

POLYMERS

→ The word polymer was derived from the Greek word
Poly = many, mers = units.

→ More number of monomer units are combined to form
Polymer.

Basic Concept of polymer:-

1. Monomer:- The repeating unit in polymer is called monomer.
-er. Eg:- Polythene monomers.

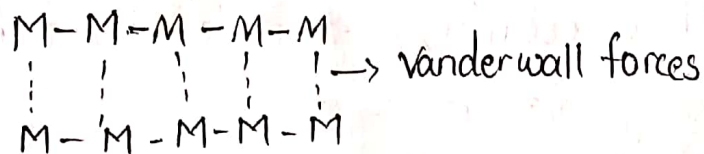
2. Functionality:-

The number of bonding sites or reactive sites present
in a monomer is called functionality.

→ Every monomer must have minimum two bonding sites
for polymerisation process.

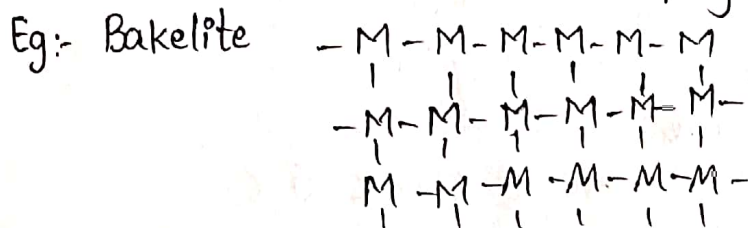
a) If the functionality of monomer is two, the reactive
sites attach side by side to each other.

→ Linear or straight chain polymers are formed.

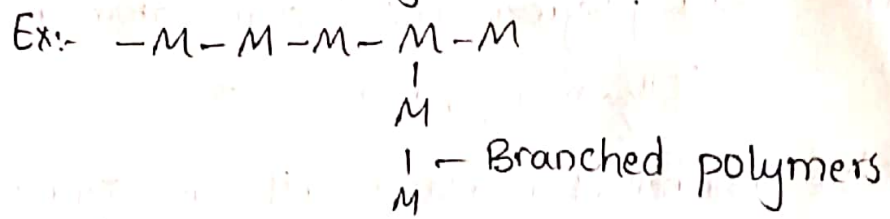


Eg:- Ethylene, styrene and VC

b) If the functionality of monomer is three, then cross-
-linked three dimensional network polymers are formed.



c) Mixture of bifunctionality and trifunctionality polymers gives the branched chain polymers.



Nomenclature of polymers:-

a) Homo polymers:- polymers obtained from same type of monomers is called homopolymers.

-> They may be linear, branched (or) crosslinked.

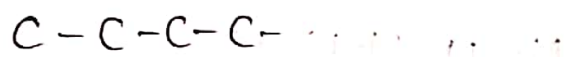
Ex:- PVC, polythene and teflon.

b) Hetero polymers:- polymers obtained from different type of monomers are called hetero polymers.

-> They may be generally linear or branched.

c) Homo chain polymers:-

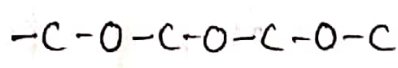
The polymer backbone is made up of same atoms. These polymers are called homo chain polymers.



Eg:- PVC, polythene.

d) Hetero Chain polymers:- polymer backbone is made up of different atoms. These polymers are called Hetero Chain polymers.

Eg:- Nylon 6,6



3) Tacticity:- The Orientation of functional groups (or) The arrangement of functional groups in polymer is called Tacticity.

a) Isotactic:- If the functional groups are arranged on the same side of the chain. It is called Isotactic Polymer.

b) Atactic:- If the functional groups are arranged randomly, then it is called Atactic polymer.

c) Syndiotactic:- If the functional groups are arranged Alternately fashion, then the polymer is called syndiotactic polymer.

When the monomers are combined to form polymers is called polymerisation.

They are of 3 types

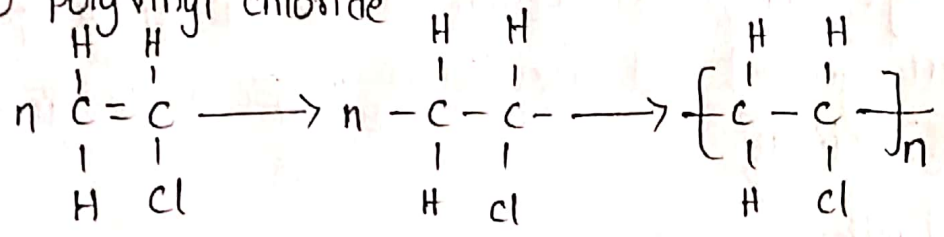
a) Addition or chain polymerisation:- (chain growth)

→ In Addition polymerisation several bifunctional monomers are combine to form polymers by addition reaction.

→ Without elimination of any byproducts.

→ The monomers containing double bonds generally Undergoes addition polymerisation and produce linear Polymer.

Eg:- ① polyvinyl chloride



PVC

② Ethylene: $\text{H}_2\text{C} = \text{CH}_2$

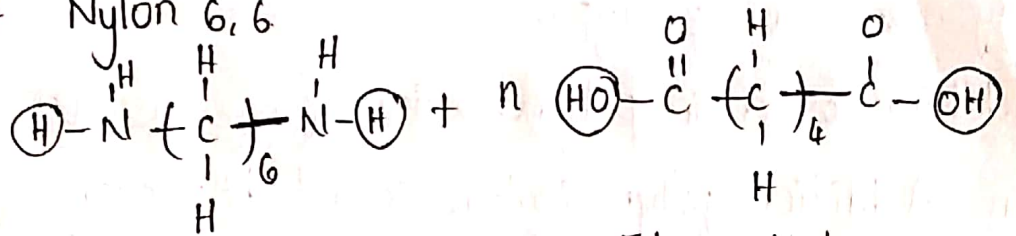
③ polystyrene: $n \text{H}_2\text{C} = \underset{\text{C}_6\text{H}_5}{\text{CH}}$

ii) Condensation polymerisation (or) Stepwise polymerisation

→ In condition polymerisation, the polymer is formed by stepwise reaction.

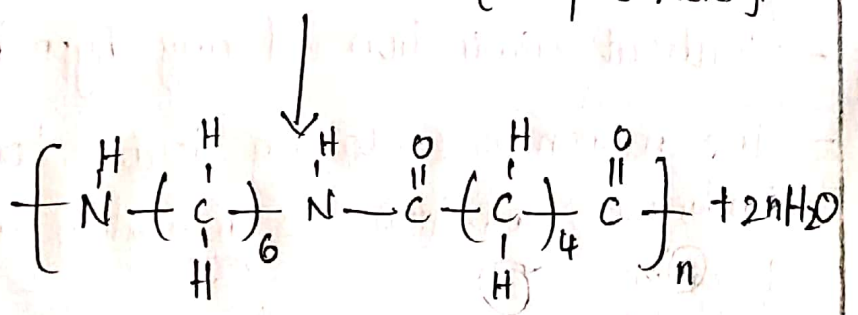
→ Between the same or different polar groups containing monomers with the elimination of small molecules like H_2O , HCl , NH_3 .

Eg:- Nylon 6,6



Hexa methylene diamine.

Tetramethylene dicarboxylic Acid (Adipic Acid).

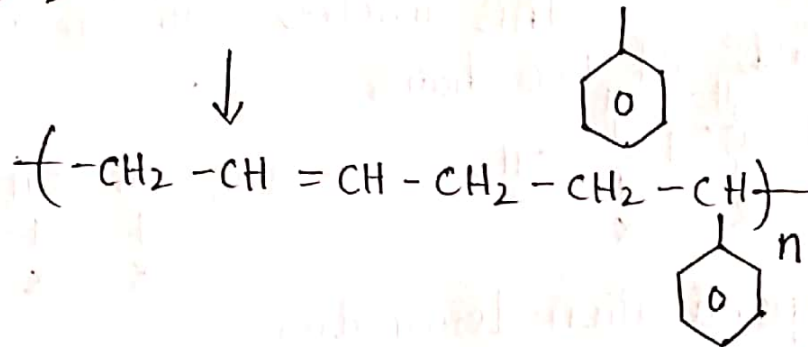
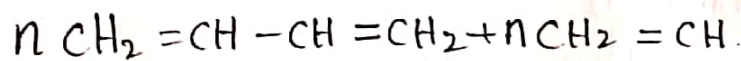


Nylon 6,6.

Copolymerisation:-

→ When two or more different types of monomers undergo simultaneously polymerisation. Then it is called Copolymerisation.

Ex:- GRS-rubber (or) SBR



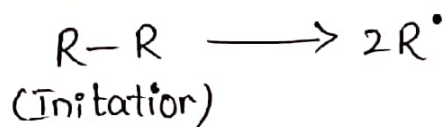
Mechanism of Addition polymerisation:-

a. Free radical polymerisation:-

The mechanism involves the following 3 steps.

(i) Initiation:-

This involves the dissociation of an initiator into two free radicals.



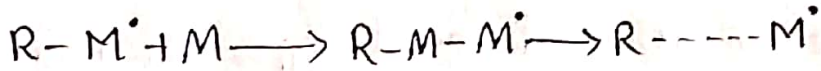
→ Then the free radicals add to the first monomer molecule.



(ii) Propagation:-

This involves the growth of polymer chain by successive addition of monomeric units resulting in the formation of polymer 'c' chain with

free radical centre.

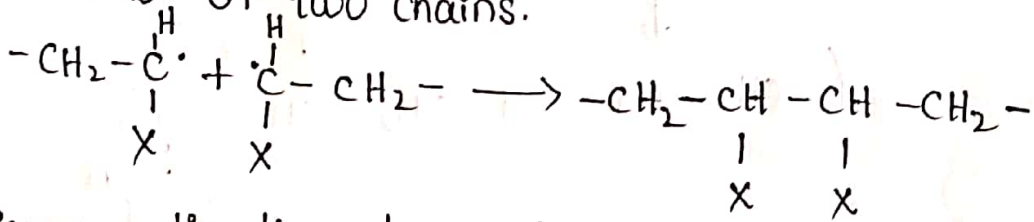


(ii) Termination:-

This can be takes place either of two

(a) Coupling termination:-

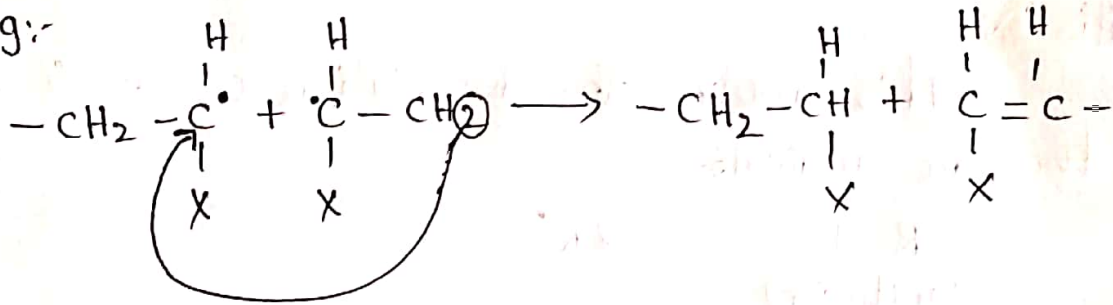
This involves collision between the active ends of two chains.



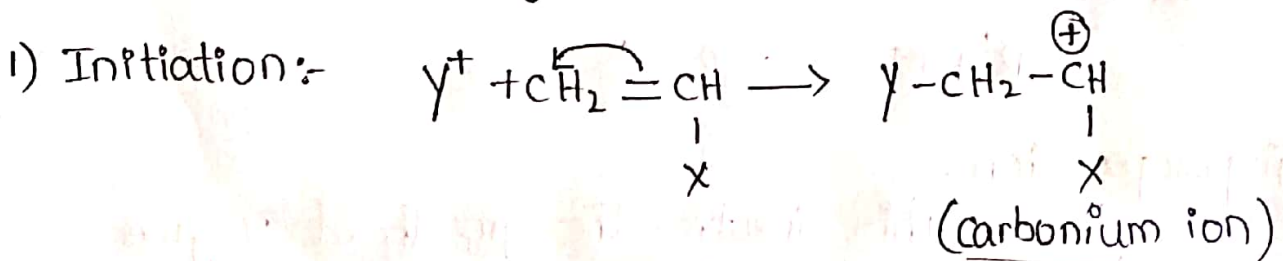
b) Disproportionation-termination:-

→ This involves the transfer of a hydrogen atom of one radical centre to another radical centre resulting in the formation of two polymer units. One is saturated and another unsaturated.

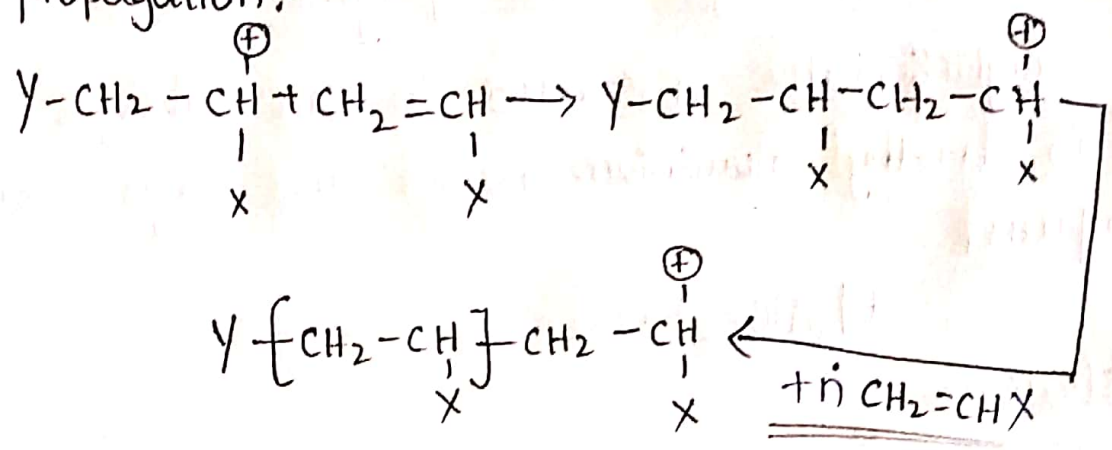
Eg:-



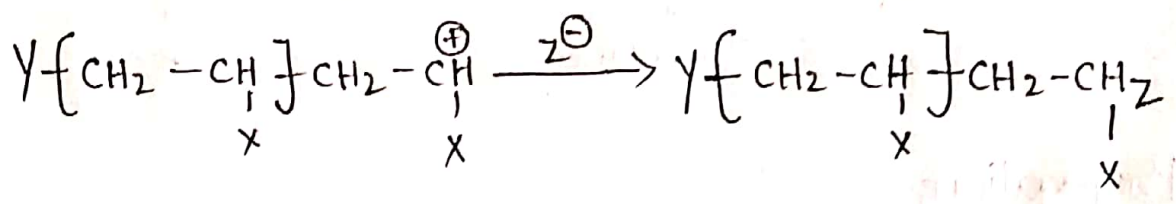
b) Cation Addition polymerisation:-



(ii) Propagation:-

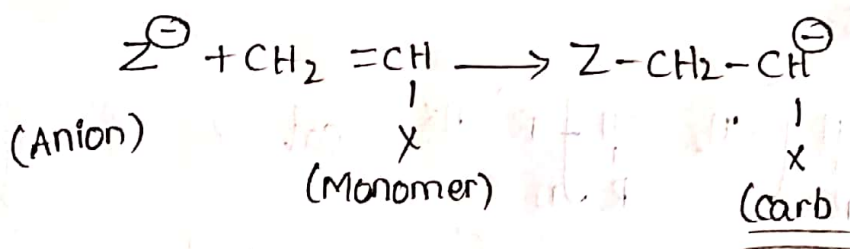


(iii) Termination:-

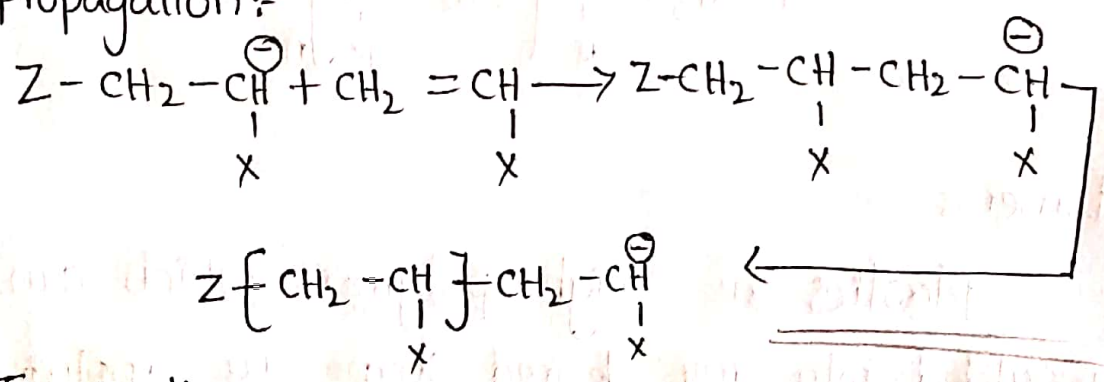


c) Anionic Addition polymerisation:-

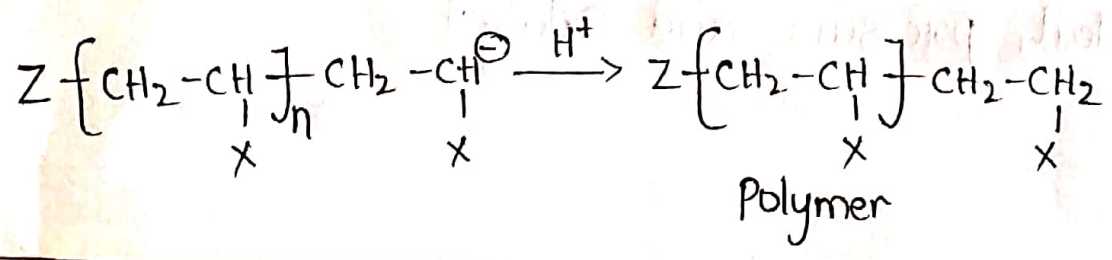
(a) Initiation:-



(b) Propagation:-

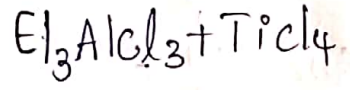


(c) Termination:-

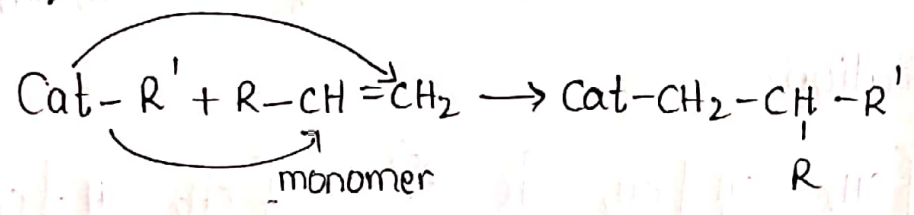


Co-ordination (or) Zeiglar-Natta polymerisation:-

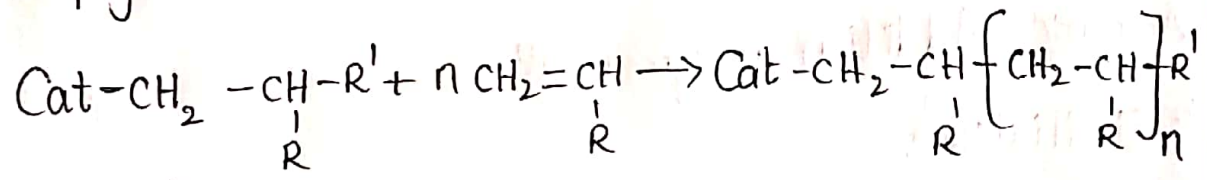
Zeiglar & Natta discovered in one catalyst that is triethyl aluminium halied and organometallic compound



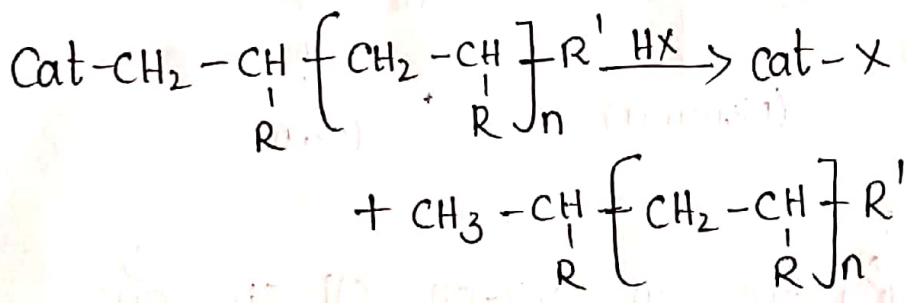
① Initiation:-



② Propagation:-



③ Termination:-



Plastomers:-

plastics are high polymers which can be moulded into any desired shape by applying the Heat, pressure and catalyst.

Properties:-

- 1) light in weight.
- 2) good thermal and electrical insulation.
- 3) low fabrication cost.
- 4) easy moulding.
- 5) Inset resistance.
- 6) Chemical inertness.
- 7) low maintenance cost.
- 8) good dimensional stability.
- 9) Corrosion resistance.
- 10) Easy workability.

Classifications of plastics:-

Plastics are classified into two types.

- ① Thermoplastics ② Thermosetting plastics.

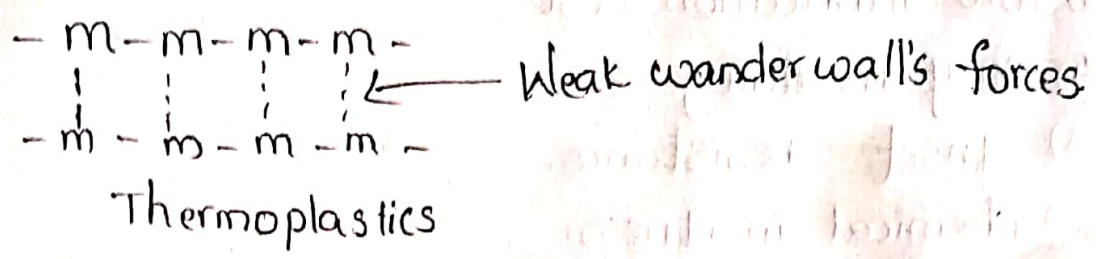
1) Thermo plastics:-

These type of polymers which become soft on heating and hard on cooling.

- On reheating, they become soft again and can be remoulded to any desired shape.
- They are formed by addition polymerisation and have linear long chain polymeric structure.

→ The chemical composition is not changed during heating or moulding operations.

→ The weak Vanderwalls forces contains b/w the thermoplastic chains



Thermoplastic	Thermosetting Plastic
<ol style="list-style-type: none"> 1. These are formed by Addition Polymerisation. 2. They are soft, weak and less brittle. 3. They soften on heating and harden on cooling. 4. They consist of linear long chain polymers. 5. They are usually soluble in some of the organic solvents. 6. They can be reclaimed from wastes. 	<ol style="list-style-type: none"> 1. These are formed by Condensation Polymerisation. 2. They are hard, strong and more brittle. 3. They are fusible on initial heating but become hard, rigid and non fusible products on further heating. 4. They consist of three dimensional network joined by strong covalent bonds. 5. They are insoluble in almost all organic solvents. 6. They cannot be reclaimed from wastes.
<ol style="list-style-type: none"> 7. There is no change in chemical composition and structure during moulding process. 	<ol style="list-style-type: none"> 7. They undergo chemical changes such as further polymerisation and cross links during moulding process.

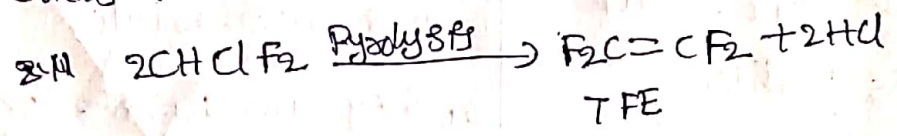
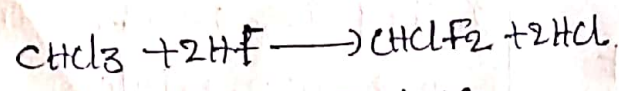
Some Important Polymers :

① Teflon :- Poly tetra fluoro ethylene (PTFE) or fluo.

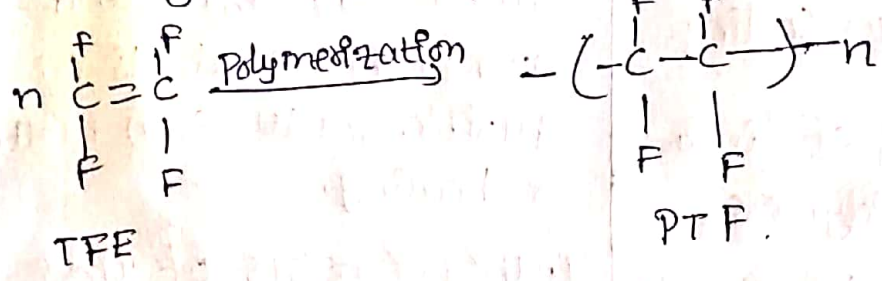
Preparation :- Teflon is obtained by the polymerization

of water-emulsion of tetra fluoro ethylene under pressure in the presence of benzoyl peroxide as catalyst.

=> The monomer, tetra fluoro ethylene (TFE) is obtained by the following reactions.



TFE undergoes polymerization, PTFE is obtained.



Properties:- a) Highly crystalline

- b) High melting point, 330°C
- c) Not soluble in any solvent.
- d) High density 2.3g/cm³.
- e) Good electrical and mechanical properties
- f) Excellent thermal stability.

uses: It is used

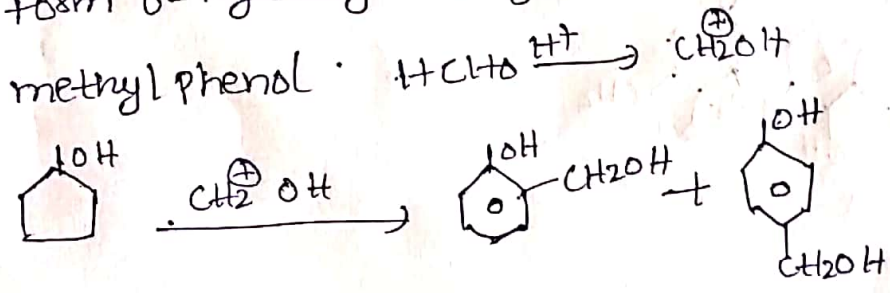
- a) For insulation of motors, generators, capacitors, transformers etc.
- b) In making stop cocks for burettes; non-lubrication bearings, chemical carrying pipes.

- c) For coating on articles like bakers trays frying pans etc.
- d) Bakelite (or) Phenol + formaldehyde resin (or) Phenol (or) Phenol Plastics.

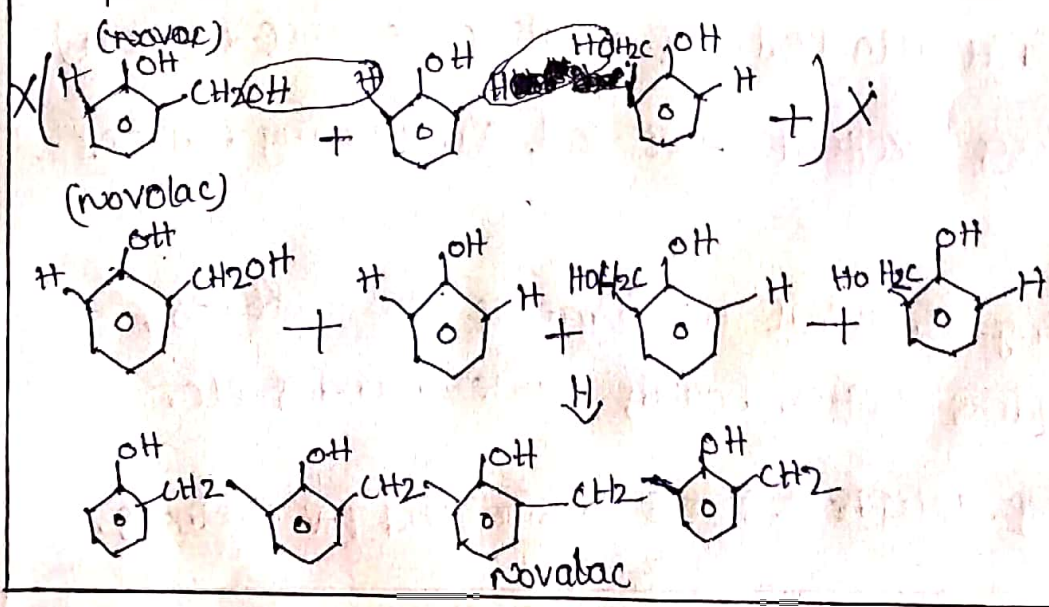
Preparation: Bakelite is obtained by the condensation polymerisation of phenol and formaldehyde in the presence of an Acid (or) alkali catalyst.

⇒ The following steps are involved

In the first step, Phenol reacts with formaldehyde to form o-hydroxy methyl phenol and p-hydroxy methyl phenol.



⇒ In the second step, Condensation between hydroxy methyl phenol and phenol occurs to give linear polymer.

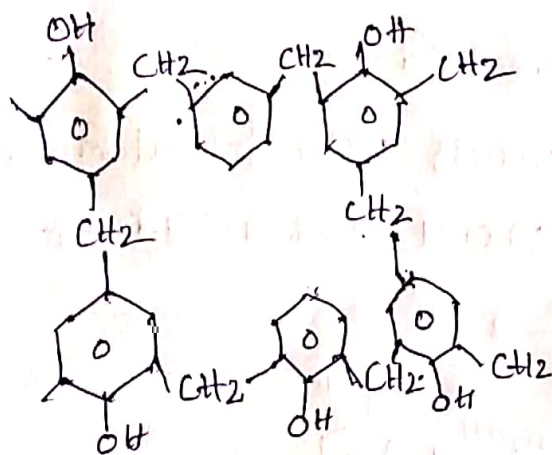


⇒ In this third step a small amount of hexamethylene tetramine is added.

⇒ It produces H_2O and NH_3

⇒ Formaldehyde converts the soluble and fusible novolac into hard, infusible solid of cross-linked three-dimensional polymer.

→ NH_3 neutralizes the Acids.



Properties:

- ⇒ Bakelite is a rigid, hard infusible solid substance
- ⇒ It is resistant to acids, salts, and most organic solvents but attacked by alkali (presence of -OH group)
- ⇒ It possesses excellent electrical insulating character.

Uses:

- ⇒ For making electrical equipments like switches, plugs, holders, switch boards, heater handles etc.
- ⇒ For making telephone parts radio and T.V. cabinets.

⇒ In paints and varnishes.

⇒ For making bearings, propeller shafts for paper industry and rolling mills

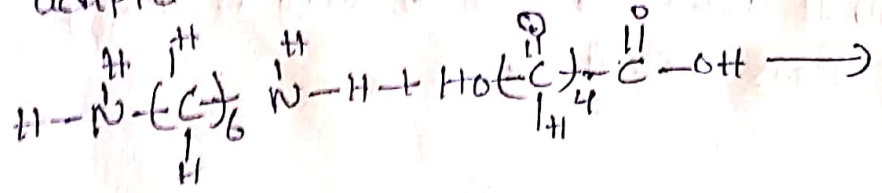
⇒ In the production of ion-exchange resins:

3) Nylon (polyamides)

The nylons have been named on the basis of the no. of carbon atoms in the monomer chain.

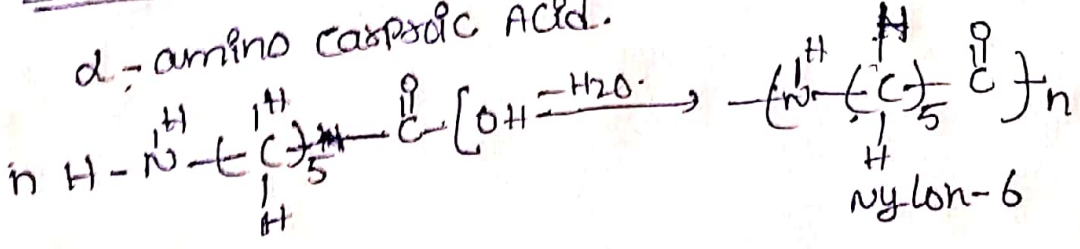
a) Nylon 6,6:-

Preparation: It is obtained by the polymerization of adipic acid with hexamethylene diamine.

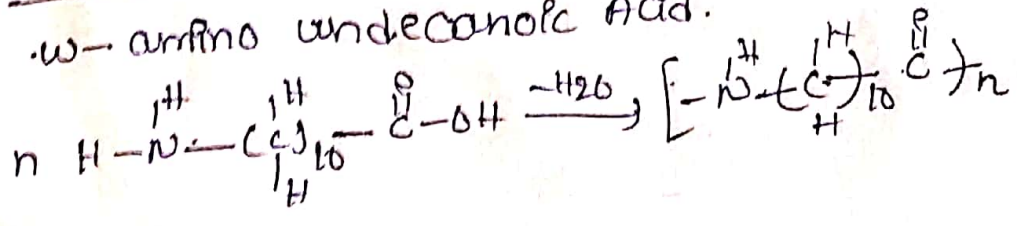


b) Nylon-6:-

Preparation: It is obtained by the self-condensation of α-amino caproic acid.



Nylon-11:- It is obtained by the self condensation of ω-amino undecanoic acid.



Properties:

- ⇒ Nylons show plastic and fibre properties.
- ⇒ They possess good mechanical properties.
- ⇒ They are insoluble in common organic solvents and soluble in formic acid and phenol.
- ⇒ They have strength and abrasive resistance.

Uses: 1) Nylon 6,6 is used as fibres for making socks,

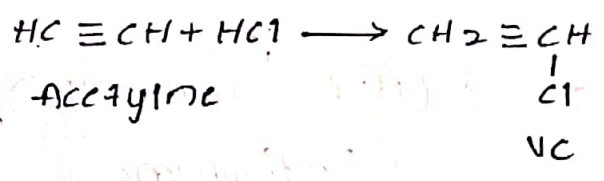
dressings, carpets, undergarments etc.

2) They are also used for making filaments, films, bristles for tooth-brushes.

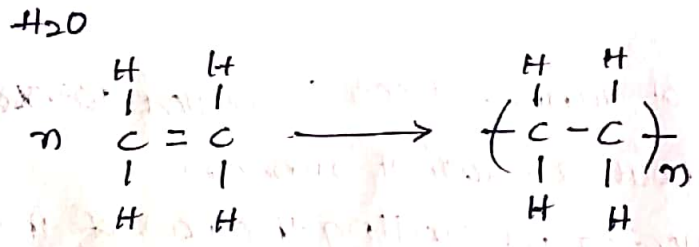
3) Nylon 6, nylon 11 are used for making moulding purpose for gears, bearings.

PVC :- Vinyl chloride is a monomer

→ vinyl chloride is prepared by reacting acetylene with HCl at 100-150°C in the presence of metal catalyst.



→ VC is heated in the presence of benzoyl peroxide (O₂)



Properties :-

- i) PVC is a colourless and odourless powder
- ii) It is non-inflammable and chemically inert
- iii) It is soluble in chlorinated hydrocarbons like
- iv) It has high resistance to light, inorganic salt and alkalis and atmospheric oxygen

Uses :-

- 1) Plasticised PVC is used for making table cloth, raincoats, coating for electric wire and cables, toilet articles, radio, T.V, components, pipes coupling valves.
- 2) Unplasticised PVC or rigid PVC is used for making refrigerators, components, pipes cycle and motor cycle mud guard, tubes, pipes etc....

Elastomers :-

→ The main sources of natural rubber is tree as *Hevea brasiliensis*

→ Natural rubber is the polymer of isoprene



2-methyl 1,3 butadiene

Polyisoprene

(Isoprene)

(Natural rubber)

Processing of N.R :-

→ The milk of rubber trees is called latex

→ It is containing about 25-40% of rubber.

→ The latex is collected by cutting the bark of the rubber trees.

→ The latex is diluted with water and filtered eliminated the impurities

→ The latex then coagulations by addition of dilutes acetic acid.

→ The coagulated rubber is called crude rubber

→ It is rolled out into sheets.

→ It is rolled out into sheets.

Crepe rubber :-

→ A small amount of sodium bisulphate the colour.

→ And passed into rollers which produce low (or) more thickness sheets. In these presence air to 40-50°C temp.

iv) accelerators :-

These shorten time required for vulcanisation and give toughness to the rubber.

For example :- 2 mercaptol and Benzothiazole added to natural rubber thus act as accelerant.

v) fillers :- These are added to give rigidity and strength to the rubber.

ex :- carbon black, zinc oxide and calcium carbonate

vi) colouring matter :-

→ These materials provide pleasing colour to the rubber product.

eg :- titanium oxide - white

Ferric oxide - red

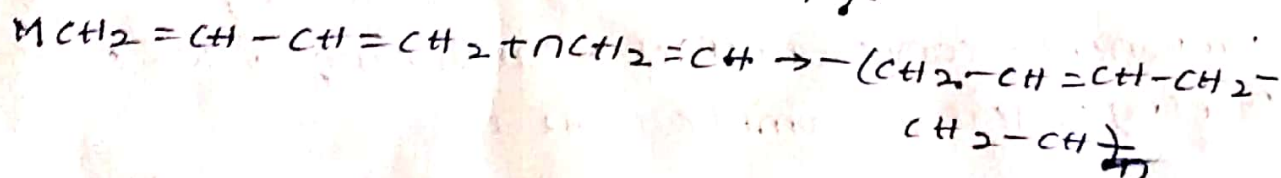
Lead oxide - yellow

Antimony oxide - cr

chromic oxide - green

Buna-S :- (oi) styrene rubber

pre :- It is produced by co-polymerization of 1,3 butadiene (75%) and styrene (25%).



Properties :- 1) It possesses high abrasion resistance and high load bearing capacity.

2) It easily oxidises in presence of ozonic atmospheric

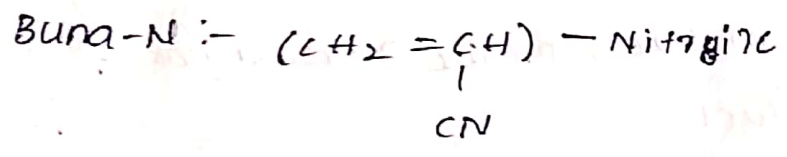
3) It swells oils and solvents.

4) It can be vulcanised in the same way as natural rubber.

uses :- a) It is mainly used for manufacture of tyre

b) It is also used for floor tiles, shoe soles, gas etc.

wire and cable in solution, adhesive tank lining



Properties :- 1) It can be vulcanised in the same way as natural rubber

2) It has good oil resistance, heat resistance and abrasion resistance

3) It is attacked by alkalis due to presence of cyanogroups (-CN)

uses :- Nitrile rubber is used for making aircraft components, conveyor belts, tank lining, gas etc.

Printing rollers, automobile parts etc.

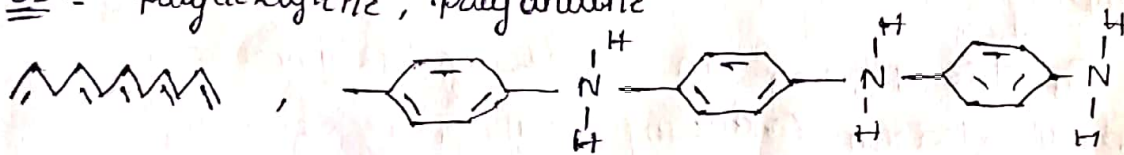
Conducting Polymers : (Polyacetylene, Polyaniline)

Polymers are poor conductors of electricity and generally used as electrical insulators and dielectric materials.

⇒ However, there are polymers with improved electrical conductivity prepared by the addition of some additives such as conducting metals like copper and silver.

⇒ An organic polymer contains with highly delocalised π electron system having electrical conductance on with metallic conductor is called a Conducting Polymer.

Ex:- Polyacetylene, Polyaniline



Classification :-

[i] π -electrons Conducting Polymers : The polymer whose back bone is made up of molecules that contain conjugated π -electrons which extended the entire polymer. It made it conducting.

[ii] Conducting element filled Polymer

This type of polymers acts as a binder i.e. which binds the conducting elements such as metaloxide.

[iii] doped Conducting Polymer :-

It is obtained by exposing a polymer to a charge transfer agent in gas or solution phase.

(iv) Blended Conducting Polymer:-

It is made by blending a conventional polymer with a conducting polymer.

(v) Inorganic or Coordination Conducting Polymer

It is a charge transfer complex containing polymer obtained by combining a metal atom with a polydentate ligand.

Synthesis

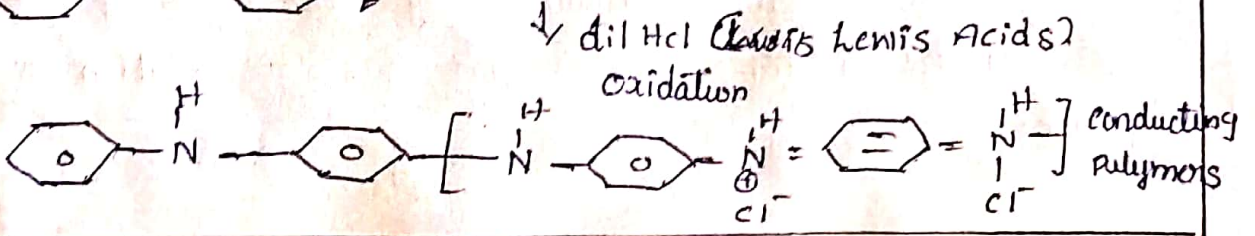
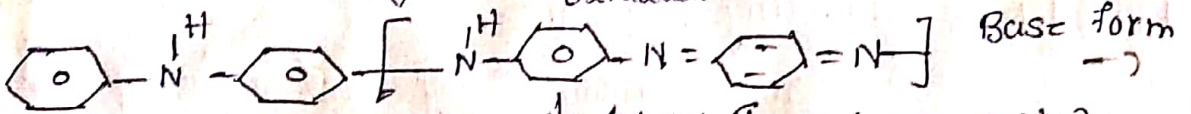
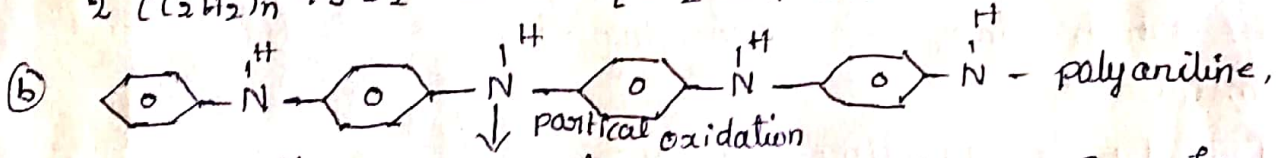
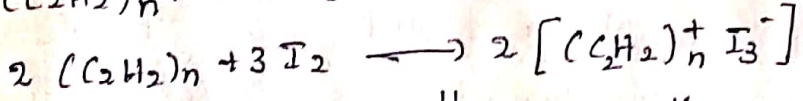
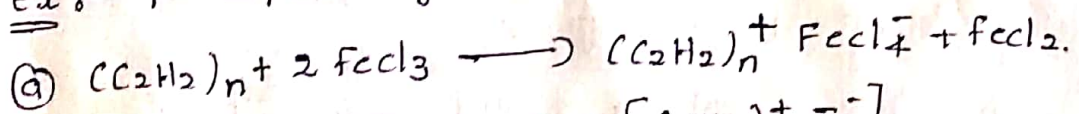
The conducting polymers like polyaniline, polyacetylene can be synthesized by doping in which charged species are introduced in organic polymers having pi- electron backbone.

(i) p- doping :-

In this process an conducting polymer or conjugated pi- electron conducting polymer is treated with Lewis Acid. Followed by oxidation takes place and creates positively charged sites as polymer backbone

=> which are current carriers for conductors.

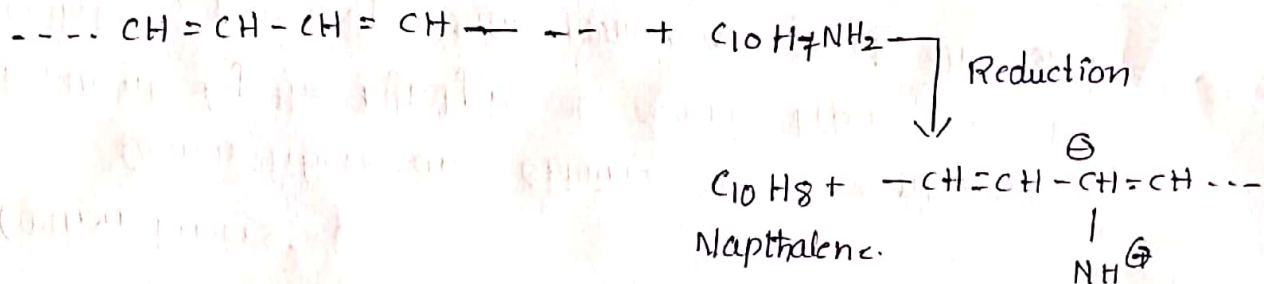
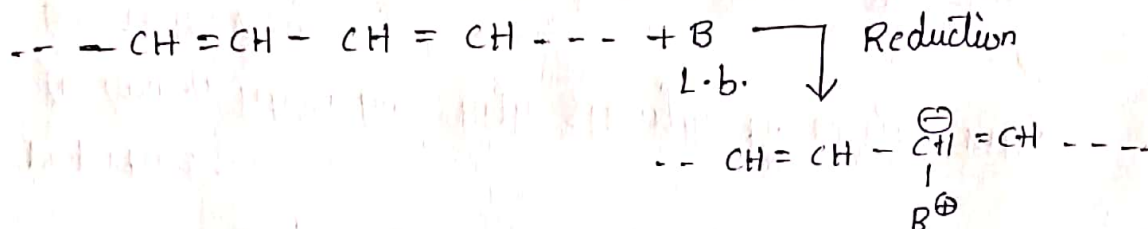
ex:- p- dopant agents are I2, Br2, AsF3.



(ii) n-doping:

In this process conjugated π -electron are treated with (Lewis base) followed by reduction takes place and creates negatively charged sites as polymer backbone which are responsible for conduction

→ Some of the general → used are Li, Na, Ca.

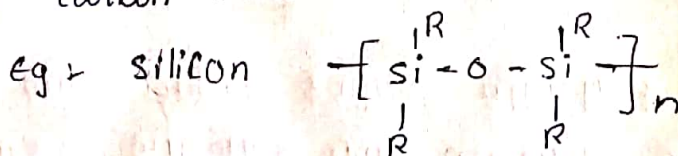


Applications :-

- ① In solar cells
- ② In photovoltaic devices
- ③ Non-linear optical materials
- ④ In telecommunication systems
- ⑤ As electrode material for commercial rechargeable batteries
- ⑥ As film membranes for gas separations
- ⑦ In wiring in aircrafts and aerospace components
- ⑧ In fuel cells as the electrolytic materials.

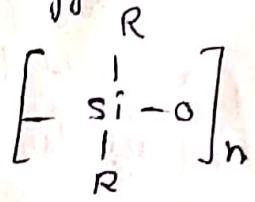
Inorganic Polymers :-

The polymer's chain backbone is made up of without carbon-carbon links is called inorganic polymer.



silicones (- silicones have alternate silicon - oxygen bonds and organic radical attached to the silicon atoms.

→ silicon is capable of forming long chains like carbon and in these chains silicon's always combined with oxygen.



Preparation :-

The monomers for silicone polymer are produced by the hydrolysis of chlorosilanes

- The unstable monomers condense to fixed silicon polymers
- silicon with alkyl halide or silicon halide with Rmg , gives organosilicon halides.

Carbon Fibers :-

Carbon fibers are obtained as a continuous filament by the pyrolysis of organic fibers such as cellulose, polyacrylonitrile (PAN) in an inert atmosphere

Properties :-

- ① Carbon fiber has high strength to weight ratio
- ② It is very rigid.
- ③ It is corrosion resistant and chemically stable.
- ④ It is electrically conductive
- ⑤ It possesses very good tensile strength.
- ⑥ It is non flammable and fire resistant
- ⑦ It is non-poisonous, biologically inert.

Advantages:-

- ① These are used as very good reinforcing materials due to
- ② High modulus specific strength and stiffness even at elevated temperatures.
- ③ Resistant to acids, base, number of solvents and moisture.

Uses:-

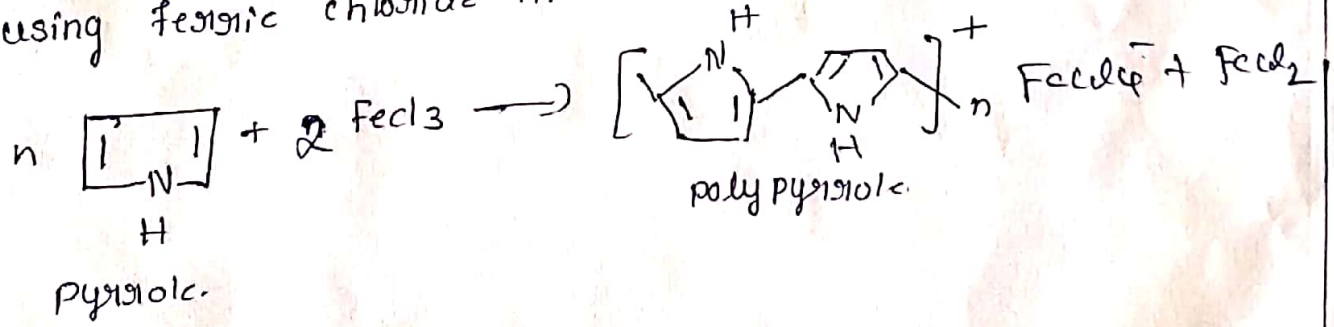
- ① They are used as reinforcing material with polyester resins (or) epoxy resins to form compositiy, which have higher specific strength than materials.
- ② they are high performance fibers, used for highly complicated works.

Poly pyrrole :-

poly pyrrole is a type of organic polymer formed by the polymerisation of pyrrole.
 → polymerisation of pyrrole may be carried out chemically

Preparation :-

poly pyrrole is prepared by oxidation of pyrrole using ferric chloride in methanol



Applications:- "

- ① Poly pyrrole is used as biosensors, gas sensors, anti electrostatic coatings, light weight rechargeable batteries.
- ② It is used in carbon compositions due to its excellent thermal stability.
- ③ It is used for manufacturing containers for protein so it can be used for drug delivery.
- ④ The blend of polypyrrole polymer, protects corrosion of metals.
- ⑤ It acts as a support for the catalyst used in fuel cells.

Stereo Specific Polymerization:-

A selective polymerization with retention of one of the enantiomers present in a mixture is considered as stereospecific polymerization.

Ex:- D and L propylene oxide molecule, poly methyl methacrylate (PMMA).

→ The stereospecific polymerization actually came into existence of Ziegler and Natta in the early 1950s established two novel polymerization systems which possess unique stereo regulating powers in isotactic specific olefin polymerization.

One of the fundamental requirements for the stereospecific polymerization catalyst is recognition of monomer to control absolute configuration of emerging chiral carbons at growing chain ends. Isotactic polystyrenes are obtainable by heterogeneous Ziegler Natta catalysis.

→ Methacrylate is one of the most extensively studied classes of vinyl monomers, in regard to the stereo regularity of the obtained polymers.

→ Methacrylate can be polymerized by the variety of polymerization systems including radical, anionic and cationic catalyst.

→ In the 1980's highly it-specific anionic polymerization of methyl methacrylate (MMA) initiated with t-butyl magnesium bromide,

→ The polymerization proceeds in a living manner without side reactions and gives a highly isotactic polymer.

→ The reaction scheme of polymethyl methacrylate is shown below.

