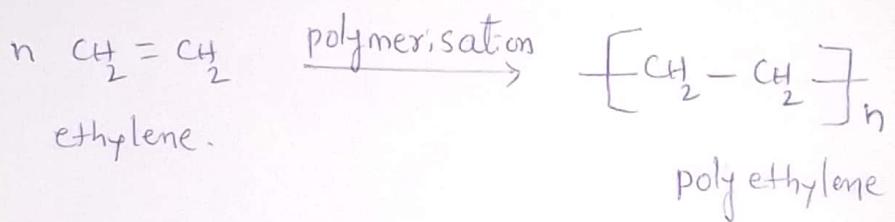


UNIT-3 Polymeric materials

The word polymer is derived from two Greek words poly means many and mers means units (or) parts.

Polymer: polymers can be defined as the large molecules (macro molecules) formed by the linking together of large number of smaller molecules called monomers.

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



Thus the repeated unit of polymer is called monomer. The number of repeating units in a polymer chain is called degree of polymerisation.

Eg: If 100 molecules of ethylene polymerize to give the polymer chain, the degree of polymerisation is 100.

→ Depending on the degree of polymerisation, there are two types of polymers.

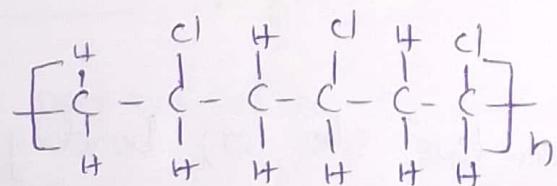
1) Oligo polymers: Those polymers whose degree of polymerisation is less than 600 are called oligo polymers.

2) High polymers: When the degree of polymerisation of a polymer is more than 600, it is called high polymer.

Tacticity: The arrangement of functional groups on carbon backbone of the polymer is called tacticity. It is mainly divided into 3 types.

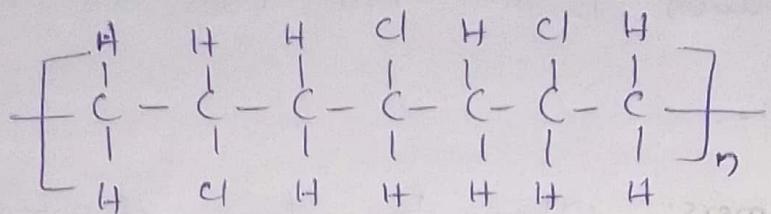
1) Isotactic polymers: The polymers in which the functional groups are arranged on the same side are called isotactic polymers.

Eg: poly vinyl chloride (P.V.C).



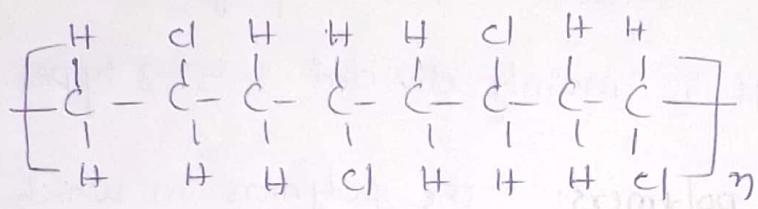
2) Atactic polymers: When there is no regular arrangement of functional groups on the carbon backbone of the polymer chain, these polymers are called atactic polymers.

Eg: poly vinyl chloride (P.V.C)



3) Syndiotactic polymers The polymers which alternate arrangement of functional groups are called syndiotactic polymers.

Eg: poly vinyl chloride (P.V.C)



Functionality of monomers

- * For a substance to act as a monomer it must have at least two reactive sites (or) bonding sites
- * The number of reactive sites (or) bonding sites in a monomer is called functionality of the monomer.
- * If two reactive sites are there in a monomer then it is called bi functional and forms linear (or) straight chain polymers.

- * A tri-functional monomer has three reactive sites and forms branched chain polymers.
- * A poly functional monomers has more than three reactive sites and forms three dimensional network polymer.

Polymerisation: The reaction in which many small molecules react to form a high molecular weight product is called polymerisation.

Types of polymerisation.

There are two types of polymerisation. They are

- a) Addition polymerisation (or) Chain polymerisation.
- b) Condensation polymerisation (or) Step polymerisation.

Addition polymerisation

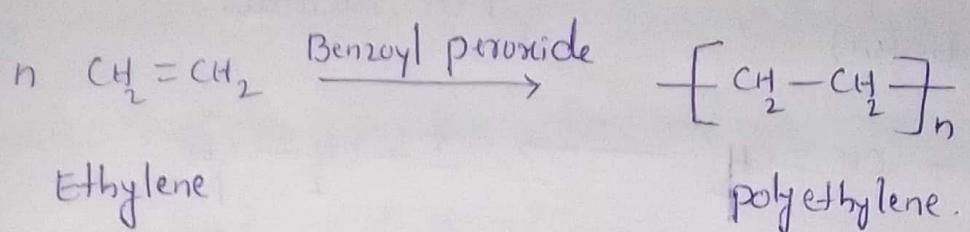
The polymerisation in which monomers add together to form a high molecular weight product is called addition polymerisation. It is also called chain polymerisation.

- * A chain polymerisation is a reaction that yields a polymer product which is the exact multiple

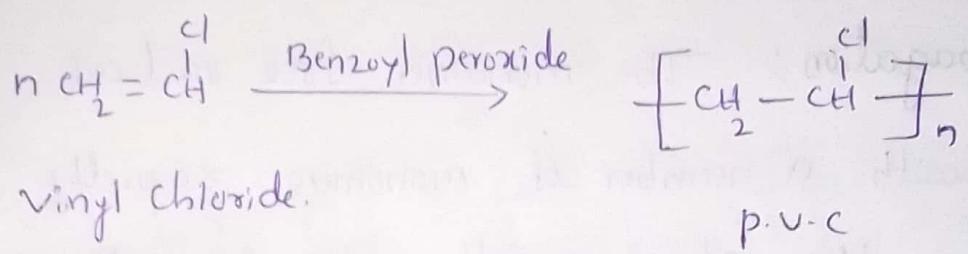
of monomers. The following are the characteristics.

- * The functionality of the monomer is a double bond and it is bi-functional.
- * The polymerisation takes place by self addition of the monomer molecules to each other through a chain reaction.
- * No bi product like H_2O , CH_3-OH etc are produced.
- * The polymer has the same chemical composition as that of monomer.
- * The mechanism is carried out in three steps i.e initiation, propagation and termination.
- * The mechanism is rapid.
- * The conversion of a π bond to σ bond takes place during the polymerisation, liberating 20 K cal / mole of energy.
- * An initiator is required to start the polymerisation reaction.

e.g. ① polyethylene produced from ethylene.



② p.v.c produced from vinyl chloride.



There are three types of chain polymerisation.

1) Free radical chain polymerisation.

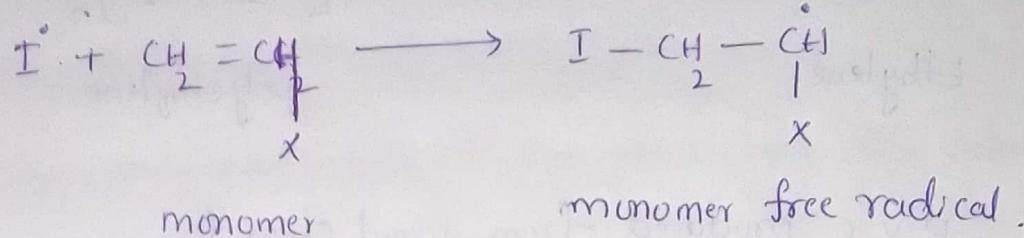
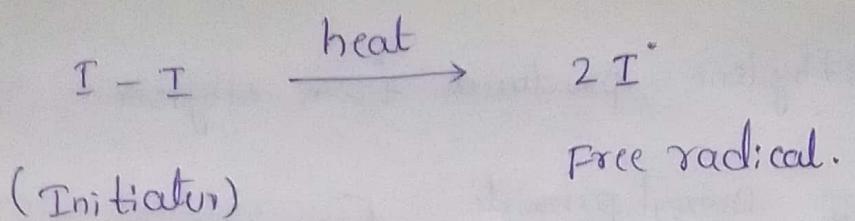
2) Ionic chain polymerisation

3) Co-ordination chain polymerisation.

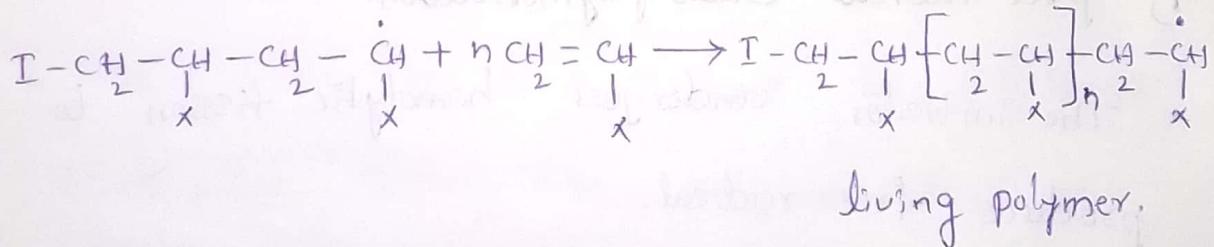
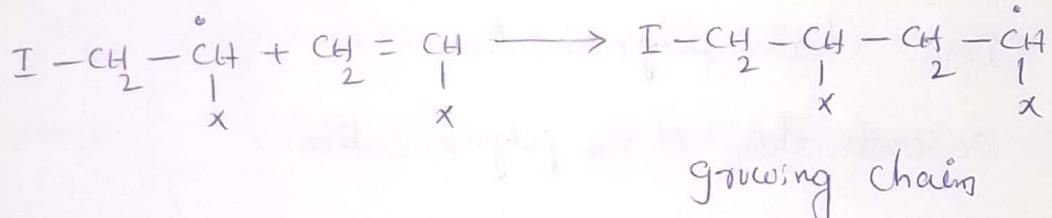
1) free radical chain polymerisation.

* The initiator undergoes homolytic fission to produce free radical.

a) Initiation: Initiators are unstable compounds and undergo homolytic fission to produce free radicals by react with π electrons.



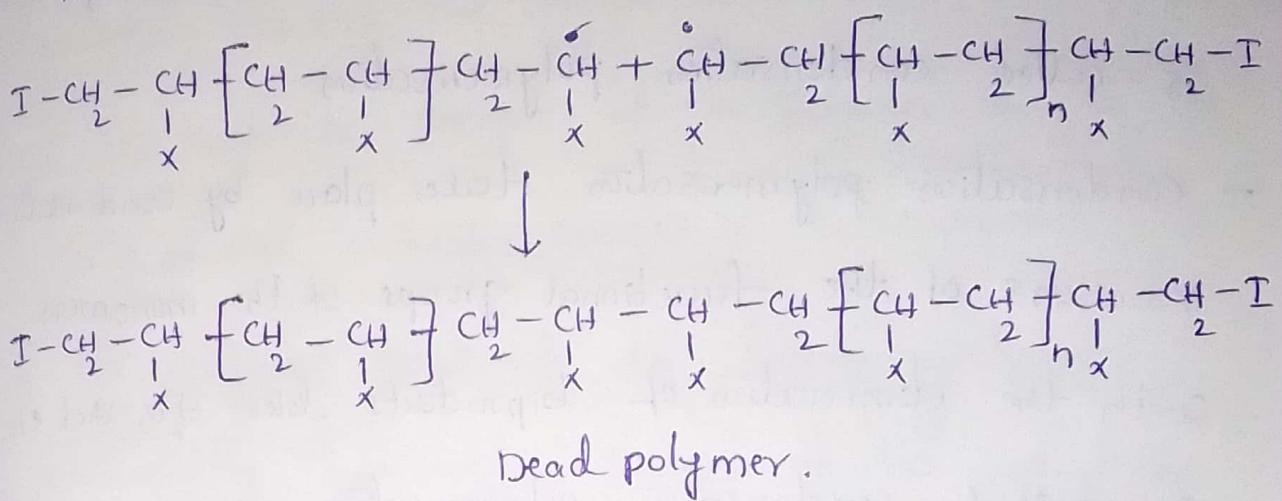
b) propagation : The monomer free radical reacts with a number of monomers rapidly resulting the chain growth with free radical site at the end of the chain producing a living polymer.



c) Termination: Termination of the growing polymer chain is carried by coupling and disproportionation resulting the dead polymer.

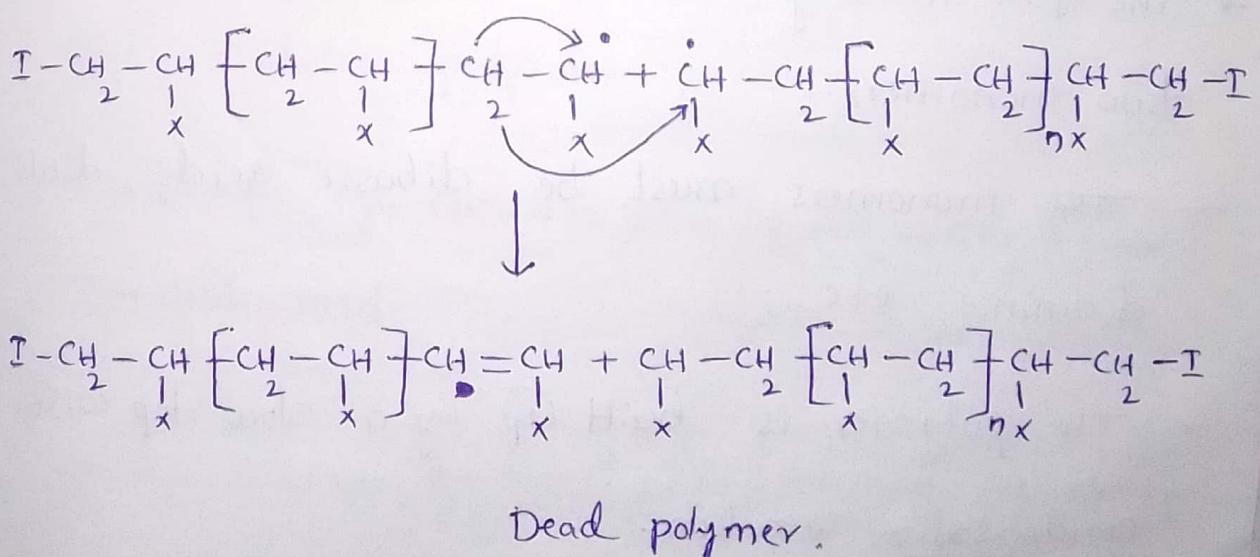
1) coupling or combination:

It involves coupling of free radical of one chain end to another free radical to form macro molecule (dead polymer).



2) Disproportionation

It involves transfer of a hydrogen atom of one radical centre to another radical centre forming two macromolecules, one saturated and another unsaturated



2) Condensation polymerisation

The polymerisation in which many small different molecules react to form a polymer with the elimination of simple molecules like H_2O , NH_3 , HCl etc is called condensation polymerisation.

* Condensation polymerisation takes place by condensation reactions of the functional groups of the monomers.

with the elimination of biproducts like H_2O , HCl etc is called condensation polymerisation.

* The following are the characteristics of condensation polymerisation.

* The monomers contain functional groups like $-OH$, $-COOH$, NH_2 , $RCOOR'$, halides etc.

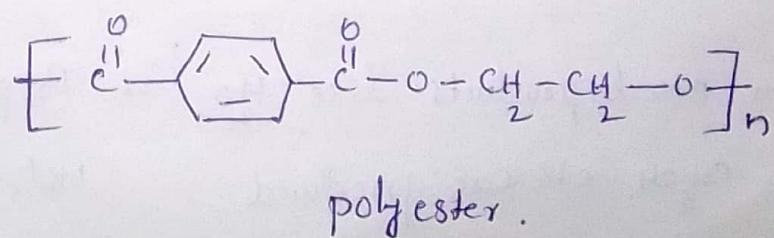
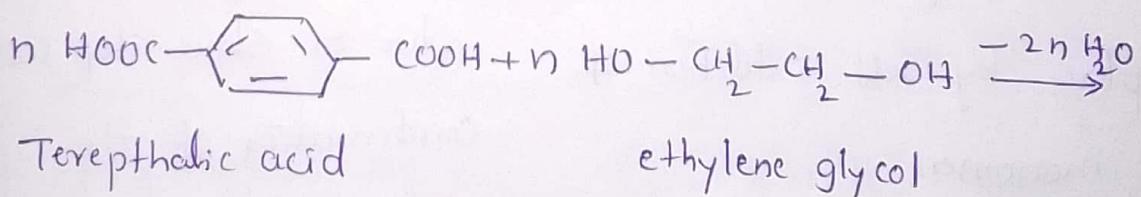
* The functionality must be two (or) more than two monomers.

* The monomers must be dibasic acids, diols, diamines etc.

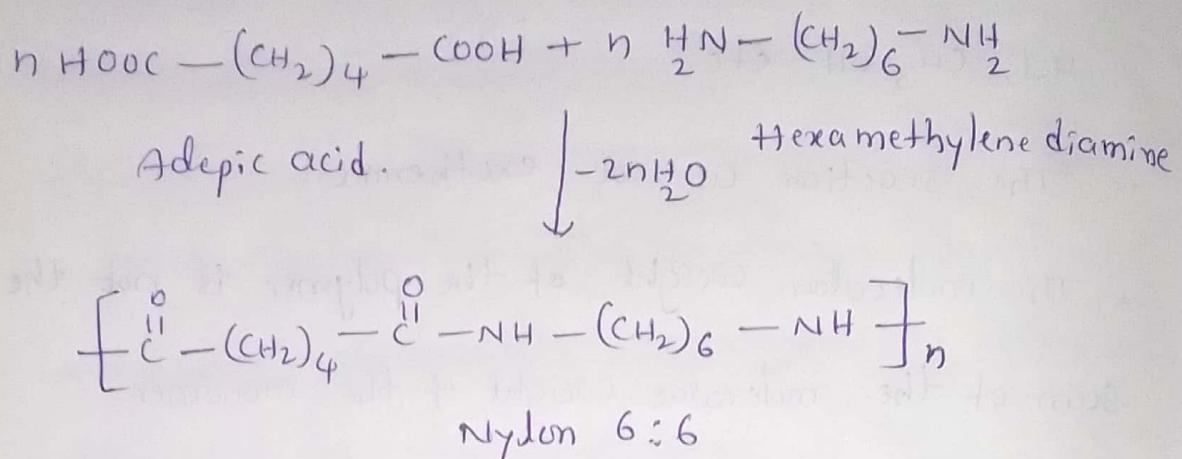
* The polymer is built up by a slow step wise condensation reaction.

- The polymerisation reaction is accompanied by the elimination of by products like HCl, CH_3OH etc.
- The reaction are not exothermic.
- The molecular weight of the polymer is not the sum of the molecular weight of the monomer.
- The polymers produced are living polymers containing functional groups at the end of the chains.
- It is not a three step mechanism of initiation, propagation and termination.
- The reaction are catalysed by catalysts.

Eg: ① The polymerisation of a diacid with diol produces polyester.



Eg ② The polymerisation of a diamine with diacid gives nylon a polyamide.



Difference between addition and condensation polymerisation

Addition

* It is also known as chain growth polymerisation

* The functionality of the monomer is double bond (with which is bi-functional).

* The polymerisation takes place by self addition of monomers.

* No biproducts like H₂O, CH₃OH etc are produced

Condensation

* It is also known as step growth polymerisation.

* The functionality of monomer bi-functional; tri (or) poly functional.

* The polymerisation is due to slow step wise condensation of the functional groups.

* Biproducts like H₂O, HCl, CH₃OH etc are produced.

- * The molecular weight of polymer is the sum of molecular weight of monomers. → The molecular weight of polymer is not the sum of molecular weight of monomers.
- * The mechanism of polymerisation is carried out in three steps - initiation, propagation, and termination. → The mechanism of polymerisation is carried out by slow step wise condensation.
- * The mechanism is rapid. → The mechanism is slow.
- * The mechanism is highly exothermic because π bond is converted to σ bond liberating 20 kcal/mole of energy. → Not exothermic.
- * An initiator is required to start the polymerisation. → A catalyst is required for the reaction.
- * Repeating units of monomers are same. → Repeating units of monomers are different.
 - Eg: polyethylene, p.v.c., polystyrene etc.
 - Eg: Bakelite, nylon, polyesters.

plastics

The high molecular weight organic polymers which can be moulded into desired shape, when subjected to heat and pressure in the presence of catalyst are called plastics.

- * All plastics are polymers but all polymers are not plastics. These polymers having property of plasticity. The term plastic and resin are synonymous.

characteristics of plastics

- * They are light in weight.
- * They possess good thermal and electrical insulating property.
- * They are corrosion resistant and chemically inert to acids, oils action of light etc.
- * plastics have easy workability i.e moulding, drilling etc.
- * Low fabrication cost. to get desired shape products.

- * They are not affected by insects, fungi, virus etc.
- * They have high tensile strength.
- * They are impermeable to water.
- * The surface of plastics are shining and glossy appearances.
- * They possess good strength and toughness.

Types of plastics

The plastics are classified into two types.

- 1) Thermo plastics
- 2) Thermo setting plastics.

1) Thermo plastics The plastics which can be softened on heating and hardened on cooling.
are called thermo plastics.

- They are formed by addition polymerisation.
- * It consists of long chain linear polymers with weak vander waal's forces of attraction.
- It can be reshaped, soft, weak and less brittle.
- * These plastics are reclaimed from waste.

* These are soluble in organic solvents.

Eg: P.V.C polyethylene etc.

Thermo setting plastics

The plastics which cannot be softened on heating once they are moulded into desired shape. are called thermo setting plastics.

- * These are formed by condensation polymerisation
- * It have three dimensional network structures.
- * They cannot be reshaped, hard, strong and more brittle.
- * These plastics cannot be reclaimed from waste.
- * Due to strong bonds and cross links they are insoluble in almost all organic solvents.

Eg: Bakelite, Nylon etc.

Difference between thermoplastics and thermo setting plastics

Thermoplastics

Thermosetting plastics.

- * These are formed by addition polymerisation

- * These are formed by condensation polymerisation.

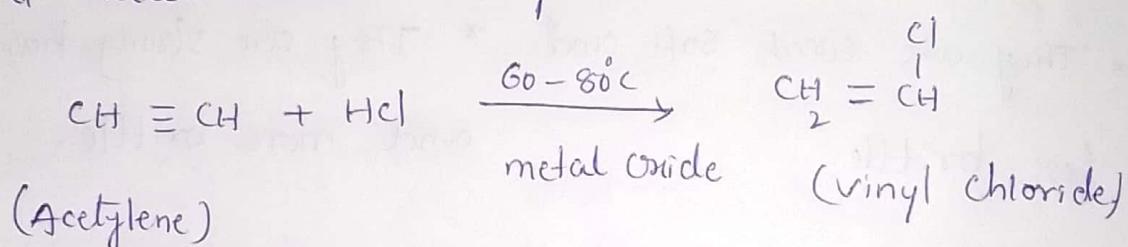
- * They consists of long chain linear polymers.
- * They softened on heating and hardened on cooling.
- * All the polymer chains are held together by weak vander waals forces.
- * They are weak soft and less brittle.
- * They can be reshaped.
- * These can be reclaimed from waste.
- * They have low molecular weight.
- * They are soluble in organic solvents
- Eg: polyethylene, p.v.c.
- * They consists of three dimensional network structure.
- * They do not softened on heating.
- * All the polymer chains are linked by strong covalent bonds.
- * They are strong hard and more brittle.
- * They cannot be reshaped.
- * These cannot be reclaimed from waste.
- * They have high molecular weight.
- * They are insoluble in organic solvents.
- Eg: Bakelite., Nylon etc.

preparation, properties and engineering applications
of plastics.

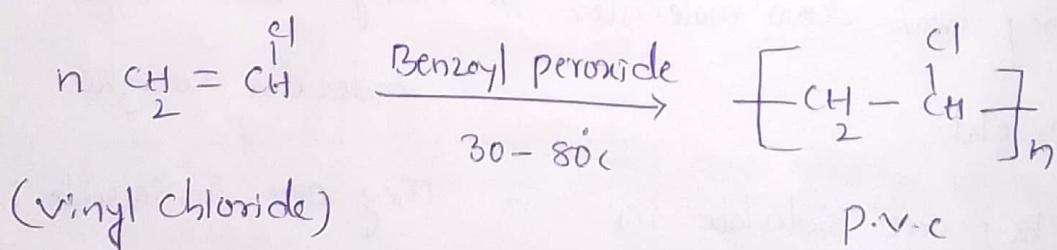
i) poly vinyl chloride (P.V.C). $\left[\text{CH}_2 - \overset{\text{Cl}}{\underset{\text{I}}{\text{CH}}} \right]_n$

preparation The monomer used for the manufacture of P.V.C is vinyl chloride.

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



* Poly vinyl chloride is produced by heating vinyl chloride in presence of benzoyl peroxide (or) hydrogen peroxide.



Properties

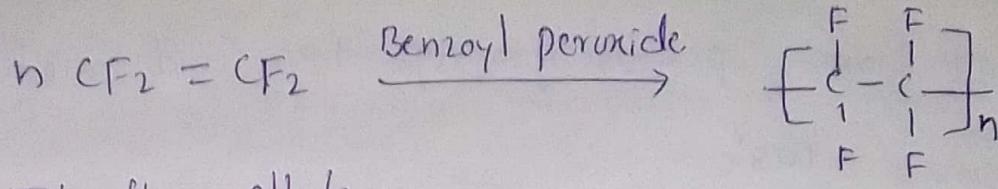
* P.V.C is a colourless, non-inflammable and chemically inert powder.

- * It has specific gravity 1.33 and melting point 148°C
- * It is resistance to atmospheric conditions like O_2 , CO_2 , and moisture.
- * p.v.c is strong brittle.
- * pvc is not stable to heat. It undergoes degradation.

Engineering applications of p.v.c

There are two kinds of p.v.c plastics.

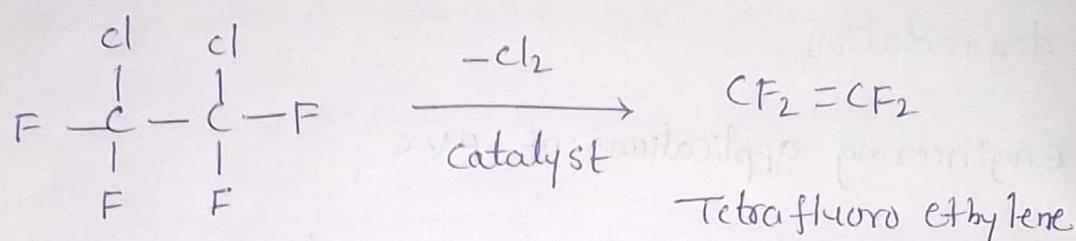
- 1) Unplasticized pvc:- It is used for making safety helmets, refrigerator components, tyres, cycle and motor cycle mudguards.
 - 2) plasticized pvc:- It is used for making raincoats, table cloths, hand bags, curtains, and electrical insulators, radio, TV components
- * Teflon (poly tetra fluoro ethylene) (or) Fluon.
- * Teflon is obtained by the chain polymerisation of tetrafluoro ethylene in presence of benzoyl peroxide as initiator.



Tetra fluoro ethylene

Poly tetra-fluoro ethylene

- * Tetra fluoro ethylene is produced by dechlorination of syn dichloro tetrafluoro ethylene in presence of a catalyst.



(syn dichloro tetra fluoro-
-ethylene).

Properties:

Teflon is also known as fluon. Due to the presence of highly electronegative fluorine atoms, Teflon has got.

- * High melting point (350°C)
- * The strong attractive force is responsible for high toughness & high chemical resistance.
- * High density $2.1 - 2.3 \text{ gm/cc}$
- * It is a very good electrical insulator.

- It possess very good abrasion resistance.
- It is very strong hard polymer that can be machined to drilling, punching etc.

Engineering applications

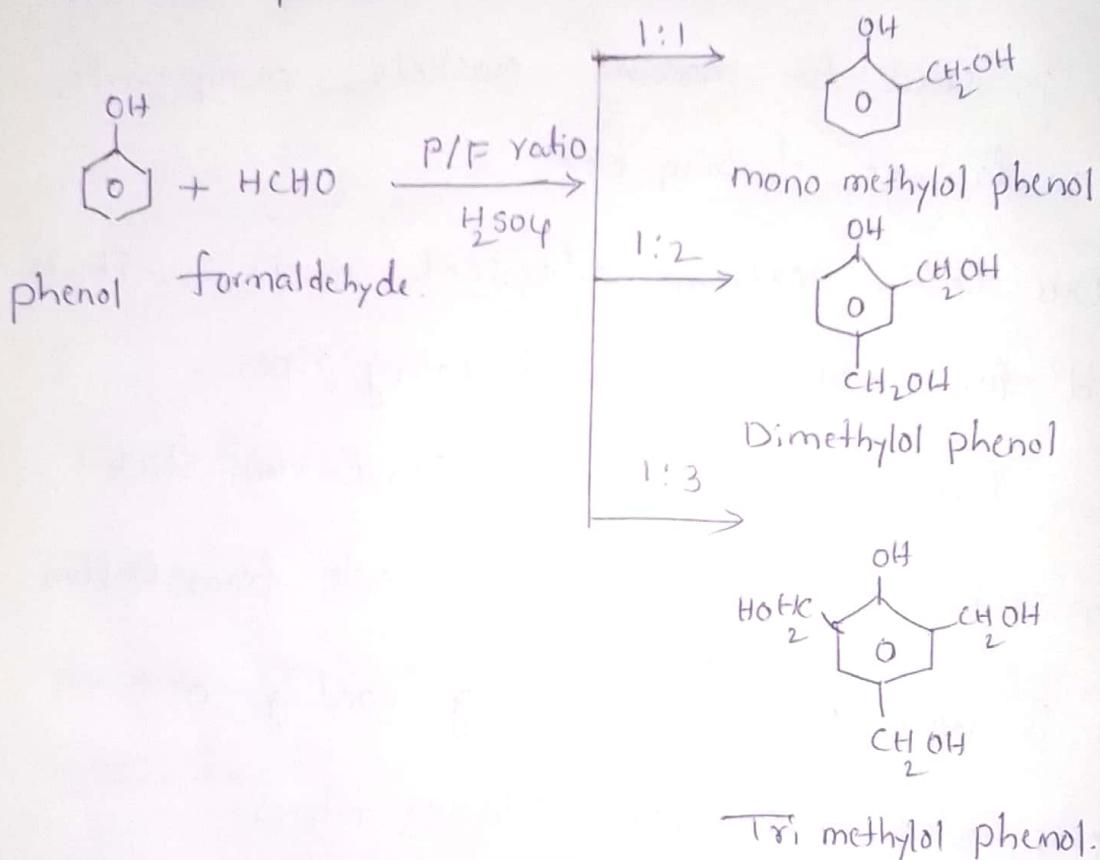
- Teflon is a very good insulating material for motors, transformers, cables, wires, fittings etc.
- It is used for making gaskets, pump parts, tank linings, tubing etc.
- Due to its extreme chemical resistance, it is used for making chemical carry pipes.
- Non lubricating bearings and non-stick stop cock for burettes are made from teflon.
- It is also used for making coating as impregnated glass fibre, asbestos fibres.

Bakelite (or) phenol-formaldehyde resin

The condensation reaction of phenol and formaldehyde in the presence of acid (or) alkali catalyst and at proper temperature produces

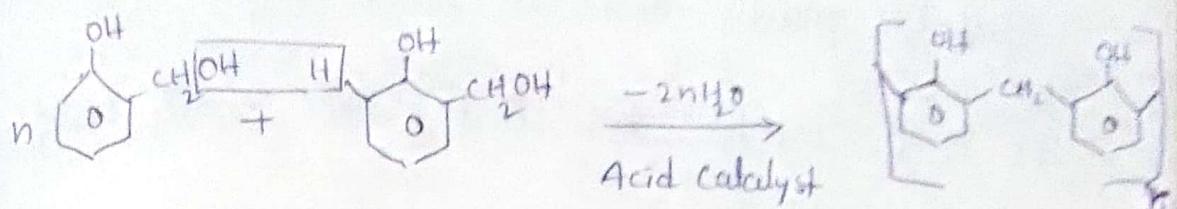
the phenol-formaldehyde resin (or) Bakelite.

I-stage: - The initial reactions of phenol and formaldehyde in the presence of acid (or) alkali catalyst and at proper tem produces mono, di, tri methylol phenols depending on the phenol-formaldehyde ratio.

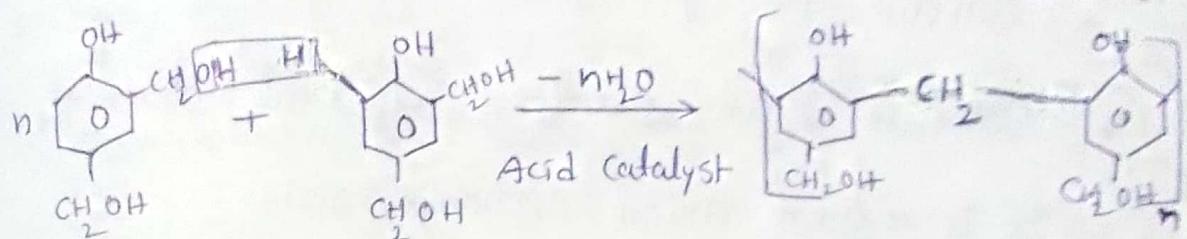


II-stage: - The mono, di, tri methylol phenols are heated to produce two types of straight chain resin by condensation of methylol group with hydrogen atom of benzene.

ring or another methylol group.

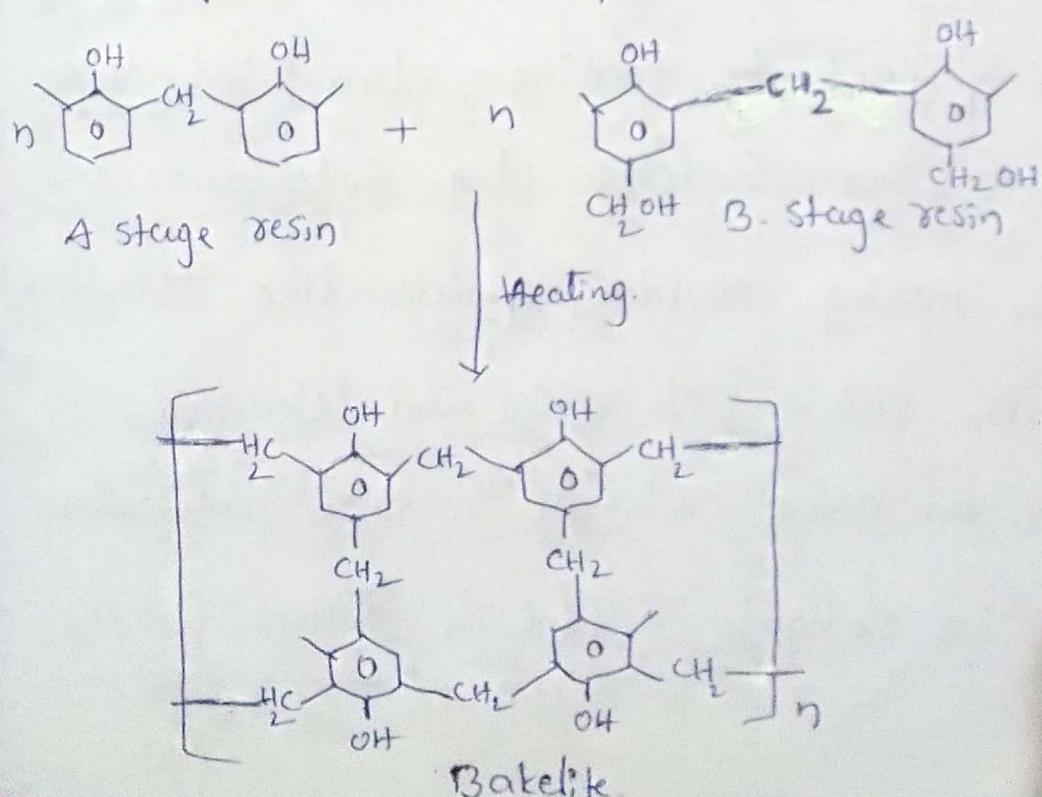


A-stage resin / Novolac



B-stage resin / Novolac

III-stage:- This stage of preparation includes heating of A stage resin and B stage resin together which develops cross linking and Bakelite plastic resin is produced.



Properties

- Bakelite plastic resin is hard, rigid and strong.
- It is a scratch resistant and water resistant polymer.
- Bakelite has got good chemical resistance.
- Bakelite is an excellent electrical insulator.
- It is a good anion exchange resin.
- It is a very good adhesive.
- Bakelite has very good corrosion resistance, resistance to atmospheric conditions like O_2 , CO_2 , moisture.

Engineering applications

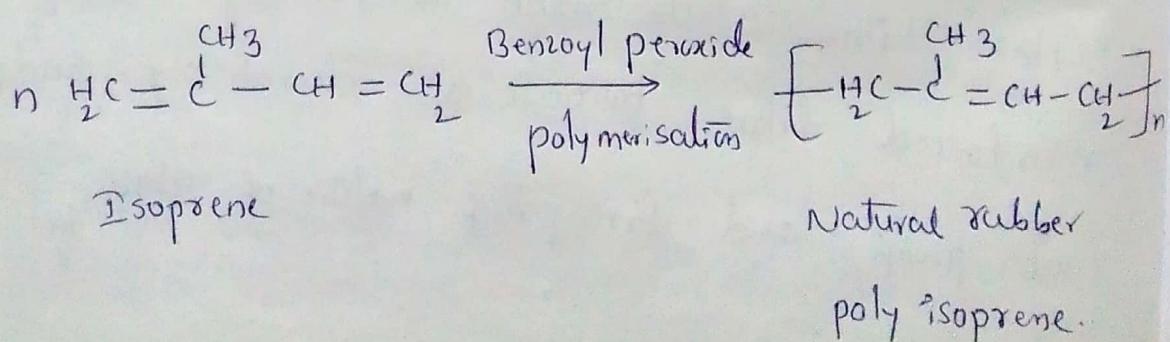
- It is used for making electric insulator parts like switches, plug, switchboards etc.
- For making moulded articles like telephone parts, cabinet of radio and television.
- As an anion exchanger in water purification by ion exchange method in boilers.

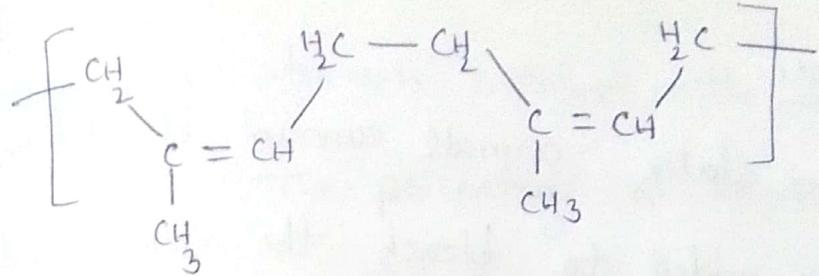
Rubbers

Those polymers which possess the property of elasticity is called rubber.

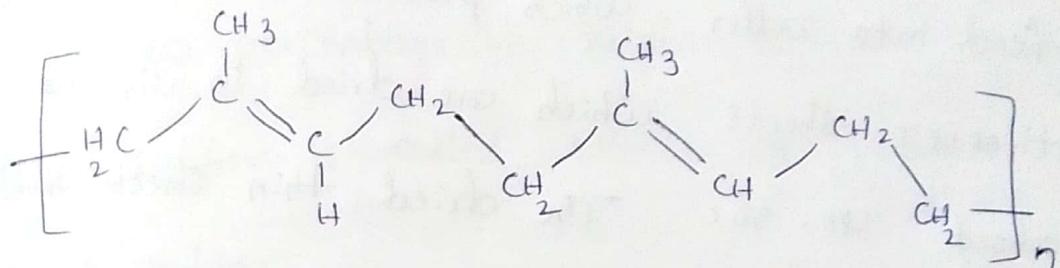
Natural rubber

Natural rubber is a high molecular weight hydrocarbon polymer represented by the formula $(C_5H_8)_n$. It is obtained from a milk emulsion called latex by tapping the bark of the tree *Hevea-brasiliensis*. The main composition of natural rubber is polyisoprene which is in the form of long coiled chains. The isoprene units polymerise to form rubber. Isoprene in natural rubber exists in two geometrical isomeric forms cis- and trans. cis-polyisoprene is present in hevea rubber, trans-polyisoprene is present in Gauyle and purcha rubber.





cis - poly isoprene



Trans - polyisoprene.

processing of natural rubber

The source of natural rubber is the latex of the tree *Hevea brasiliensis* by cutting the bark of

rubber tree the milky colloidal rubber milk is obtained - The main constituent of rubber latex is 25 - 45% of rubber and the remaining are water, protein and resinous materials.

The rubber latex is coagulated by using 5% acetic acid and made into sheets. The rubber sheets are cured under mild heat and then subjected to further processing.

Crepe rubber

To the rubber latex a small amount of sodium bisulphite is added to bleach the colour and feed into roller which produce 1mm or more thickness sheets which are dried in air at about $40-50^{\circ}\text{C}$. The dried thin sheet of rubber is known as smoked crepe rubber.

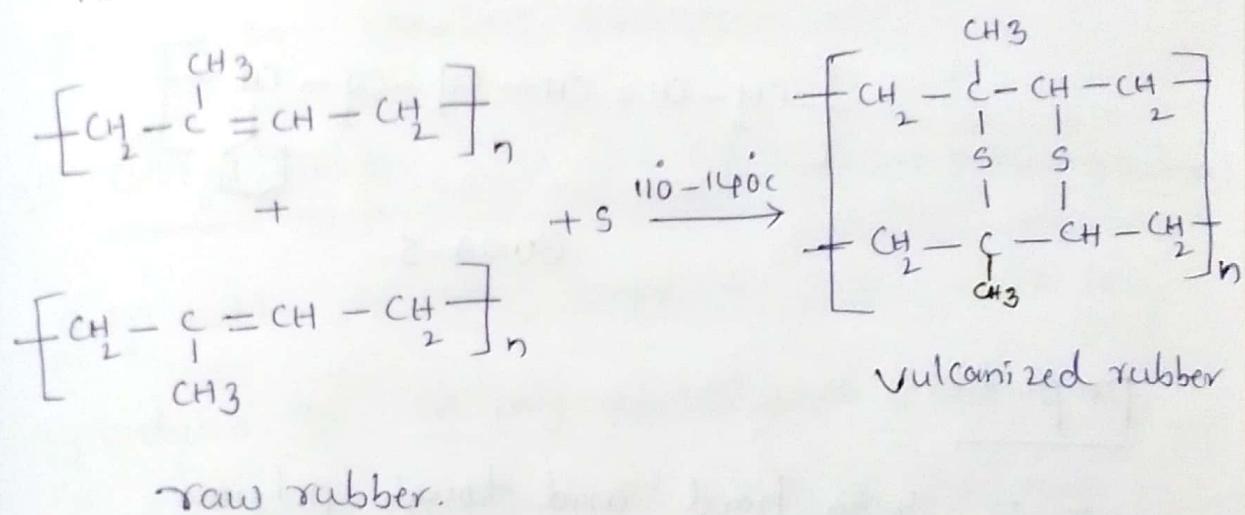
Vulcanisation of rubber

The raw or crude rubber is very little useful because it has very undesirable properties such as low tensile strength, possesses elasticity only over a limited range of temperature. To improve the properties of rubber Charles Goodyear in 1839 compounded the raw rubber with some chemicals and heated to $110-140^{\circ}\text{C}$. "The process of heating raw rubber with Sulphur at $110-140^{\circ}\text{C}$ is called vulcanisation".

* The vulcanisation process Sulphur combine chemically at the double bonds of the different chains producing sulphur cross linkings

imparting strength increases, the brittleness also increases. The percentage of Sulphur added is in the range of 0.5 to > 35%.

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



Elastomers (or) Synthetic rubbers

i) BUNA-S (or) styrene butadiene rubber or GRS

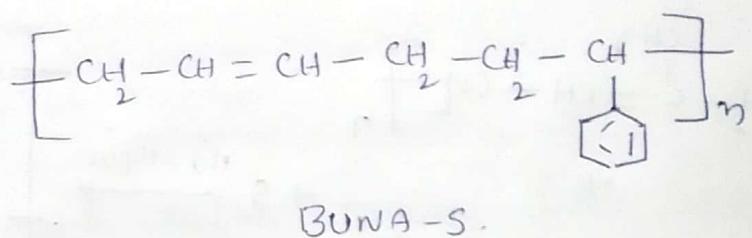
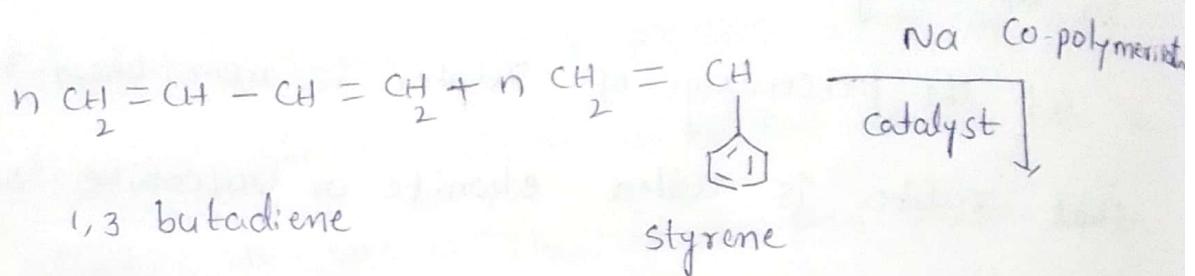
Buna-S (or) styrene rubber or GRS (Government rubber - styrene) or Ameripol.

BU — Butadiene — monomer

NA — sodium — catalyst

S — styrene — monomer.

→ Buna-S is produced by the co-polymerisation of butadiene (75%) and styrene (25%) using sodium as a catalyst.



Properties

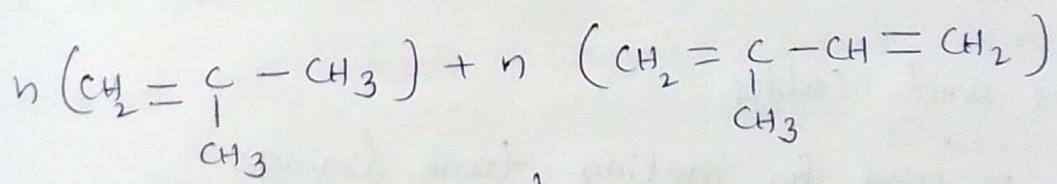
- It is strong hard and tough polymer.
- It is vulcanized by sulphur monochloride (S_2Cl_2) or sulphur.
- It is a good electrical insulator.
- It possess excellent abrasion resistant.
- It is resistant to chemicals but swell in oils and attacked by even traces of ozone present in the atmosphere.
- It possess high load bearing capacity and resistance.

Applications

- * It is used in manufacture of tyres, wires, and cable insulators.
- * It is used in the foot wear industry for making shoes, shoe soles and foot wear components.
- * It is used in production of floor tiles, tank linings in chemical industries etc.

2) Butyl rubber (or) GR-I (Government rubber-isobutene)

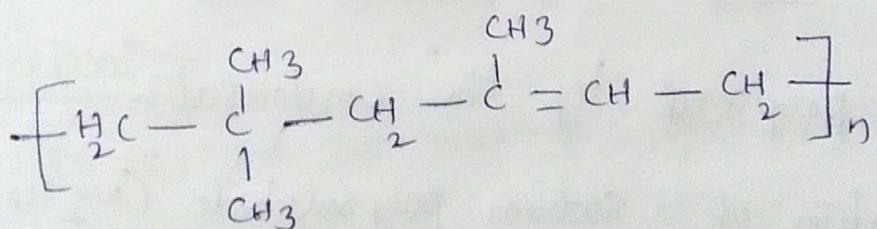
Butyl rubber is also known as GR-I. It is produced by co-polymerisation of isobutene with small amount of (1-5%) isoprene.



Isobutene



Isoprene.



Butyl rubber.

Properties

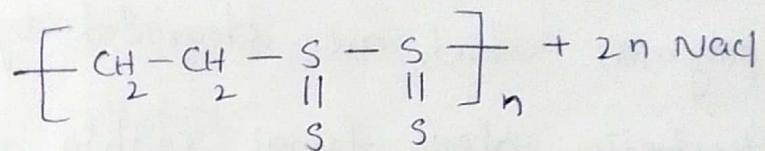
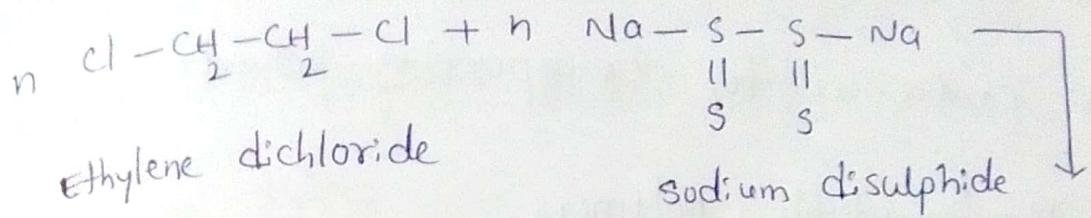
- It is a strong and tough synthetic rubber.
- It possess high abrasion resistance.
- It has high resistance to atmospheric gases and ozone.
- It is a good electrical insulator.

Applications

- Butyl rubber is used for making cycle tyres and automobile tubes.
- It is used for making automobile parts and conveyor belts in food processing industry.
- It is used as an insulator for high voltage wires and cables.
- It is used for making tank linings.

3) Thiokol rubber, Poly sulphide rubber or GIR-P

Thiokol is prepared by the condensation polymerisation of sodium poly sulphide (Na_2S_4) and ethylene dichloride.



Thick oil rubber.

properties

- * Thiokol rubber possess strength and impermeability
 - * Thiokol rubber can not be vulcanized and cannot form hard rubber.
 - * It possesses extremely good resistance to mineral oils, fuels, oxygen, solvents, ozone and sunlight.
 - * Thiokol rubber possesses low abrasion resistance.

Applications

- Applications

 - * It is used for making gaskets and seals for printing rolls.
 - * Thiokols are used for lining hoses for conveying gasoline, tank linings

- It is used in military air craft
- * containers for transporting solvents

Biodegradable polymers

The polymers which are degraded by microorganisms like bacteria, algae, fungi within a suitable period so that the polymers and their degraded products do not cause any serious effects on the environment are called biodegradable polymers.

Types of biodegradable polymers

Biodegradable polymers are classified into two types.

- 1) Natural biodegradable polymers
- 2) Synthetic biodegradable polymers.

1) Natural biodegradable polymers

Natural biodegradable polymers are produced in nature by all living organisms.

Groups of natural biodegradable polymers.

Natural biodegradable polymers are grouped into four types.

1) polysaccharides

e.g.: starch, cellulose

2) proteins

e.g.: Gelatin, Casein, Silk, Wool.

3) Aliphatic polyesters

e.g.: poly hydroxy alkanoates

4) Others

e.g.: Lignin, Shellac, natural rubber.

2) Synthetic biodegradable polymers.

These polymers are produced from chemicals or biological sources that are biodegradable.

There are a number of biodegradable synthetic polymers they are

1) poly-lactic acid

2) poly vinyl alcohol

3) poly vinyl acetate

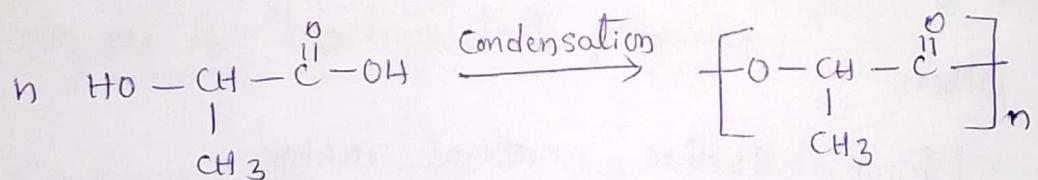
4) poly amide esters

Important biodegradable polymers.

1) poly lactic acid.

poly lactic acid is a biodegradable aliphatic thermoplastic polymer. It is derived from renewable sources such as starch, sugar cane etc.

Preparation poly lactic acid is obtained by the condensation polymerisation of lactic acid in the presence of acid or base catalyst.



Lactic acid poly lactic acid

Properties of PLA:

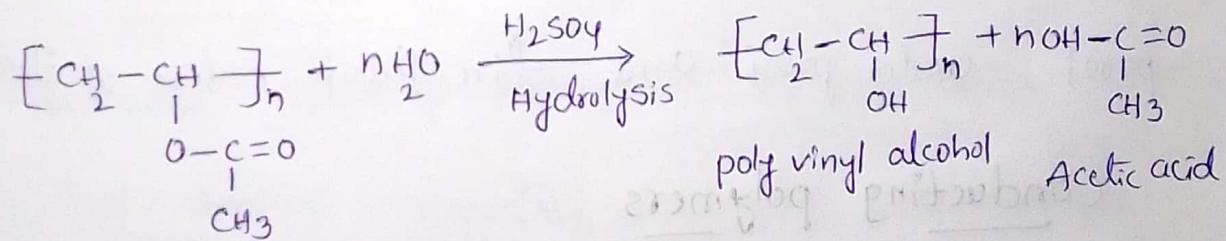
- * The glass transition temperature of PLA is 60-65°C
- * PLA possess melting point 173 - 178°C
- * PLA possess good bio-compatibility, processability
- * PLA possess high strength.
- * PLA is a chiral compound existing a poly L-lactic acid.

Applications of PLA

- PLA is used for making medical implants like screws, pins, anchors etc.
- * It is used in a number of biomedical applications like drug delivery devices and dialysis media.
- * It is used in the preparation of bio plastics for packing food and disposable table ware.
- * It is also used for making compostable packing materials, food packing etc.

2) poly vinyl alcohol

Polyvinyl alcohol is a poly hydroxy polymer containing number of OH⁻ groups. It is readily obtained from hydrolysis of poly vinyl acetate.



Properties: * It is a colourless, odourless, tasteless.

- * It is unaffected by all oils, greases, fats, hydrocarbons,
- * high tensile strength and flexibility.

- * high chemical resistance and water soluble polymer.
 - * Viscosity range from 5 to 55 centipoise.
- Applications * It is used in the paper and textile industry.
- * It is used in food packing industry.

Fibre reinforced plastics

Fibre reinforced plastics are produced by reinforcing a plastic matrix with a high strength fibre materials such as glass, graphite, alumina, carbon, boron, Be and aromatic polyamide.

- * Natural fibres such as sisal, asbestos are also used for reinforcement.
- * Glass fibre is the most extensively used reinforced fibre because of durability, acid-proof, water proof and fire proof nature of glass.

conducting polymers

Those polymers which conduct electricity are called conducting polymers.

Reason for the conduction in the polymers.

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

Eg: polyacetylene, polyaniline.

Preparation of conducting polymers.

Doping:- Doping is the process by which conductivity of the polymers may be increased by creating negative or positive charge on the polymer backbone by oxidation or reduction.

Types of doping There are two types

1) p-doping :- creating a positive site on polymer

backbone called p-doping Eg: I_2 , Br, $AlCl_3$

2) n-doping :- creating a negative site on the

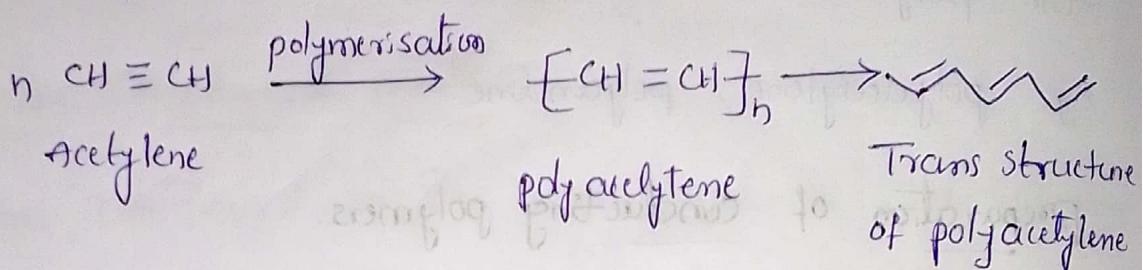
polymer backbone called n-doping Eg: Na, K,

T, naphthalide.

Important conducting polymers.

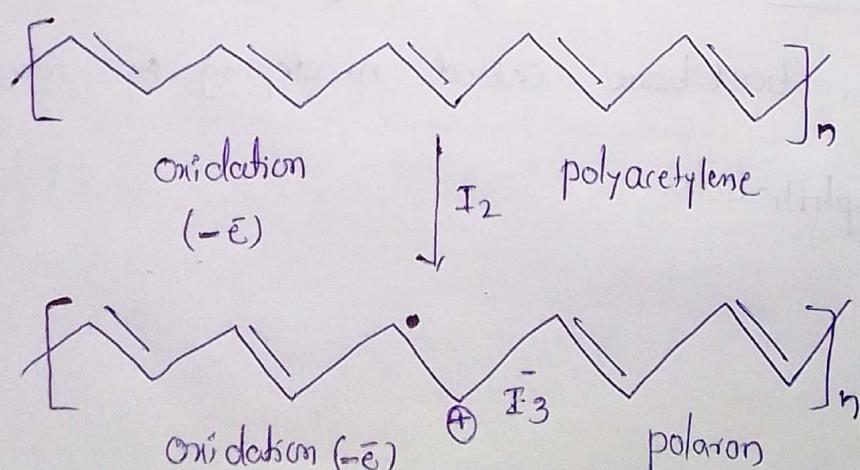
Polyacetylene Preparation:-

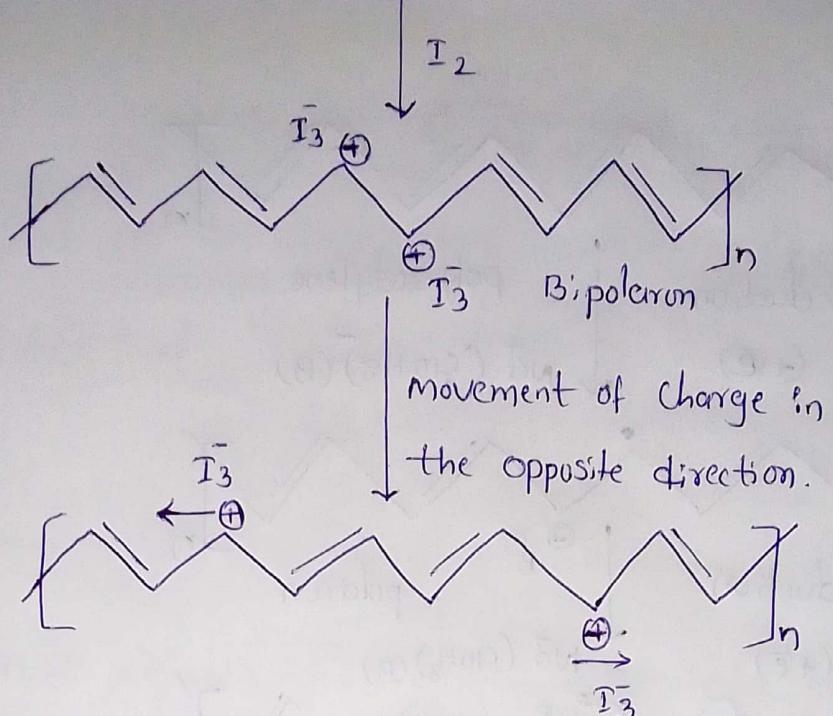
Polyacetylene is prepared by the addition polymerisation of acetylene.



Mechanism of conduction polyacetylene

- p-doping :- p-doping is done by oxidation of a polyacetylene with iodine vapour or Lewis acid
- During oxidation the iodine molecules remove an electron from polyacetylene chain and becomes I_3^- . Now the polyacetylene chain carrying the +ve charge called polaron.

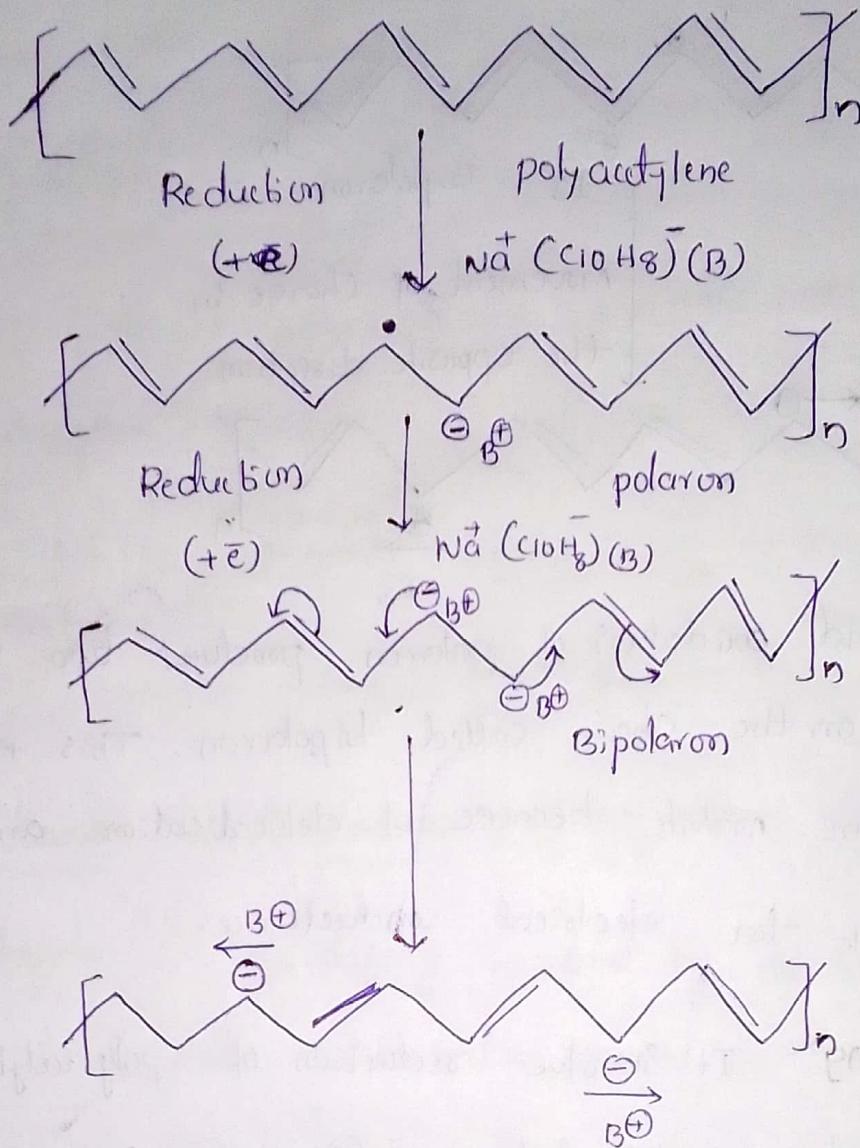




* The second oxidation of polaron produces two +ve charges on the chain called bipolaron. These +ve charges are mobile because of delocalisation and responsible for electrical conductance.

n-doping It involves reduction of polyacetylene with sodium naphthalide $\text{Na}^+(\text{C}_{10}\text{H}_8)^-$. During the reduction, sodium naphthalide donates an electron to polyacetylene chain. Now the polyacetylene carrying -ve charge this is called polaron.

* The second reduction of polaron to produce two -ve charges on the chain called bipolaron. These -ve charges are mobile because of delocalisation and responsible for electrical conductance.



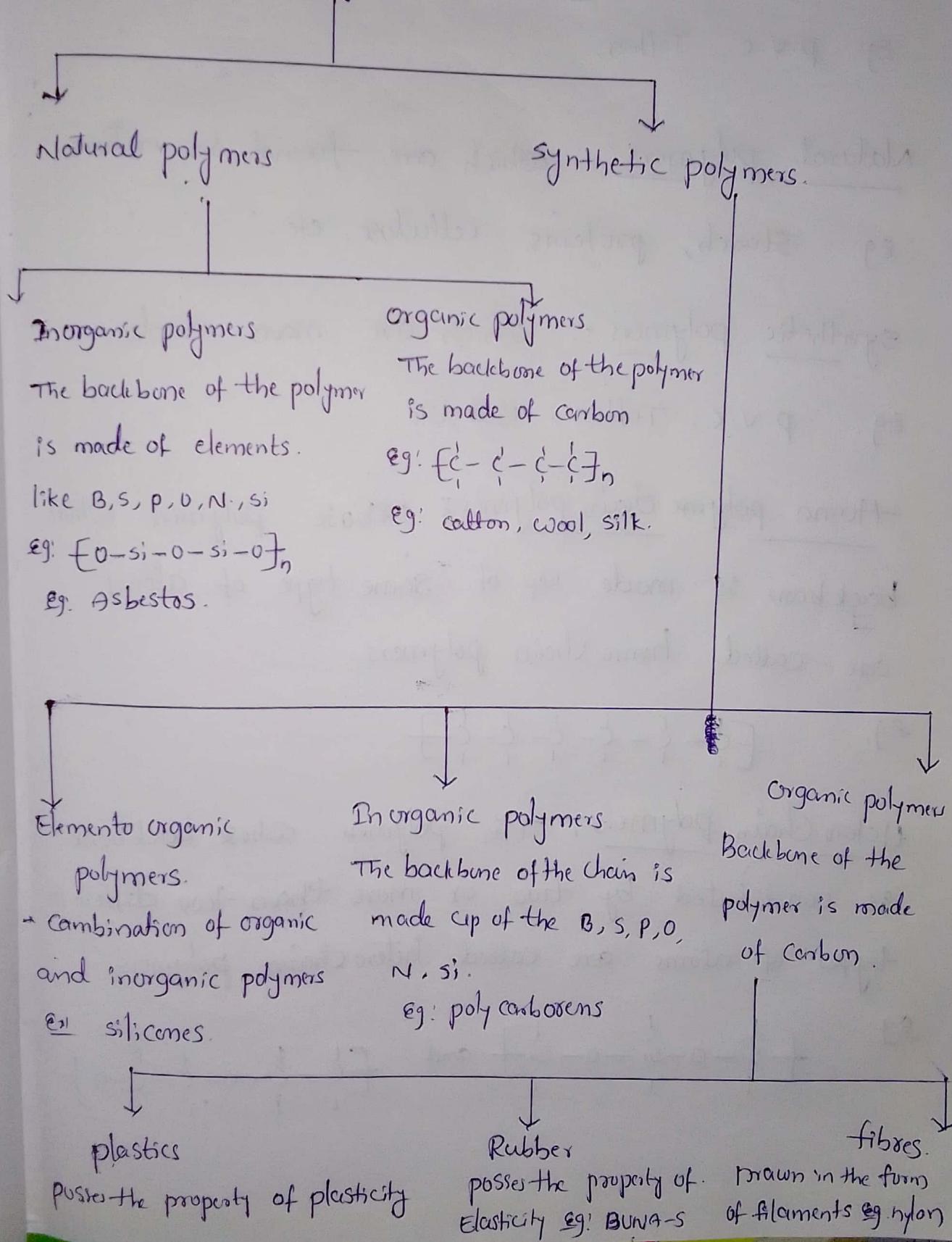
Applications of conducting polymers

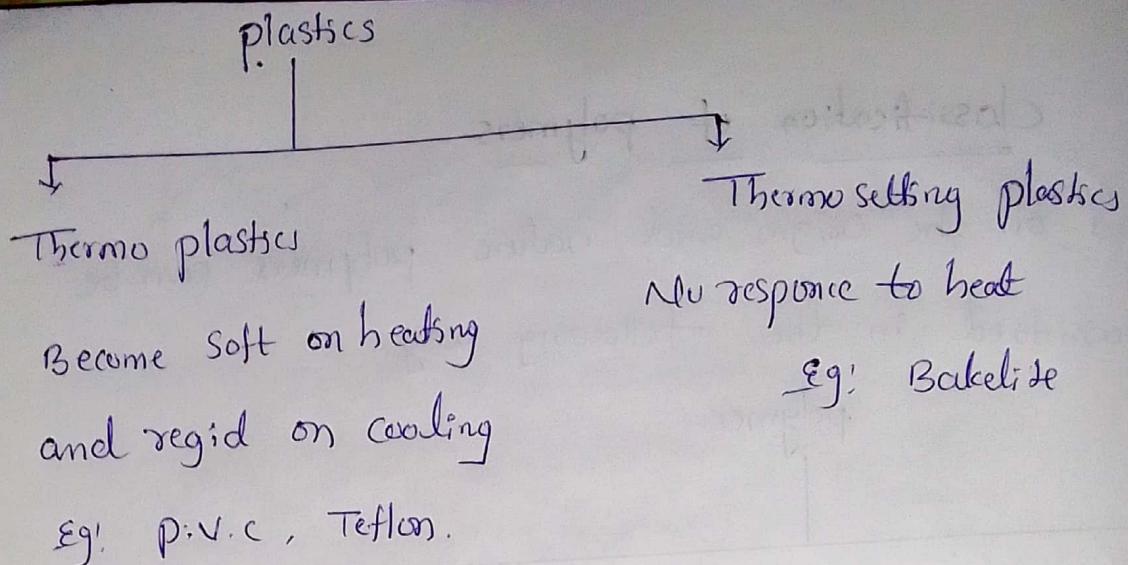
- * Conducting polymers are used in solar cells.
- * It is used in telecommunication system.
- * It is also used as a very good electrode material for rechargeable batteries.
- * It is used as a membrane film for gas separations
- * It is used for making analytical sensors.
- * It is used for making ion exchangers.

Classification of polymers

Based on the origin and nature polymers can be classified in the following way.

polymer.





Natural polymers: which are found in nature

e.g.: starch, proteins, cellulose, etc.

Synthetic polymers :- which are man made

e.g.: P.V.C., Teflon, Bakelite.

Homo polymer chain polymers: Those polymers whose backbone is made up of same type of atoms are called homo chain polymers.

e.g.: $\left\{ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \right\}$

Hetero chain polymers: The polymers whose backbone is constituted by two or more than two different types of atoms are called hetero chain polymers.

e.g.: $\left\{ \text{Si}-\overset{\cdot}{\underset{\cdot}{\text{O}}}-\overset{\cdot}{\underset{\cdot}{\text{Si}}}-\overset{\cdot}{\underset{\cdot}{\text{O}}}-\overset{\cdot}{\underset{\cdot}{\text{Si}}} \right\}$ and $\left\{ \text{C}-\overset{\cdot}{\underset{\cdot}{\text{C}}}-\overset{\cdot}{\underset{\cdot}{\text{O}}}-\overset{\cdot}{\underset{\cdot}{\text{C}}}-\overset{\cdot}{\underset{\cdot}{\text{C}}}-\overset{\cdot}{\underset{\cdot}{\text{O}}} \right\}$