

UNIT - IV

Definition :-

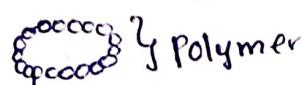
→ It is a branch of chemistry which deals preparation, properties and application of polymer materials.

→ The word polymer is derived from Greek language. Poly means "many" mer means "parts" (or) simple molecules.

Polymer :- It is a large molecule which is prepared from the combination of monomers.

Monomer :- It is a simple molecule which is used in preparation of polymer.

Polymerization :- It is a chemical reaction of which two (or) more monomers combined together to form a polymer.



It is obtained after Monomers

Classification of polymerization :- Chain polymerization.

→ Addition polymerization (OR) chain polymerization.

It is a polymerization reaction at which two (or) more monomers combine together to form a polymer without elimination simple molecule is known as addition polymerization:

Example:- PE, PVC, Teflon

Condensation polymerization (or) step polymerization:-

It is a polymerization reaction at which two (or) more monomers combined together to form with elimination of simple molecule like H_2O , NH_3 etc. Alcohols, NH_3 is known as condensation polymerisation.

Example:- Bakelite, Nylons.

~~co-ordination (or) stereo specific (or) Ziegler-Natta polymerization~~

co-ordination (or) stereo specific (or) Ziegler-Natta polymerization

It is a polymerization reaction at which two (or) more monomers combined together to form a Polymer in the presence of catalyst is known as co-ordination polymerization.

Example:- LDPE, HDPE

Co-polymerization:-

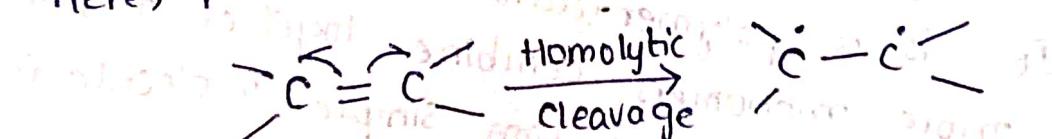
It is a polymerization reaction at which two different monomers combine together to form entirely different polymer.

Example:- Buna-S, Buna-N.

Mechanism addition polymerization:-

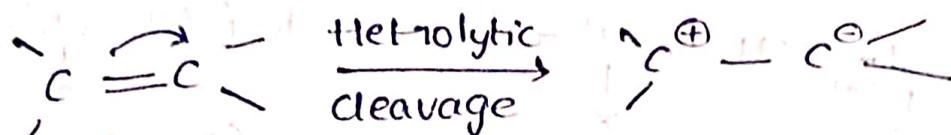
Homolytic cleavage:-

The bond is shifted towards both sides of the carbon elements is known as Homolytic cleavage. Here, product is free radicals.



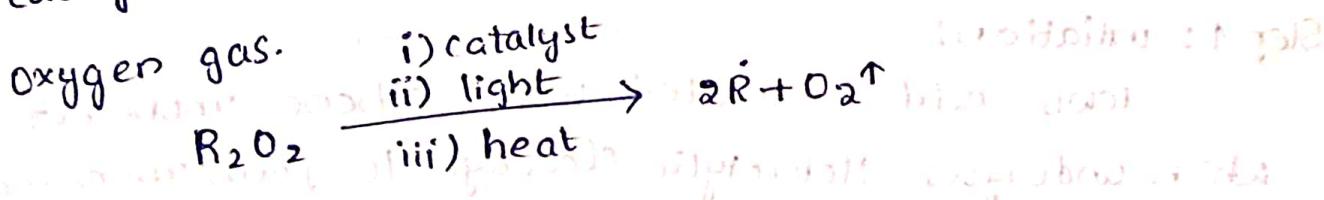
Heterolytic cleavage:-

The bond is shifted towards single side of the carbon elements is known as Heterolytic cleavage. Here, product is cations and Anions.



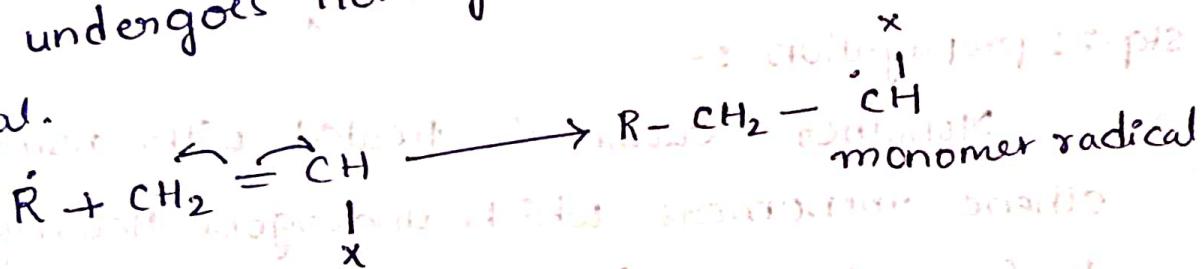
Free Radical Mechanism:-

Dialkyl peroxide undergoes in the presence of catalyst, light heat to form alkyl radicals and oxygen gas.



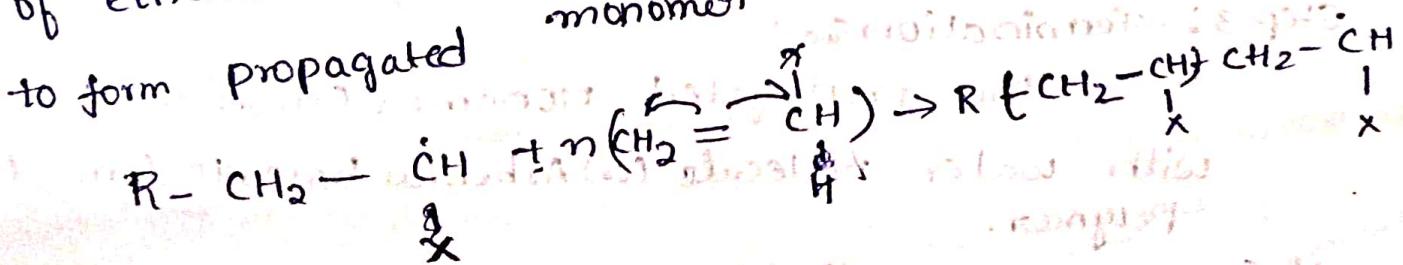
Step 1 : Initiation:-

Alkyl radical is treated with ethene monomer which undergoes homolytic cleavage to form monomer radical.



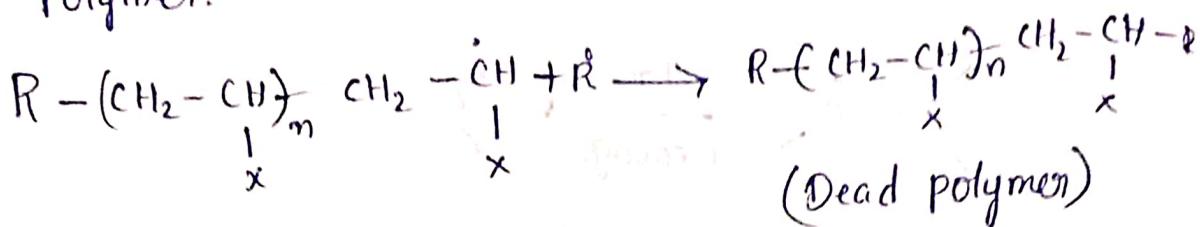
Step 2 : Propagation:-

Monomer radical is treated with 'n' number of ethene monomers which undergoes homolytic cleavage to form propagated monomer radical.



Step 3: Termination :-

The propagated monomer radical is treated with alkyl radical from initiator to form Dead Polymer.

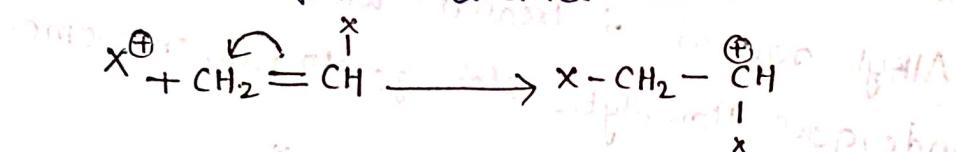


2. Cationic Mechanism:-

Lewis acids are electron pair acceptors.

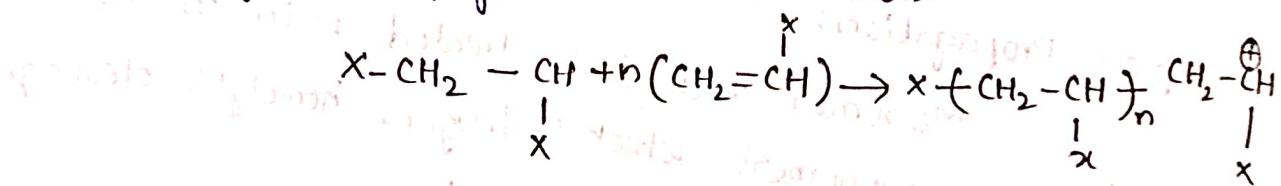
Step 1: Initiation:

Lewis acid is treated with ethene monomer which undergoes heterolytic cleavage to form monomer cation.



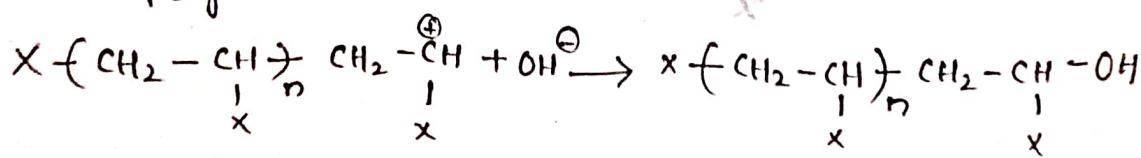
Step 2: Propagation :-

Monomer cation is treated with number of ethene monomers which undergoes heterolytic cleavage to form propagated monomer cation.



Step 3:- Termination:-

The propagated monomer cation is treated with water molecule (or) Arrhenius base, to form Dead Polymer.

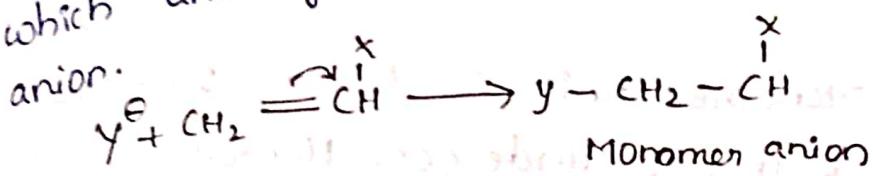


③ Anionic Mechanism:-

Lewis base are electron pair donors:

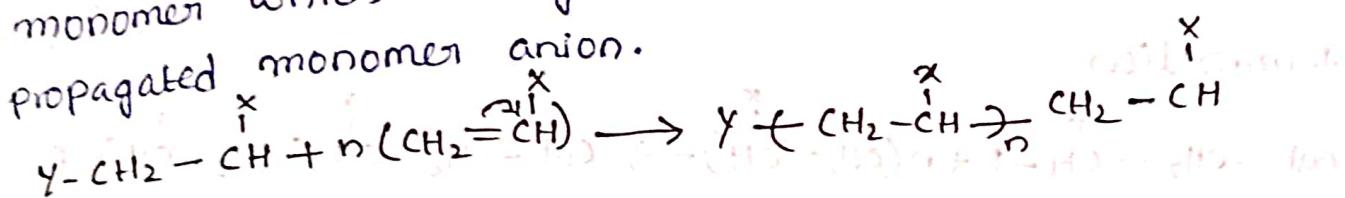
Step 1 :- Initiation reaction:-

Lewis base is treated with ethene monomer which undergoes Heterolytic cleavage to form monomer anion.



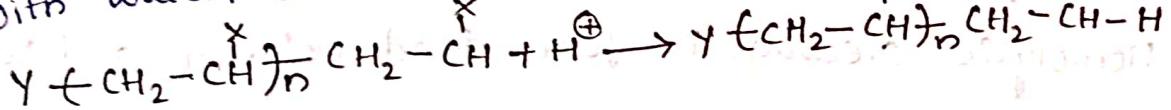
Step 2 :- Propagation:-

Monomer anion is treated with number of ethene monomer which undergoes Heterolytic cleavage to form propagated monomer anion.



Step 3 :- Termination:-

The propagated Monomer anion is treated with water molecule (HOH) Arrhenius acids forms Dead Polymer.



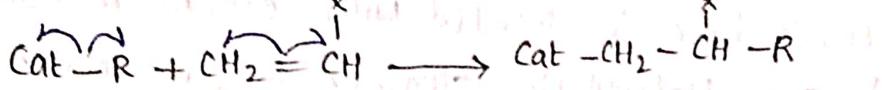
- * Lewis acids are Initiators in cationic mechanism.
Lewis acids means electron pair acceptors which have deficiency of electrons that why Lewis acids are designated as X^+
- * Lewis bases are Initiators in anionic Mechanism. Lewis bases means electron pair donors which have efficiency of electrons that why Lewis bases are designated as Y^-

Mechanism of co-ordination Polymerisation:-

Ziegler proposed catalyst materials (transition metal halides $TiCl_3$ or $TiCl_4$), Natta proposed co-catalyst material (R_3Al) - Tri Alkyl Aluminium to give dead Polymer.

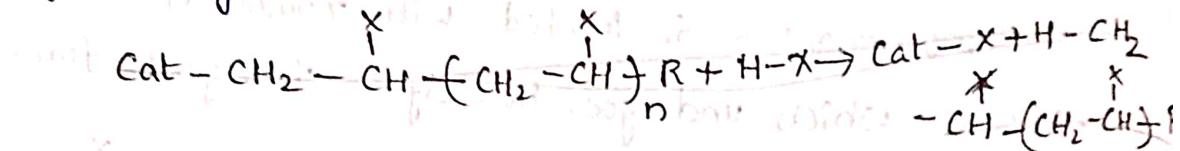
Initiation:-

Ziegler Natta catalyst is treated with ethene monomer. Here both undergo Homolytic cleavage to form Ziegler Natta monomer unit.

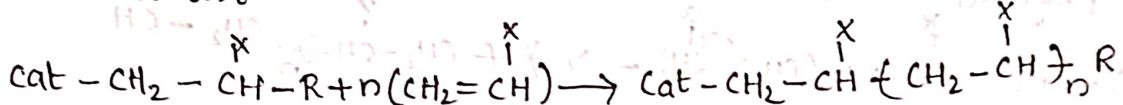


Propagation:-

Ziegler Natta Monomer unit is treated with no. of ethene monomer both undergo Homolytic cleavage to form Ziegler Natta propagates monomer unit \times .

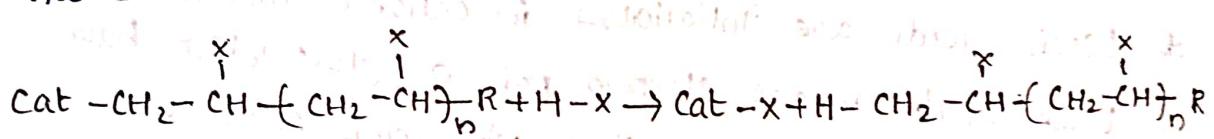


Termination:-



Termination:-

The Ziegler Natta propagated monomer unit is treated with Hydrogen halide (HCl , HBr , HF , HI) both core undergoes Homolytic cleavage to form dead polymer and catalyst Halide.



1. Functionality of Monomers:-

The number of reactive side (or) functional group present in a monomer is known as functionality of Monomers.

On the basis upon reactive sides numbers function of monomer are divided into three types.

1. Unfunctionalized monomers
2. Mono functionalized monomers
3. Poly functionalized monomers

(i) Bifunctional monomer:-

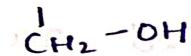
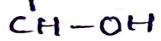
The monomer which consists two reactive sides in its structure is known as bi function monomer.

Ex:- Ethene ($\text{CH}_2=\text{CH}_2$)

(ii) Trifunctional monomer:-

The monomer which consists of three reactive sides in its structure is known as tri function monomer.

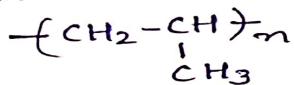
Ex:- Glycerol $\text{CH}_2\text{-OH}$



(iii) Polyfunction monomer:-

The monomer which consists of many sides in its structure is known as poly function monomer.

Polypropylene



② Degree of Polymerisation:-

The number of repeating units (or) monomers present in the basic chain of polymer is known as Polymerisation.

→ The degree of polymerisation value is low which gives low molecular weight polymers.

→ The degree of polymerisation value is high which gives high molecular weight polymers.

on based upon degree of polymerisation value the polymers are divided into two types. Those are

1. Chain polymers
2. Cross linked polymers

Oligopolymers:-
The polymers which consists degree of polymerisation value is below 600 is known as Oligopolymers.
→ oligopolymers could not satisfy engineering properties.

High polymers:-

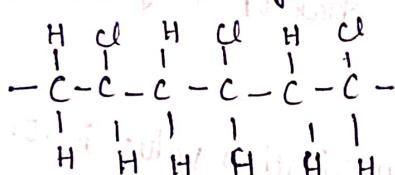
The polymers which consists degree of polymerisation value is above 600 is known as High polymers.
→ High polymers satisfies the engineering properties.

Tacticity of polymers:-

The orientation of functional groups, present basic chain of the polymer is known as tacticity polymers.
on based upon orientation of function groups
Tacticity of polymers are divided into three types.

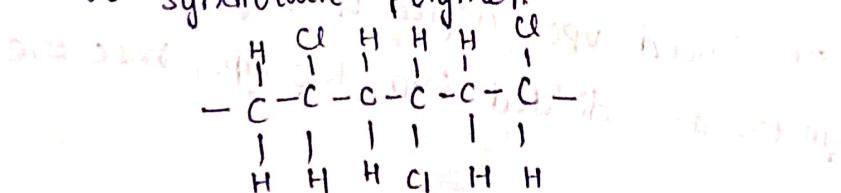
(1) Isotactic polymers:-

The functional groups are arranged in the same side of the basic chain of the polymer is known as Isotactic polymers.



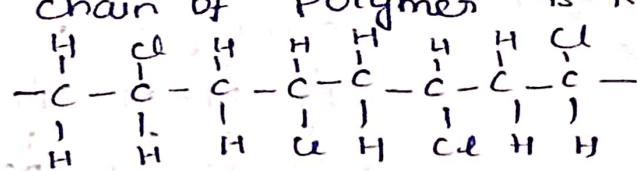
(2) Syndiotactic polymers:-

The functional groups are arranged in alternative side of basic chain of polymer is known as Syndiotactic polymers.



3. Astatic Polymers :-

The functional groups are arranged in randomly of basic chain of polymer is known as Astatic Polymer.



plastomers (or) plastics :-

the materials which having high molecular weight organic polymers which exhibits plasticity nature that is which are moulded into desirable shape is known as plastomers (or) plastics.

on the based upon ~~additive~~ temperature plastics are divided into two types those are

1. Thermoplastics (or) softening plastics.

a. Thermo setting plastics (or) hardening plastics.

Difference Plastics

between Thermoplastics and Thermo setting resins - propal state of plastic

THERMOPLASTIC

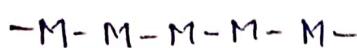
1. The plastics which are soften on heating and harden on cooling is known as Thermo plastics.
2. Thermoplastics undergoes addition polymerisation.

THERMO SETTING PLASTICS

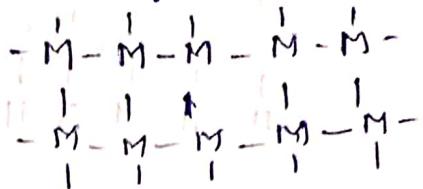
- b. The plastics which are donot converted into soften state by applying maximum amount of temperature and pressure because once they are exhibit in fixed state is known as thermosetting plastics.
3. Thermo setting plastics under goes condensation polymerisation.

3. Thermo setting plastics under goes condensation polymerisation.

3. Thermoplastics are linear shape of plastics because of monomers are arranged in chain wise manner



3. Thermosetting plastics are crosslinked. Shape of plastic because of monomers are arranged in step-wise manner



4. Thermo plastics are under goes reversible process

5. Thermoplastic are soluble in organic solvents

6. Thermo plastics having weak van der wall forces.

7. Thermo plastics are reclaimed from waste.

8. Thermo plastics are weak, soft and less brittle.

9. Thermoplastics are having shape change conversion.

10 Examples are PVC, Teflon

4. Thermosetting plastics under goes irreversible process.

5. Thermosetting plastics are insoluble in organic solvent

6. Thermosetting plastics are having strong covalent bonding forces.

7. Thermosetting plastics are not reclaimed from waste

8. Thermosetting plastics are hard, strong and more brittle

9. Thermosetting plastics are having no shape change conversion.

10. Examples are Bakelite, Nylon

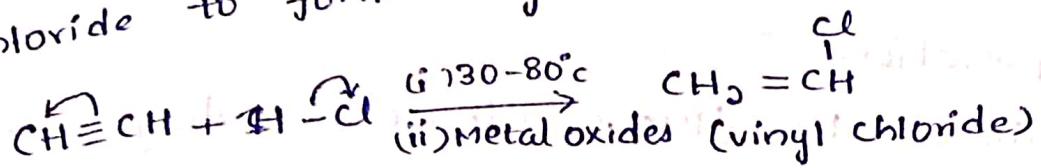
Some important plastics are used in daily life :-

Poly vinyl chiroide :-

PVC is prepared by addition Polymer is of vinyl chiroide monomers that is without elimination of simple molecules.

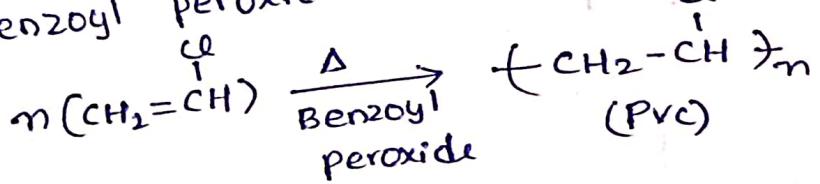
Monomer preparation:-

Ethyne is treated with hydrogen chlorig which undergoes heterolytic cleavage in the presence of temperature ($30^{\circ}-80^{\circ}\text{C}$) and metal oxides as a catalyst to form vinyl chloride to form vinyl chloride monomer.



Polymer preparation:-

The number of vinyl chloride monomers undergoes addition polymerization in the presence of temperature and Benzoyl peroxide as a catalyst to form poly vinyl chloride



Properties:-

- * Water Resistance
- * electrical resistance
- * chemical resistance
- * Absorbtion resistance
- * Thermal resistance
- * Tensile strength
- * Abrasion resistance.

Application:-

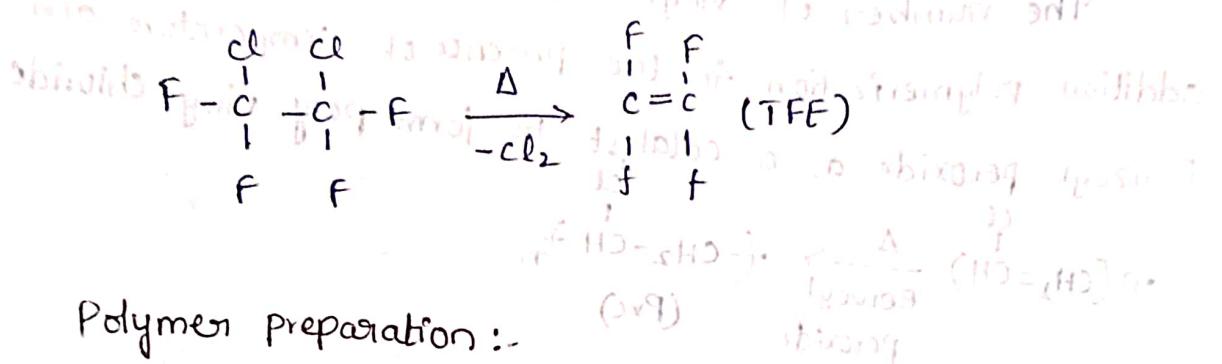
- * PVC is used in preparation of water pipes which are used in agriculture, domestic and industrial sectors.
- * PVC is used in the preparation of chemical containers.
- * PVC is used in the manufacturing of radio and television parts.
- * PVC is used in electrical Wires.

Teflon (or) PTFE :-

Teflon is prepared by addition polymerization of Tetra fluoro ethene monomer that is without elimination of simple molecules.

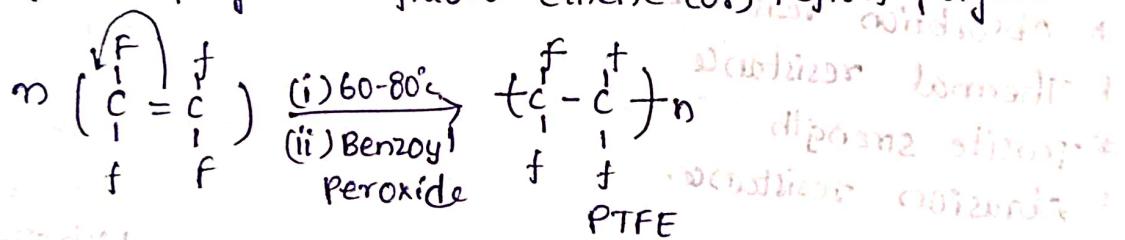
Monomer preparation :-

The dichloro tetra fluoro ethane undergoes dechlorination in the presence of temperature to form tetra fluoro ethene.



Polymer preparation :-

The 'n' number of tetra fluoro ethene undergoes addition Polymerization in the presence of temperature ($60-80^\circ\text{C}$) and Benzoyl peroxide as catalyst to form poly tetra fluoro ethene (or) Teflon polymer.



Properties :-

- * Water resistance
- * electrical resistance
- * Absorption resistance
- * Thermal resistance
- * tensile strength
- * Chemical resistance
- * Abrasion resistance

Applications:-

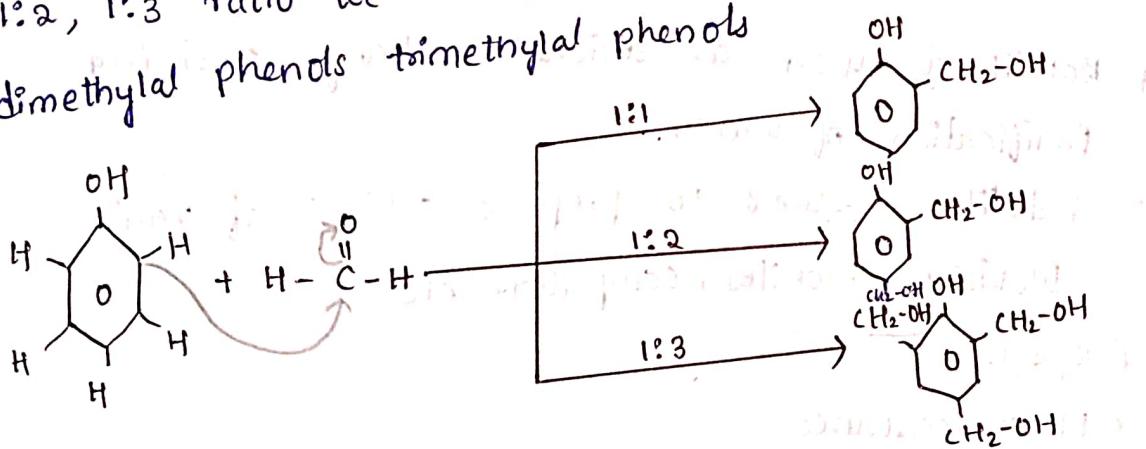
- * Teflon is used in the preparation of Burette stop corks.
- * Teflon is used in the preparation of non-stick coating utensils.
- * Teflon is used in shirt buttons, toothbrushes, hair combs, umbrella handles.
- * Teflon is used in chemical carrying pipes.

Bakelite (or) phenol formaldehyde Resin:-

Bakelite is prepared by condensation polymerisation of phenol and formaldehyde monomers that is with elimination of simple molecules.

Step-1:- Preparation of monomethyl phenols:-

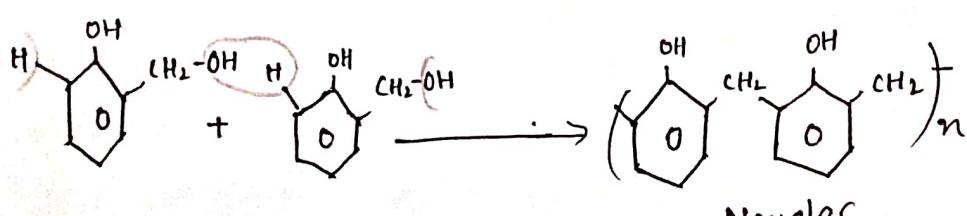
Phenol is treated with formaldehyde in 1:1, 1:2, 1:3 ratio we will get monomethyl phenols, dimethyl phenols, trimethyl phenols



Step-2:-

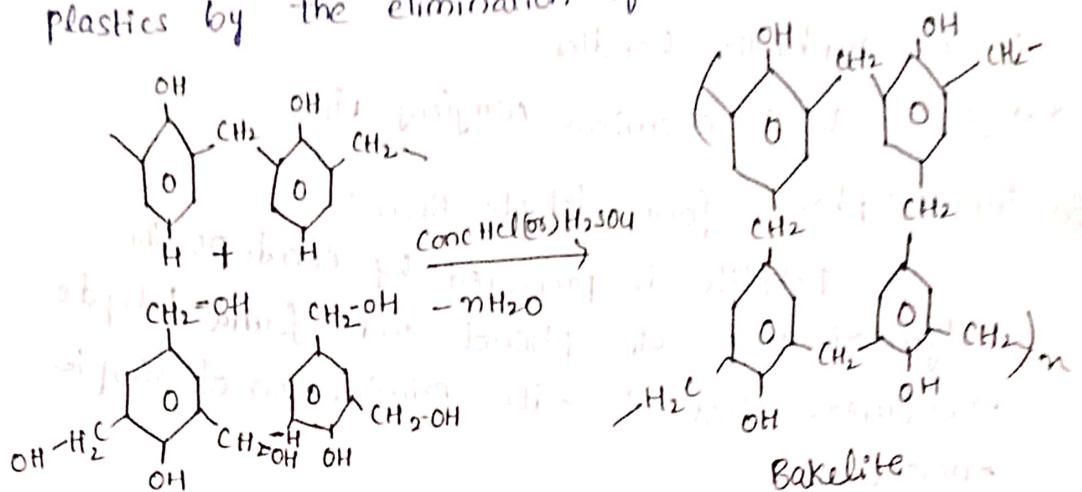
Preparation of Navolac:-

The combination of monomethyl phenols in the presence of glacial acetic acid as a medium to form Navolac plastic (linear polymer)



Step 3:- Preparation of Bakelite:-

The Novolac linear polymer is treated with $\text{CH}_2=\text{OH}$ methylol phenols and dimethyl phenols in the presence of conc. HCl (or) $\text{Conc. H}_2\text{SO}_4$ to form Bakelite plastics by the elimination of water molecules.



Applications :-

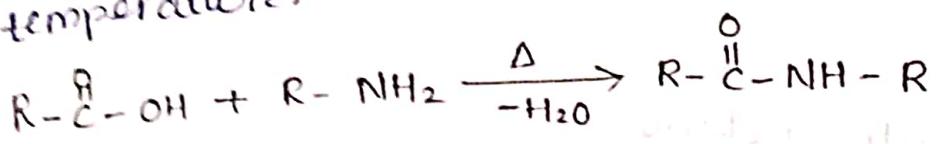
- * Bakelite is used to prepare electrical switches
- * Bakelite is used as anion exchange resin in purification of water.
- * Bakelite is used to prepare cabinets of radios, television, mobiles, computers etc.

Properties :-

- * Water resistance
- * Electrical resistance
- * Chemical resistance
- * Absorption resistance
- * Thermal resistance
- * Tensile strength
- * Abrasion resistance

Nylons (or) Poly Amides

Nylons are prepared by the combination of carboxylic acid and amines in the presence of temperature.



on based upon monomers, carbon elements numbers nylons are divided into three types.

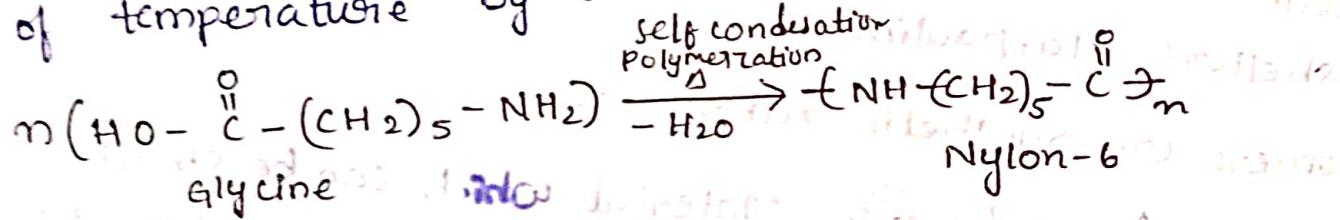
those are:- (i) Nylon-6

* (ii) Nylon-6,6

(iii) Nylon-6,10

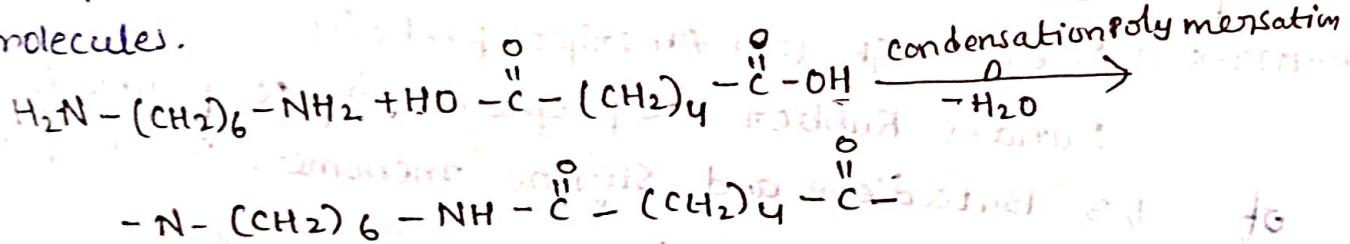
(i) Nylon-6:-

Nylon-6 is prepared by self condensation polymerization of amino caproic acid (or) Glycine in the presence of temperature by the elimination of water molecule.



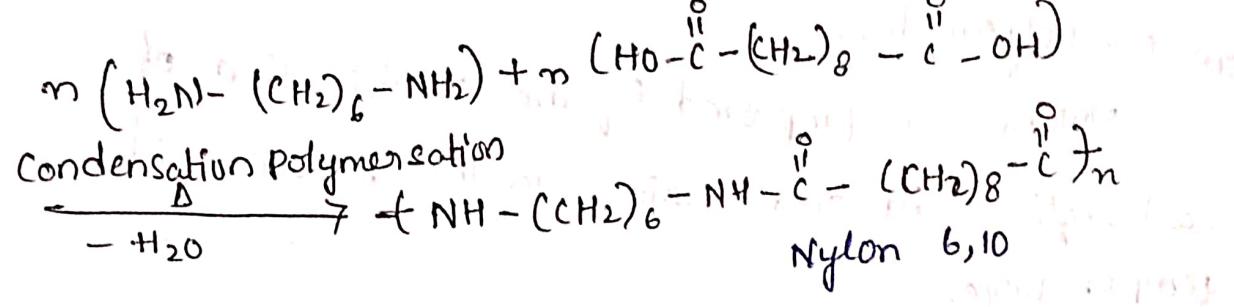
(ii) Nylon-6,6:-

Nylon-6,6 is prepared by condensation polymerization of Hexamethylene diamine and Adipic acid in the presence of temperature with elimination of water molecules.



3. Nylon-6,10:-

Nylon-6,10 is prepared by amide condensation polymerization of hexamethylene di-amine and sebacic (or) Decane Dioic acid in the presence of temperature with elimination of water molecule.



Properties:-

- * It is a thermoplastic polymer.
- * It is a linear polymer.
- * It is a tuff tough polymer.
- * High tensile strength.
- * High chemical resistance.

Applications:-

- 1. Strings of musical instruments like guitar, violin etc.
- 2. Bristles of tooth brush.
- 3. Nylon nets, Nylon parachutes.
- 4. seat belts and ropes and shelters, tarpaulines.

Elastomers (or) Synthetic rubbers:

A polymeric material which can be stretched at least twice its original length but it returns into original shape as soon as stretching forces are released. It is known as elastomers.

Examples- BUNA-S Rubber, Buna N-Rubber.

Buna-S Rubber :- (GRS (or) Ameripol rubber):-

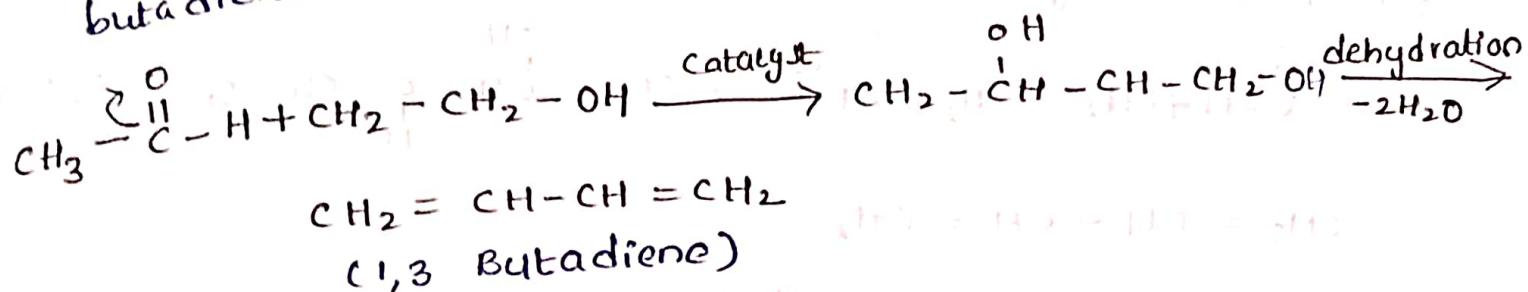
Buna-S Rubber is prepared by co-polymerization of 1,3 Butadiene and styrene monomers in the presence of sodium acts as catalyst.

* It is a black rubber by copolymer of 1,3-butadiene and styrene.

* It is a thermoplastic polymer for preparing all of bisphenol monomers.

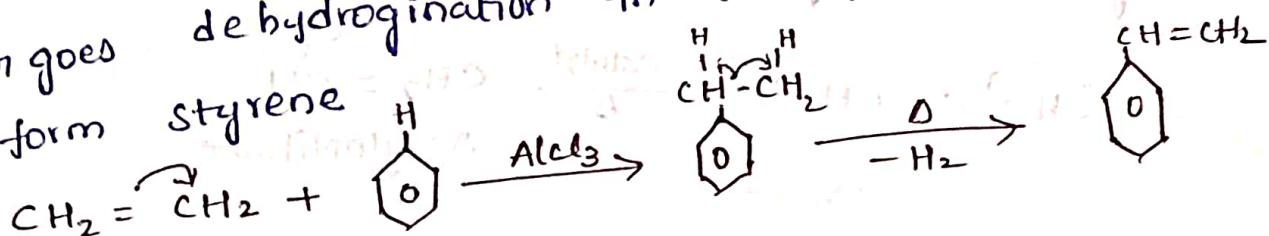
* It is a polymer which is used for acid anhydrides.

Preparation of 1,3 Butadiene:-
 Buna-S Ru Acetaldehyde is treated with ethyl alcohol in the presence of catalyst to form 1,3 butadiene by the elimination of water molecules.



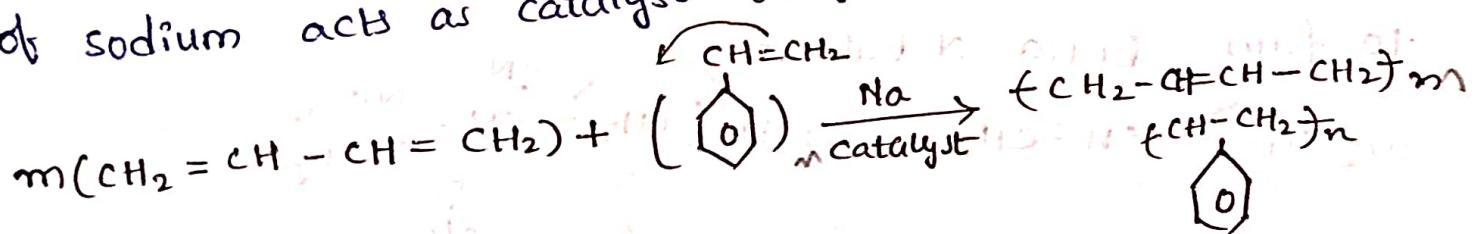
Preparation of Styrene:-

Ethene is treated with benzene in the presence of AlCl_3 acts as catalyst to form ethyl benzene further which undergoes dehydrogenation in the presence of temperature to form styrene.



Preparation of Buna-S Rubber:-

1,3 Butadiene is treated with styrene in the presence of sodium acts as catalyst to form Buna-S Rubber.

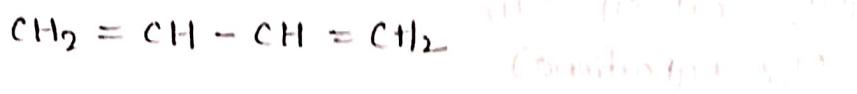
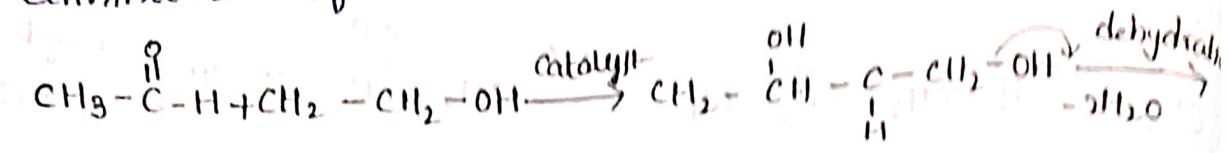


Buna-N Rubber (or) Nitrate Rubber:-

Buna-N rubber is prepared by co-polymerization of 1,3 Butadiene and acrylonitrile monomer in the presence of sodium acts as catalyst.

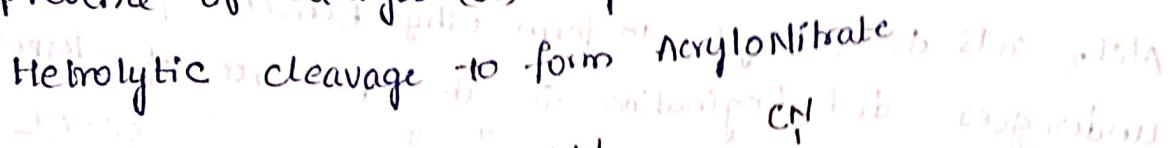
Preparation of 1,3 Butadiene:-

Acetaldehyde is treated with ethyl alcohol in the presence of catalyst to form 1,3 butadiene by the elimination of water molecule.



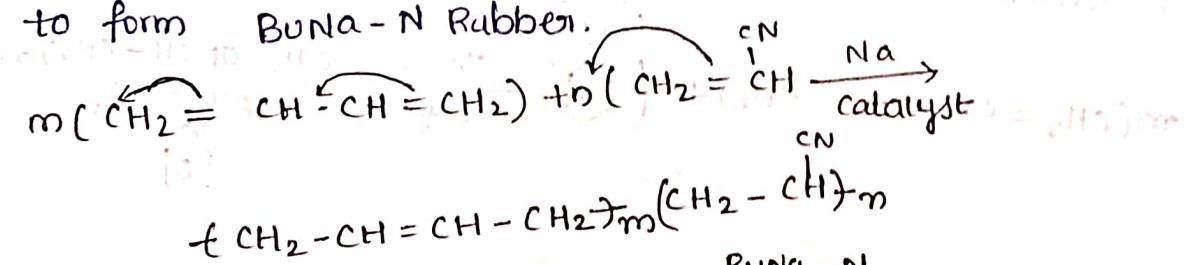
Preparation of Acrylonitrile:-

Ethyne is treated with hydrogen cyanide in the presence of catalyst (or) temperature both undergoes hydrolytic cleavage to form Acrylonitrile.



Preparation of Buna - N Rubber:-

1,3 butadiene treated with Acrylonitrile monomer in the presence of sodium acts as catalyst to form Buna - N Rubber.



Properties:-

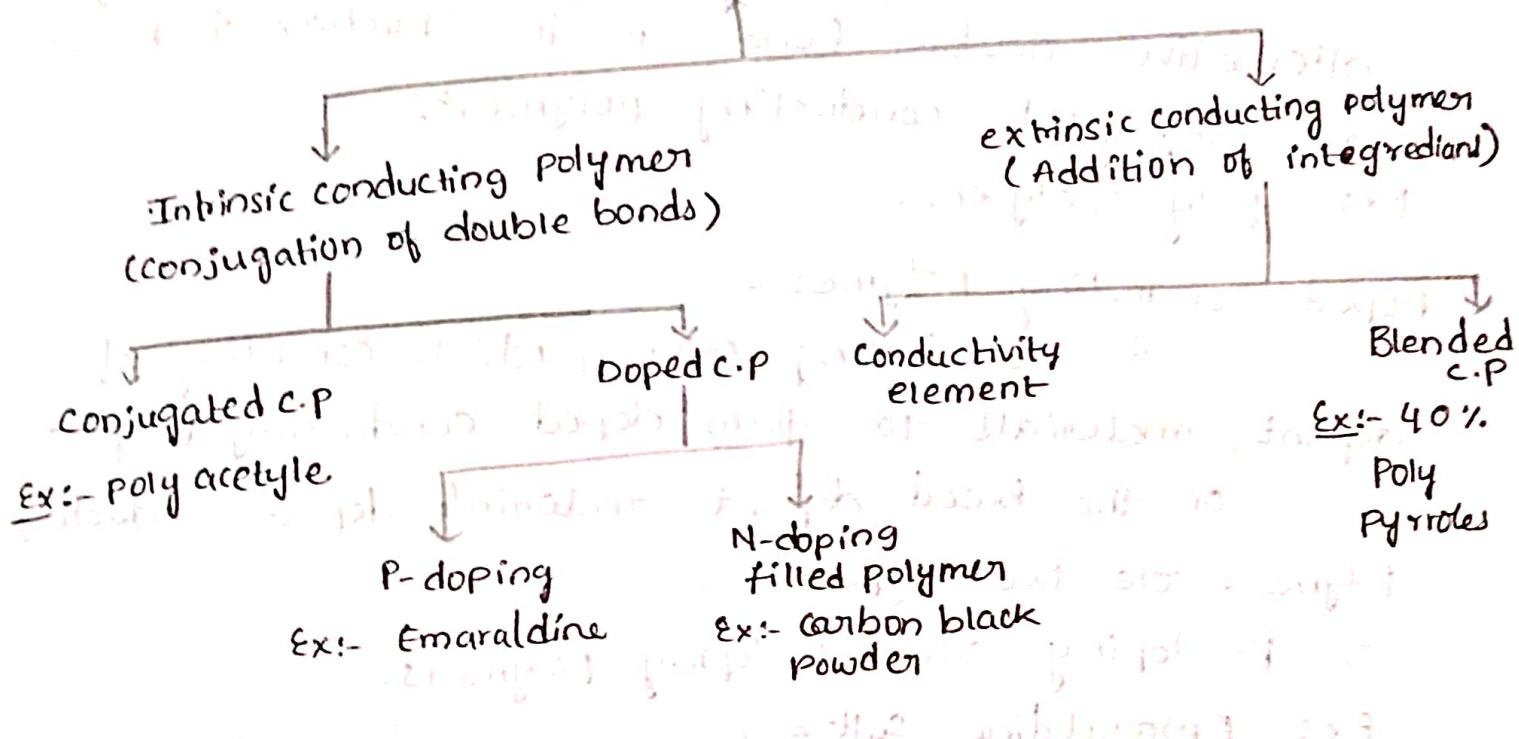
1. It is strong and tough polymer.
2. Vulcanised with Sulphur element.
3. Resistant to atmospheric conditions.
4. Excellent abrasion resistance.
5. Resists chemicals swells in oils.

Applications:-

1. used in insulation of electrical wires
2. used in foot wear components like shoes, and shoe soles.
3. It is used in conveyer belts in excellator etc.
4. It is used in manufacturing of motortires, belts etc.

conducting polymers:-

types of conducting polymers



conducting polymer :-

The polymers which exhibits conductivity state due to the presence of conjugated double bonds and addition of ingredients is known as "conducting polymers". These core blocks upon conductivity those are.

divided into two types those are.

→ intrinsic conducting polymers

→ extrinsic conducting polymers

ex/poly aniline

Intrinsic conducting polymers:-

The polymers which consist of conjugated double bonds to form intrinsic conducting polymer further intrinsic conducting polymers are divided into two types.

Those are

1. Conjugated conducting polymers.

2. Doped conducting polymers.

Conjugated conducting polymers:-

The conducting polymers which having alternative double bonds in its structure is known as "conjugated conducting polymer".

Ex:- Poly acetylene.

Doped conducting polymers:-

The conducting polymer which consisting of dopant materials to form doped conducting polymers.

On the based dopant material doped conducting

Polymers are two type i.e.,

⇒ P-doping and N-doping polymers.

Ex:- Emeraldine salt.

Extrinsic conducting polymers:-

The conducting polymers which have prepared from addition of ingredients is known as extrinsic conducting polymers.

On based upon ingredient these are divided into two types.

1. conductivity filled polymers.

2. Blended Conducting Polymer.

conductivity element filled polymers:-

The conducting polymer which consists conductivity element as a filter is known as "conductivity element filled polymer".
Ex:- carbon black powder.

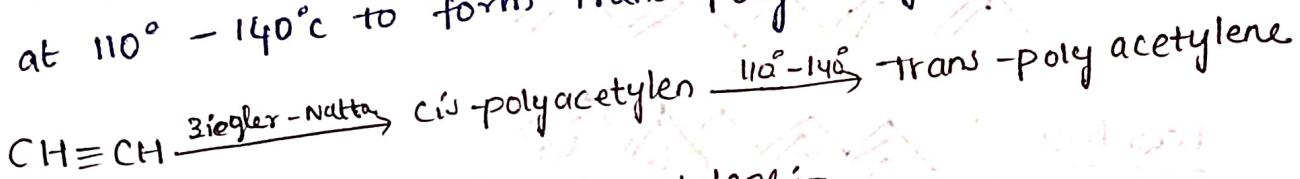
Blended conducting polymers:-

The conducting polymers which are mixed with foreign substance / other ingredients is known as blended conducting polymers.

Ex:- 48% poly Pyrrole

Poly acetylene:-

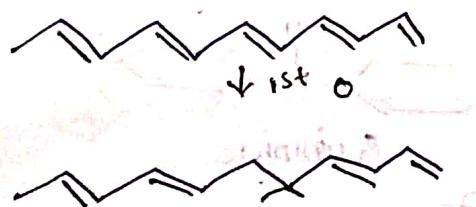
Ethyne / acetylene is treated with Ziegler Natta catalyst to form cis - polyacetylene further we will supply temperature at $110^{\circ} - 140^{\circ}\text{C}$ to form trans - poly acetylene.



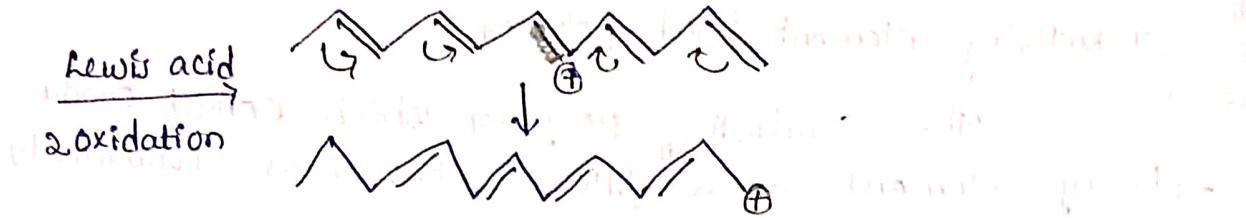
p-doping mechanism of polyacetylene:-

Trans polyacetylene is treated with Lewis acids which undergoes oxidation reaction, to form polaron (Radical cation), further we will add excess amount of Lewis acids to form bi polar (dication)

finally, the delocalization of double bonds we will get p-doping polyacetylene.



polaron (radical cation)

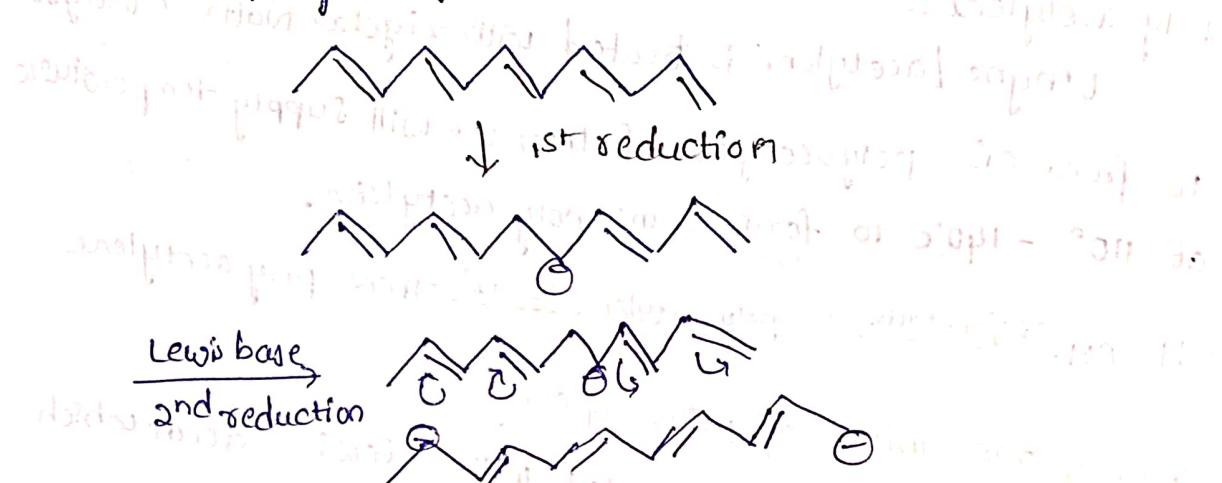


N-doping Mechanism of polyacetylene:-

Trans polyacetylene is treated with lewis bases which undergoes reduction reaction to form Polaron (radical anion) further we will add excess amount of lewis bases to form bipolaron (di anion)

finally, the delocalization of double bonds, we will get

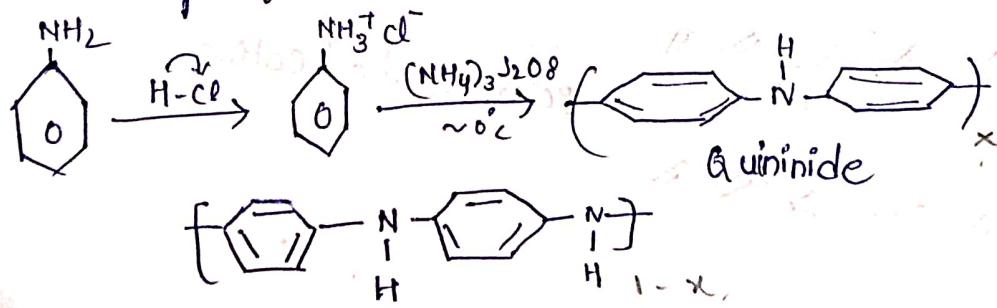
n-doping polyacetylene



Polyaniline:-

Polyaniline is prepared by aniline is treated with hydrogen chloride, to form anilinium chloride, further which is subjected to Ammonium pure sulphate ($(\text{NH}_4)_2\text{SO}_4$) in the presence of 0°C and continuous stirring to form poly aniline

(Mixing of Quinide and Benzenoid rings)



Benzinoid

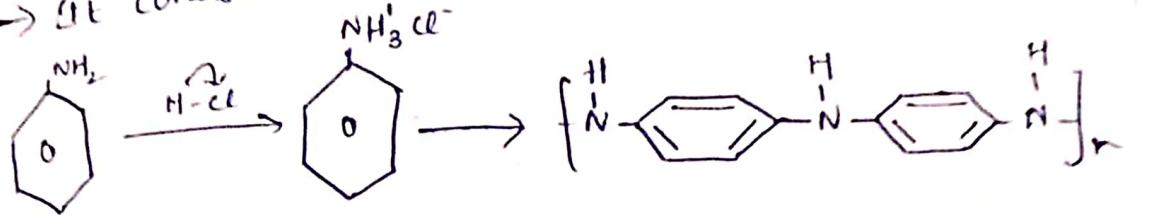
Types of polyaniline:-

leuco emeraldine:-

The x value will be zero in basic chain of the polyaniline which have only benzoquinonoid rings.

→ It is completely reduced and colorless material.

→ It consists N groups which acts as insulators.



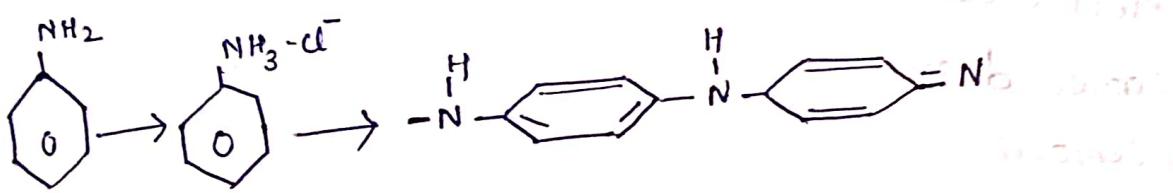
ferromagnetic:- (pernigraniline)

The x -value will be '1' in basic chain of the poly

aniline which have only quinonoid rings.

→ It is completely oxidised and purple colour material.

→ It consists only $-N$ groups which acts as insulators.



Emeraldine base:-

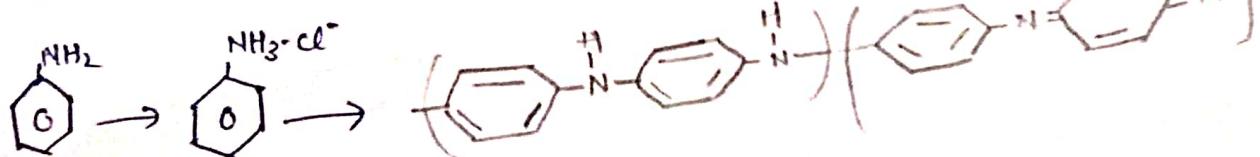
The x value will be 0.5 in basic chain of the poly

aniline which consist of mixed benzoid and quinonoid

polarized, not neutralized and blue colour material.

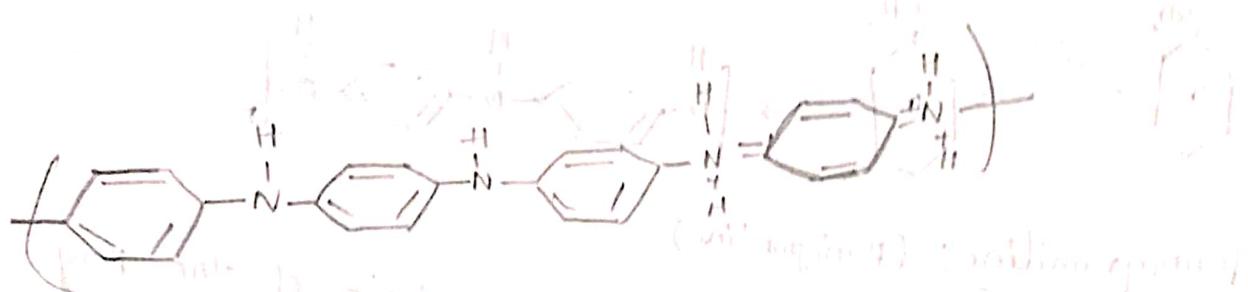
→ It is partially polarized, not neutralized and blue colour material.

→ It consists $N-H$, $-N$ groups which acts as insulators.



Emeraldine salt:-

- The x value is 0.5 is basic chain of the polyaniline which consists of mixed benzoid and quinonoid.
- It is partially polarised, neutralised and green colour material.
- It consists -N-H, -N groups and acts as conductor.



Applications:-

- Conducting polymers used as super capacitors.
- Solar cells.
- EMP shielding components (electromagnetic induction).
- Thermo electric devices.
- Electro chronic devices.
- Chemical sensors.