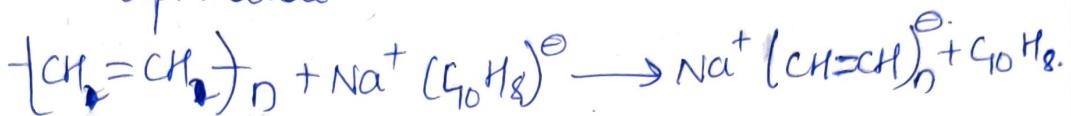


Process: P-doping:

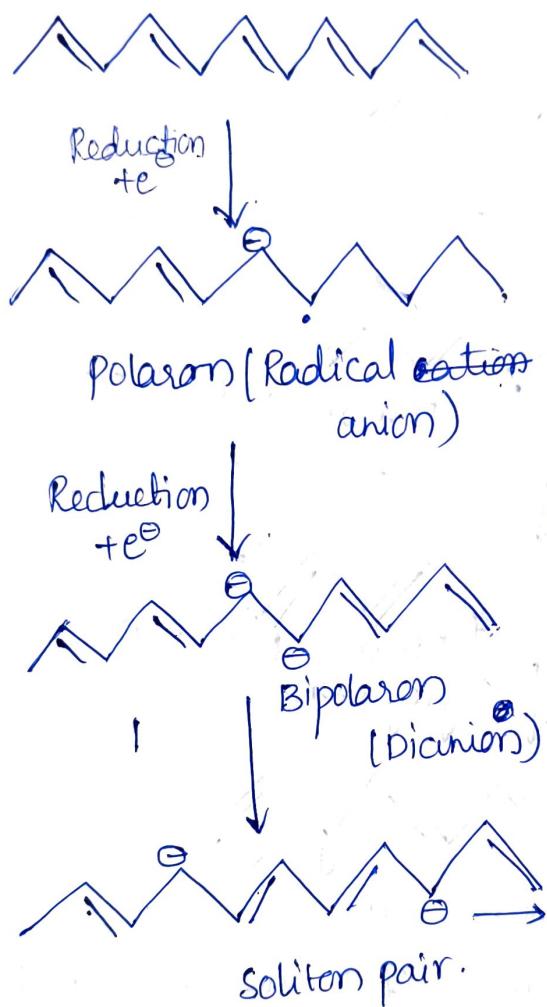


- During oxidation; removal of π electron from polymer backbone leads to formation of delocalised radical ion called polaron.
- Second oxidation results two positive charge carriers in each chain called bipolaron, which are mobile because of delocalisation.
- Delocalisation charge carriers are responsible for conductance when placed in electric field.

n-doping: This is done by reduction process. For conductance polymers having conjugation is treated with lewis base like sodium naphthalide.



Process!



Applications:

1. To make rechargeable, light weight batteries which are small in size.
2. Analytical sensors for P^H , O_2 , NO_2 , SO_2 , NH_3 and glucose.
3. Making ion-Exchanges, electromagnetic screening materials.
4. Electronic device - such as transistors & diodes, making solar cells. & photovoltaic devices.

Biodegradable polymers:

Polymers which undergo degradation by naturally occurring microorganisms like algae, fungi and bacteria.

Requirements:

- Production of non-toxic products.
- Controlled rate of degradation.
- Capable of maintaining good mechanical integrity until degradation.

Factors affecting degradation:

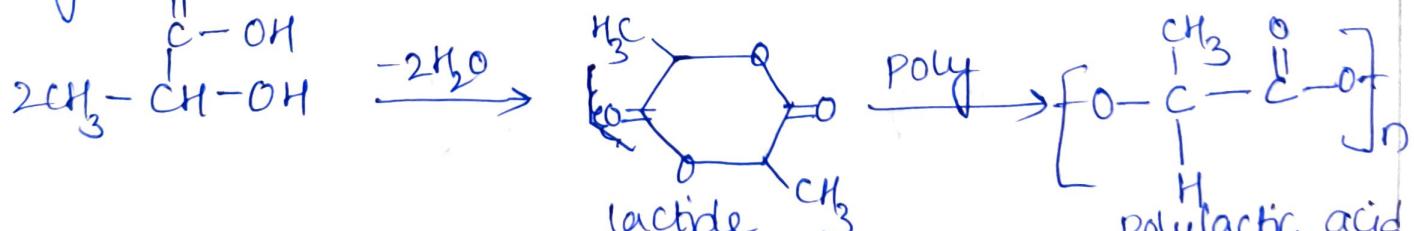
- Molecular weight of polymer.
- Amount of crystallinity of polymer.
- Hydrophobicity of polymer.
- Environment which surrounds the polymer.

Polylactic Acid (PLA):

It is a biodegradable thermoplastic polyester.

It is derived from renewable source such as starch,

Sugarcane etc.



It is produced by catalytic dimerisation of lactic acid resulting in the formation of lactide monomer.

Properties :

- It is stable to UV radiation, good resistance to moisture, high strength.
- It possess high melting point $173-178^{\circ}\text{C}$.
- PLA is a chiral compound existing as poly-L-lactic acid

Application :

- medicinal implants like screws, pins, anchors
- It is used in a number of biomedical application like drug delivery device and dialysis media.
- Preparation of bioplastic for packing food and disposable table ware.
- packing materials, food packing.

Polyvinyl Acetate Alcohol:

Polyvinyl alcohol is prepared by polymerising vinyl acetate and it is converted to PVA.



Properties :

- Excellent film forming, emulsifying and adhesive properties.
- It is resistant to oil, grease and solvents.
- High tensile strength and flexibility.

Polyvinyl alcohol :

Polyvinyl alcohol is prepared by first polymerising vinyl acetate and the resulting polyvinyl acetate is converted to PVA.



Properties:

1. It has excellent film forming, emulsifying and adhesive properties.
2. It is resistant to oil, grease and solvents.
3. It has high tensile strength and flexibility.

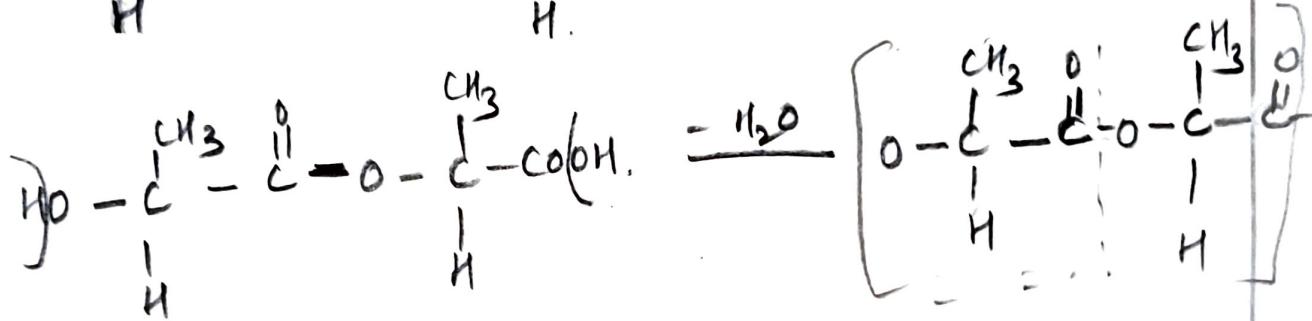
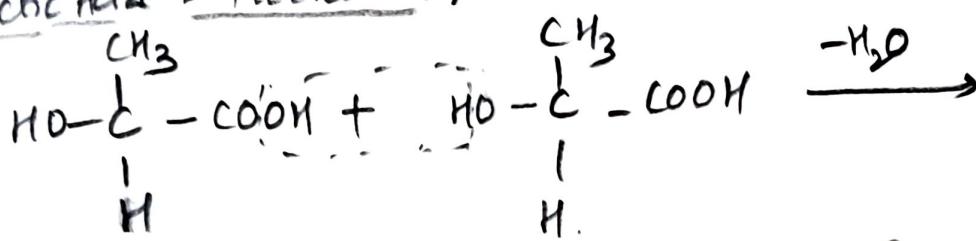
Application:

1. It is used in eye-drop and hard contact lens solution as a lubricant.
2. It is used as a protective chemical resistant gloves.
3. It is used as a film in water transfer printing process.

Applications:

1. It is used as sizing agent in textile industry.
2. It is used as protective chemical - resistant gloves.
3. used as film in water transfer printing process.
4. used in eye drops and hard contact lens solution as lubricant.

Poly Lactic Acid - Mechanism:



lactic
acid
unit after condens.