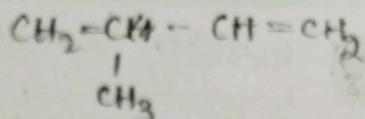
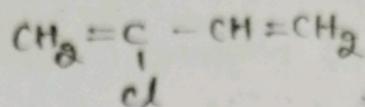


2 methyl 1,3 butadiene



2 chloro 1,3 butadiene.

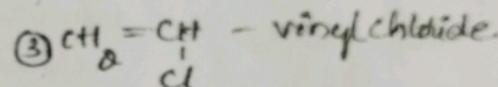
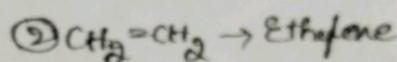
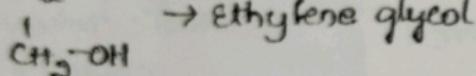


### FUNCTIONALITY OF MONOMERS:

The minimum no. of bonding sites (or) reacting sites present in a monomer is called as functionality.

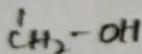
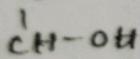
- \* If the functionality of monomer has 1 is called mono functionality. Ex:  $\text{CH}_3\text{OH} \rightarrow$  methanol  $\text{CH}_2=\text{Cl}$  Ethyl chloride
- \* If the functionality of monomer is 2 is called bi functionality

Ex: ①  $\text{CH}_2-\text{OH}$



- \* If the functionality of monomer is 3 is called tri functionality.

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



- \* If the monomer has more than 3 as a functionality that is called as poly functionality

Ex: Phenol formaldehyde resin (Bakelite)

② Urea formaldehyde resin

NOTE: The above monomers are mixing to produce straight chain (or) linear chain polymers, branched chain polymers and cross-linked polymers.

### TACTICITY OF POLYMERS: / stereospecific polymer

Tacticity - orientation.

The orientation of functional groups in a polymer takes place in orderly (or) disorderedly manner with respect to the main chain - this is known as tacticity (or) stereospecific

The resulting tacticity of polymers are following three types

1. Isotactic polymers (same side of the main chain)
2. Syndiotactic polymers (Alternate side)
3. Atactic polymers

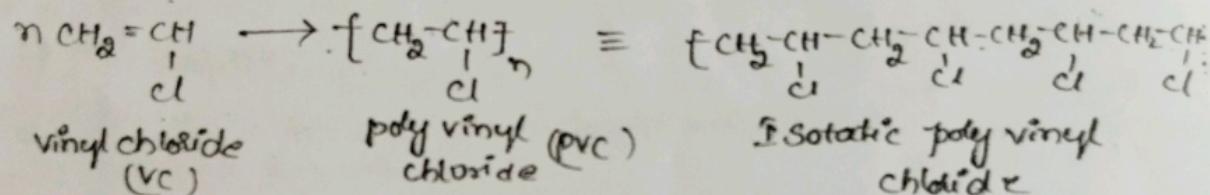
### 1. Isotactic polymers:

The functional groups are arranged in a polymer in such a way that all the same functional groups face same side with respect to the main chain.

Ex: PVC, PAN, PS, etc

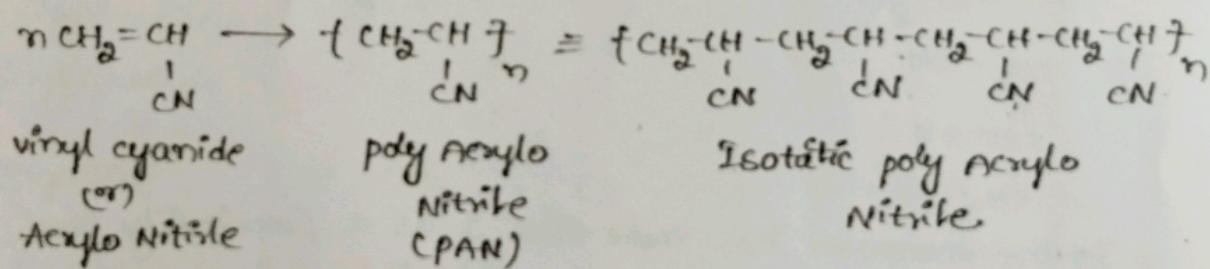
chloride

#### ① PVC:

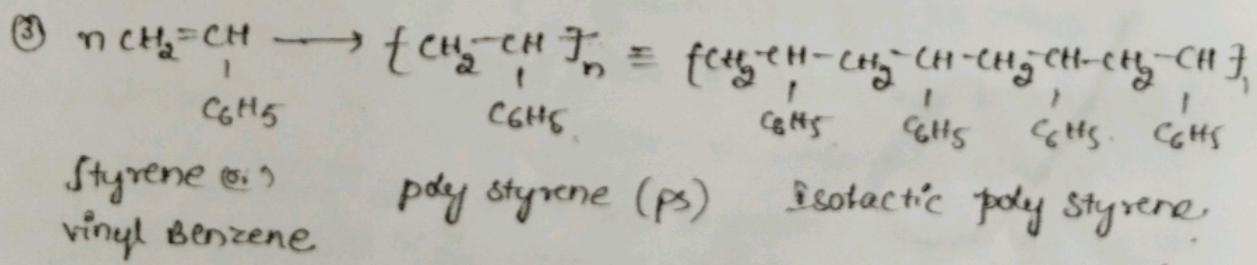


ide.

#### ② PAN

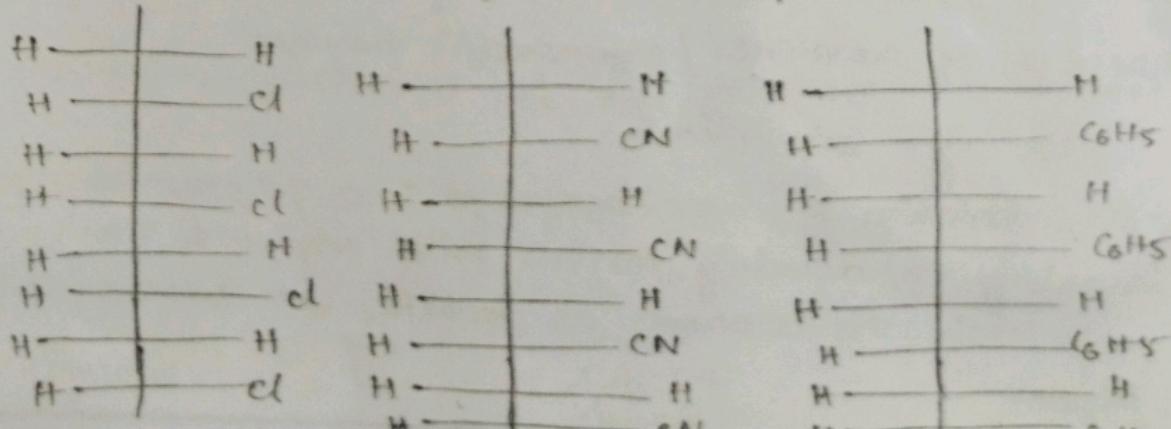


it



ht

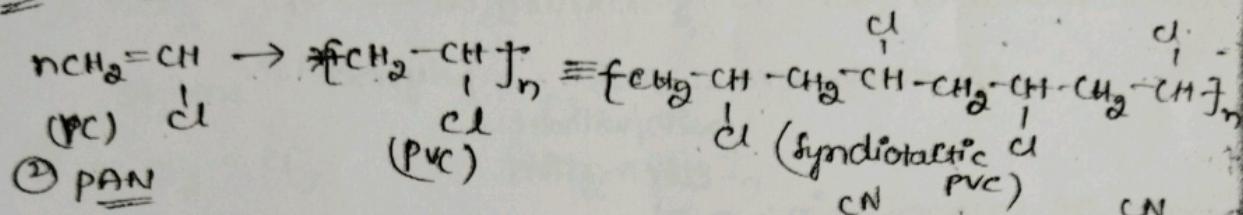
Stereo form of Isotactic PVC & Isotactic PAN & Isotactic PS are:-



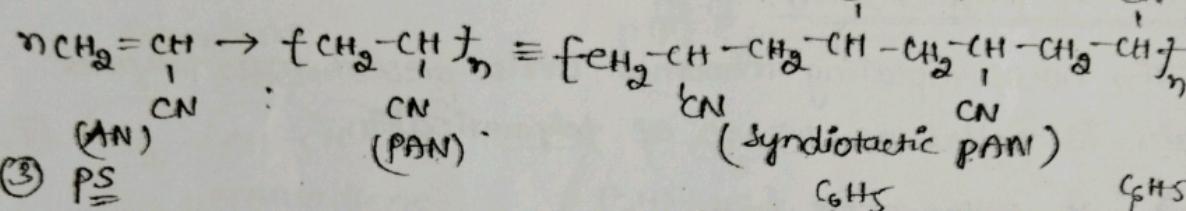
## 2. syndiotactic polymers:

The functional groups are arranged in a polymer alternatively with respect to main chain.

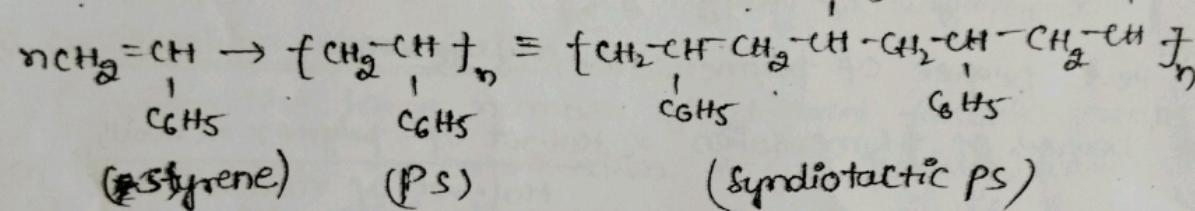
Ex: ① PVC



② PAN



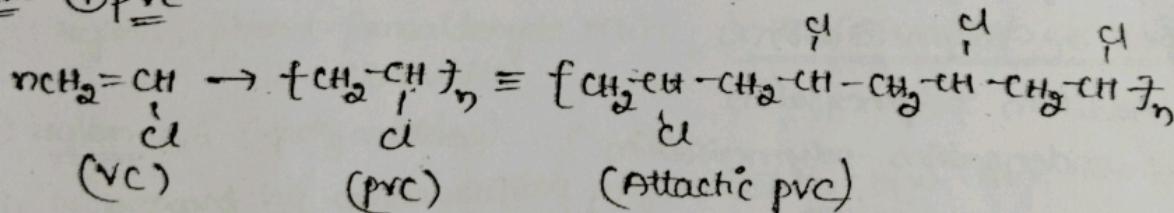
③ PS



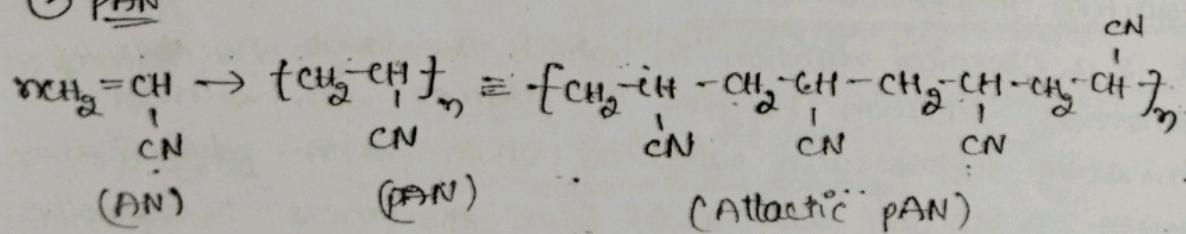
## 3. Atactic polymers:

The functional groups are arranged in random around to the main chain.

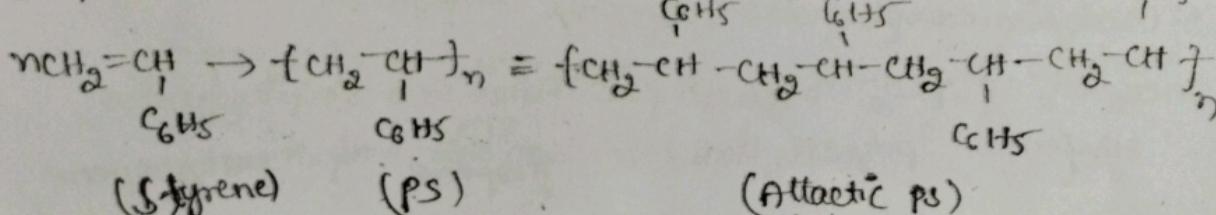
Ex: ① PVC



② PAN



③ PS



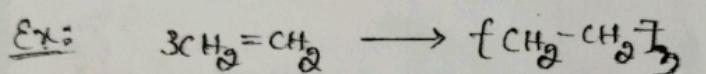
Polymerisation: It is a chemical reaction

when the large number of monomers combine together and form a polymer with (or) without elimination of smaller molecules (such as  $H_2O$ ,  $HCl$ ,  $CH_3OH$  etc)

$n$  monomers  $\longrightarrow$  polymer  
with/without  
elimination

\* Degree of Polymerisation: (D.P.)

The no. of repeating monomer units present in a polymer chain is called as degree of polymerisation.



Here, Degree of polymerisation is 3

\* Degree of polymerisation =  $\frac{\text{Mol. wt of polymer network}}{\text{Mol. wt of monomer unit}}$

$$D.P. = \frac{3 \times 28}{28} = 3 \text{ for } CH_2=CH_2 \text{ (Ethylene)}$$

\* The ratio of molecular weight of polymer network to molecular weight of single monomer unit is called as Degree of polymerisation.

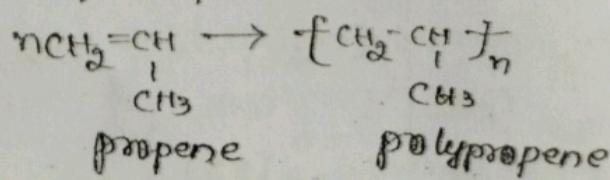
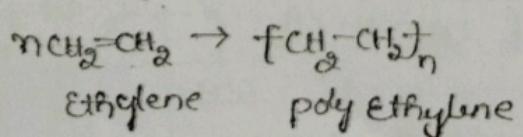
Types of Polymerisation:

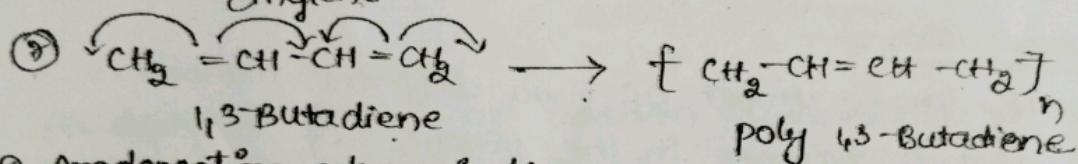
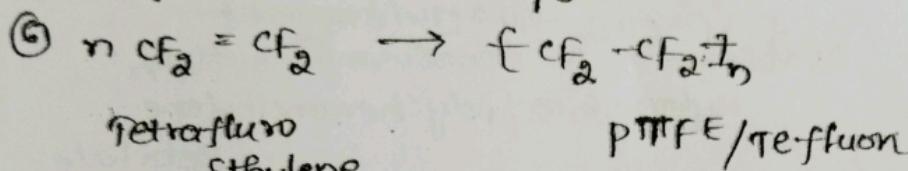
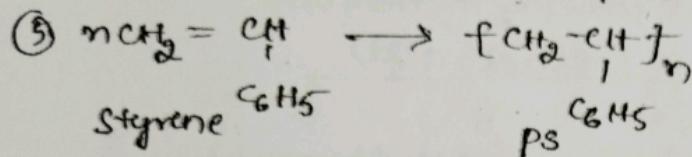
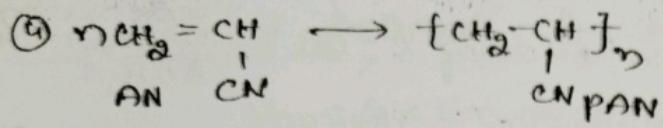
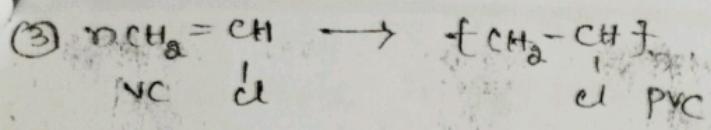
1. Addition polymerisation
2. Condensation polymerisation
3. co-polymerisation.

1. Addition polymerisation:

It is a chemical reaction in which the large number of monomers add to give a polymer with/without elimination. It is also called as chain growth polymerisation because of by self addition of same monomers to each other through a chain reaction.

Ex: ① Olefine compounds      ② vinyl compounds





## 2. Condensation polymerisation:

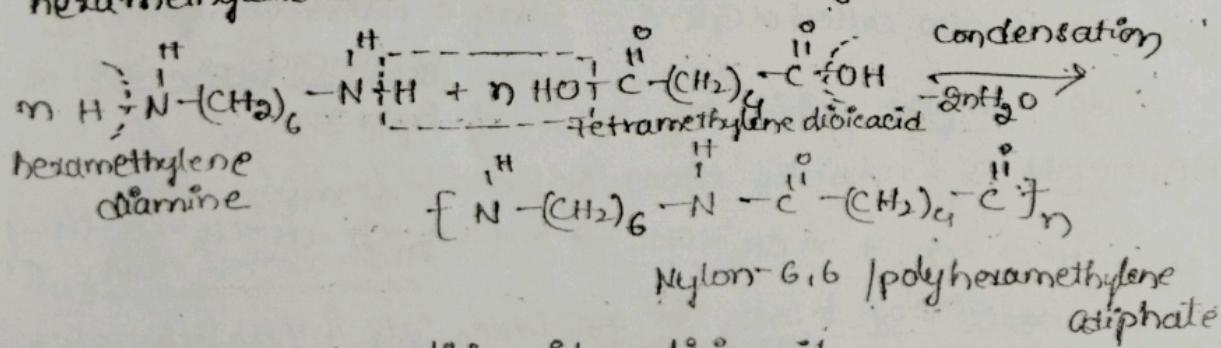
when the large number of different function groups of the monomers on condensation to give (produce) one polymer with elimination of small monomers is known as condensation polymerisation.

It is known as Step-wise polymerisation because of by condensation b/w two different functional groups of the monomers to each other through a step-wise reaction.

Ex: Nylons, phenol-formaldehyde resin, urea-formaldehyde resin  
(Bakelite)

① Nylon-6,6 (polyamides) are equal to molecular weight polymers.

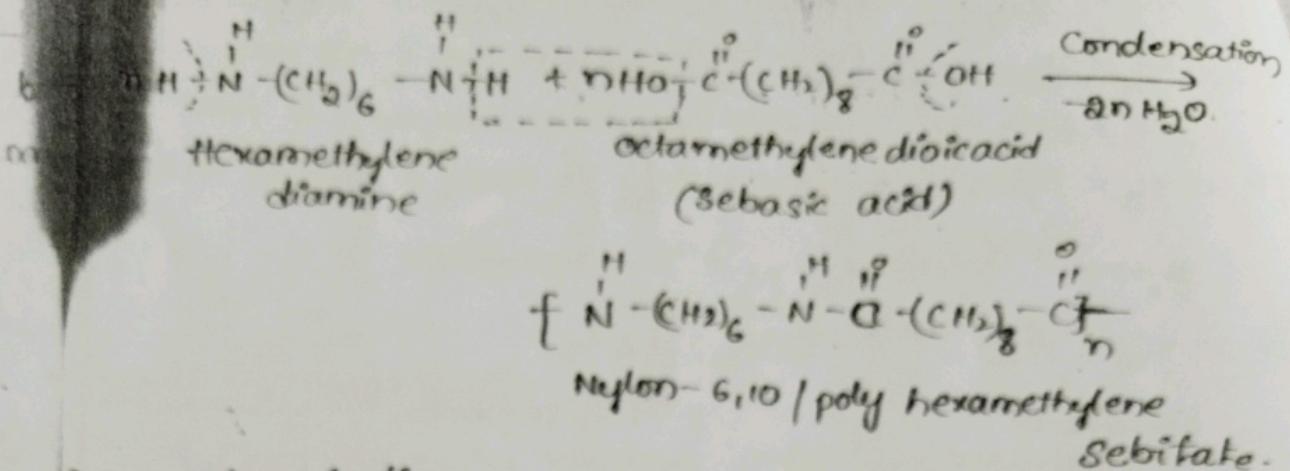
It is prepared by condensation polymerisation b/w large number of different functional groups of the monomers like as hexamethylene diamine and tetramethylenedioic acid.



tetramethylene dicarboxylic acid - adipic acid

octamethylene dioic acid - sebasic acid

② Nylon-6,10



### 3. CO - polymerisation :

when the large number of two different monomers combine to give a polymer in the presence of catalyst is called as co-polymerisation. It is also called as joint polymerisation.

Ex: Buna-S , Buna-N

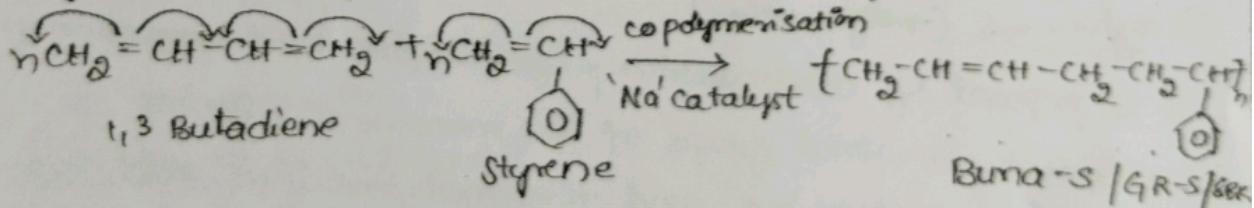
## ① Buna - S

### Bu - 1,3Butadiene

Na- Na catalyst

S - Styrene

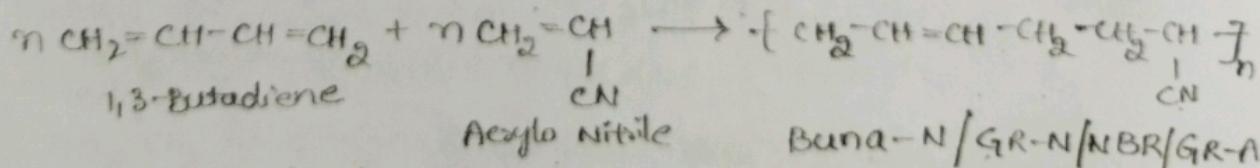
It is prepared by co-polymerisation of 1,3-Butadiene & Styrene in the presence of sodium catalyst



Buna-S is also called as GR-S — Gummie rubber co-styrene

SBR - Styrene (Buna-S) rubber  
Butadiene

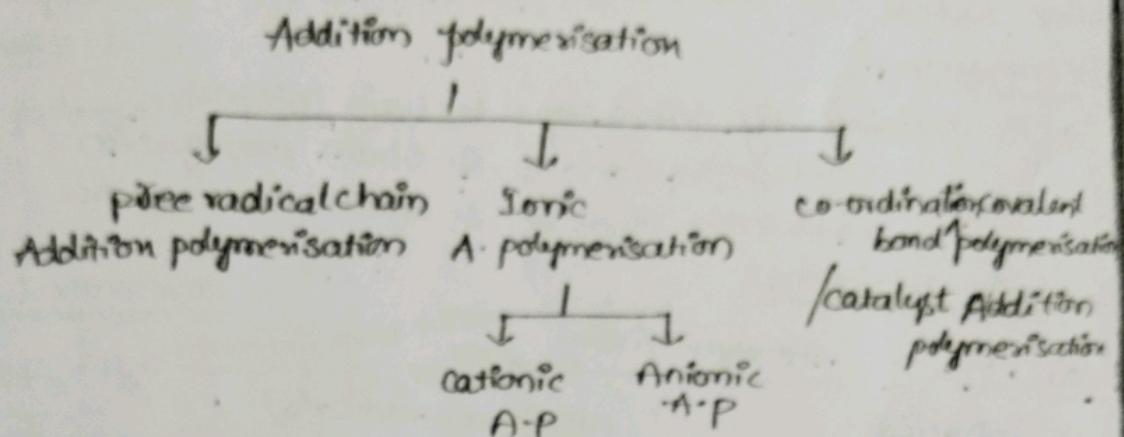
## ② Buna - N



Buna-N is also called as G.R.N - Goodyear rubber co - Nitrile  
NBR - Nitrile butadiene rubber  
G.R.N - Goodyear rubber & Acrylonitrile

Reaction NEE  
It is prepared by the copolymerisation of 1,3-Butadiene & Acrylonitrile in the presence of Na catalyst.

### MECHANISM OF ADDITION POLYMERISATION:



According to process of addition polymerisation is classified into mainly 3 types.

1. free radical AP

2. Ionic AP

3. co-ordination covalent bond AP / catalyst AP. This is further classified into cationic & Anionic AP

The mechanism of any addition polymerisation based on the following 3 steps :

1. chain initiation

2. chain propagation

3. chain termination.

#### 1. chain initiation:

In this step, how we get chain initiator from selective suitable initiators is determined.

#### 2. chain propagation:

In this step, how we get living polymer (chain-growth polymer) from the chain initiator is determined.

#### 3. chain termination:

In this step, how we get dead polymer (addition polymer) from living polymer) chain initiator is determined.

## MECHANISM OF FREE RADICAL POLYMERISATION

The polymerisation process which initiated by a free radical is known as free radical chain polymerisation.

### Mechanism:

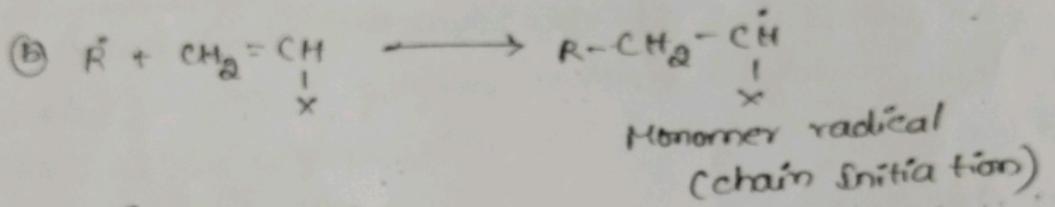
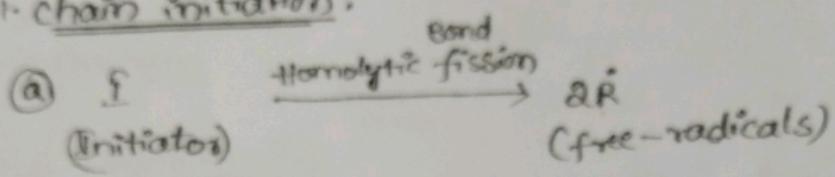
It is followed by three steps:

1. chain initiation
2. chain propagation
3. chain termination.

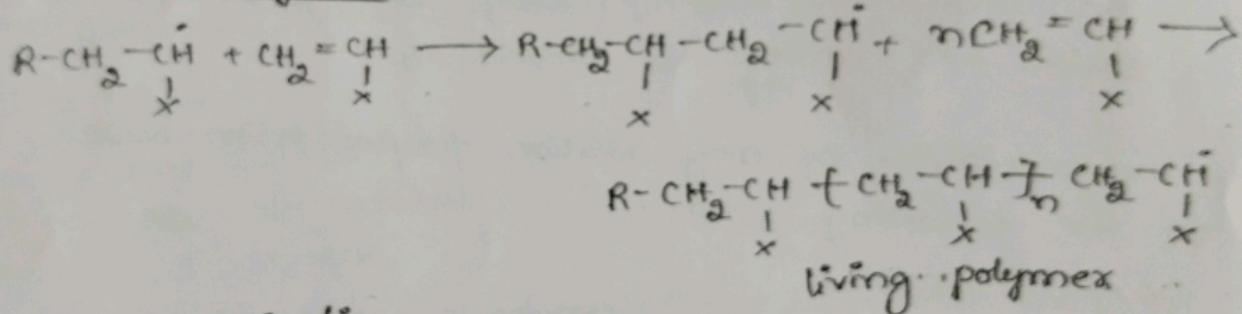
chain  
initiation

chain  
reaction

#### 1. chain initiation:

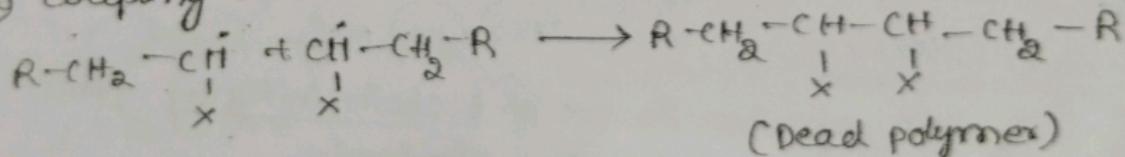


#### 2. chain propagation:

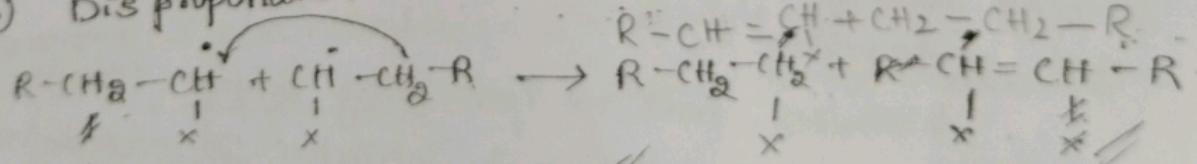


#### 3. chain termination:

##### (a) coupling reaction



##### (b) Disproportionation



## MECHANISM OF CATIONIC CHAIN POLYMERISATION:

The polymerisation process which is initiated by a cation. This polymerisation takes place when electron donating groups like  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$  are present in a monomer. These groups stabilize the carbonium ion formation.

solvent, be  
Lewis acid  
co-Catalyst  
Mechanis

81

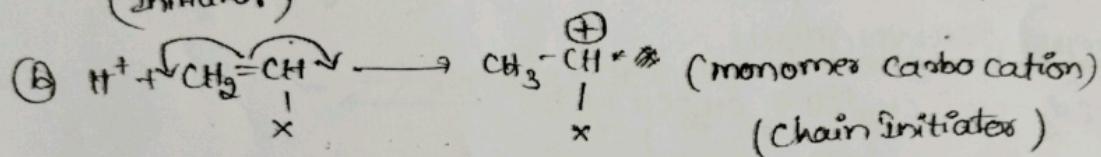
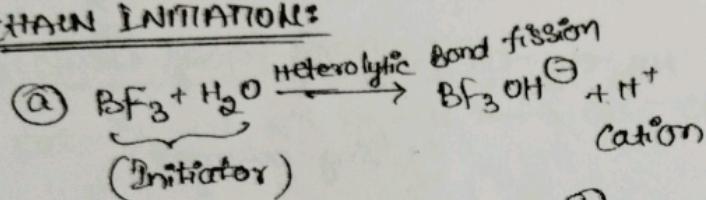
It is carried out at low temperature and in a non-polar solvent but in this polymerisation suitable initiators are Lewis acids like  $\text{BF}_3$ ,  $\text{AlCl}_3$  etc and mixing with co-catalysts like  $\text{Hg}^0$ ,  $\text{Hg}$ ,  $\text{HBr}$  etc.

### MECHANISM:

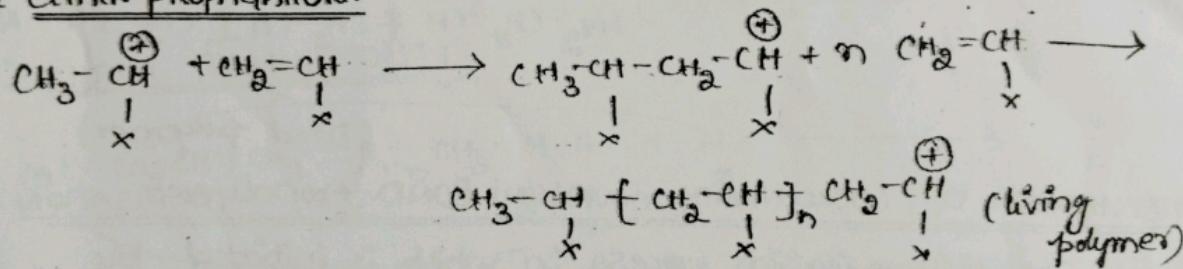
It is followed by three steps.

1. chain initiation
2. chain propagation
3. chain termination

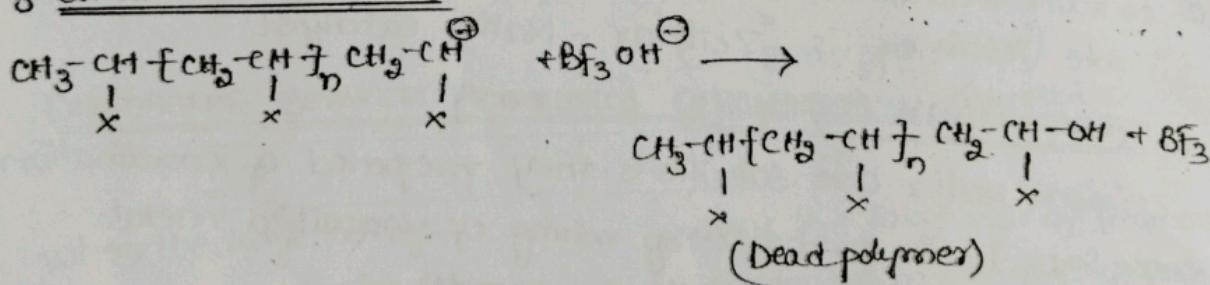
### 1. CHAIN INITIATION:



### 2. CHAIN PROPAGATION:



### 3. CHAIN TERMINATION:



### MECHANISM OF ANIONIC POLYMERISATION:

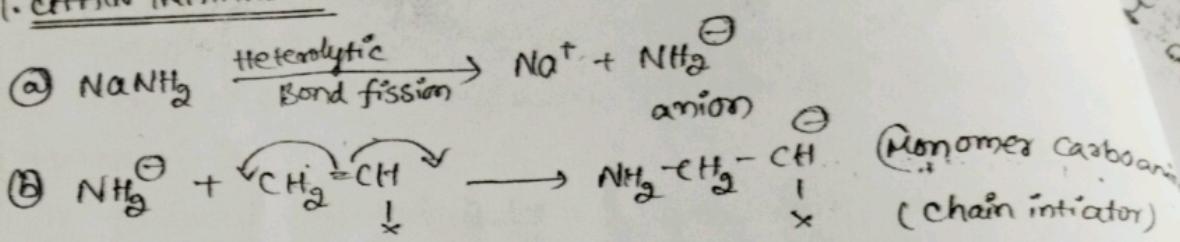
The polymerisation process in which is initiated by a anion. This polymerisation takes place when Electron accepting groups like Lewis bases, like  $\text{KNi}_2$ ,  $\text{NaNi}_2$ ,  $\text{NaP}^-$ .

### MECHANISM:

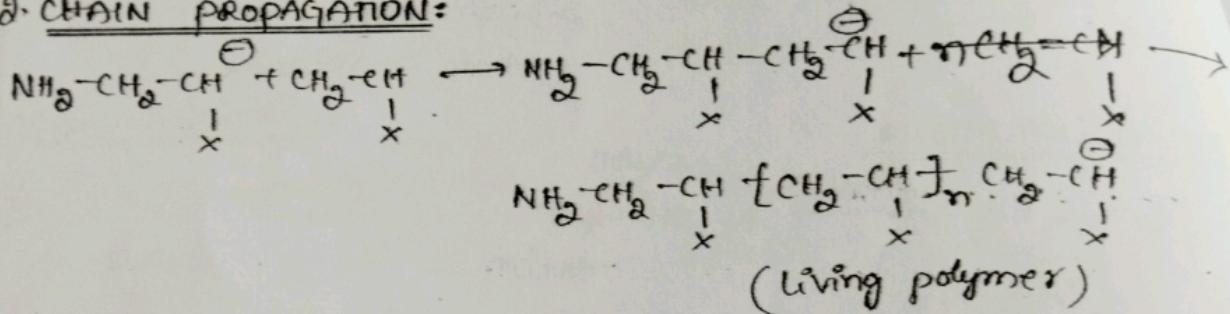
It is followed by three steps.

1. chain initiation
2. chain propagation
3. chain termination

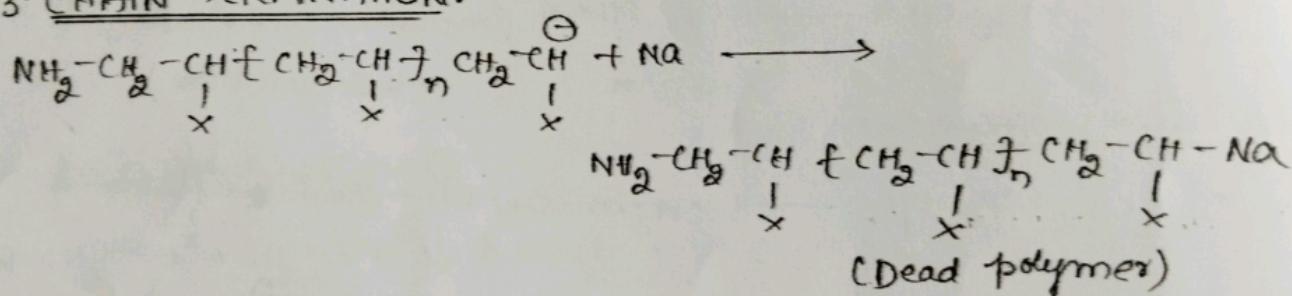
## 1. CHAIN INITIATION:



## 2. CHAIN PROPAGATION:



### 3. CHAIN TERMINATION:

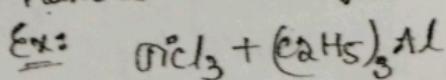


### MECHANISM OF COORDINATION COVALENT BOND AND POLYMERISATION:

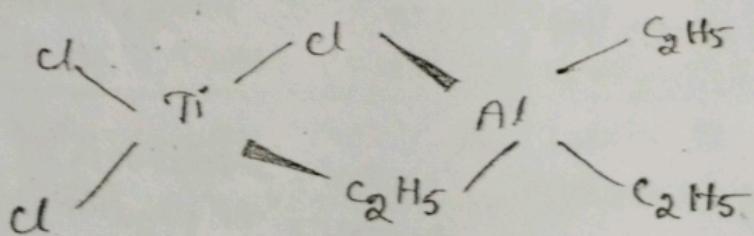
The polymerisation process in which is initiated by a coordinate covalent bond (catalyst). In this polymerisation suitable initiator is "Zeigfar - Natta catalyst."

ZEIGLER-NAFFA CATALYST: [2M \*\*\*]

ZEIGLER - Natta  
Zeigler, Natta are scientists. They prepared a coordination complex. It is prepared by mixing of transition metal halides and organo metallic compounds.



titanium chloride triethylaluminium

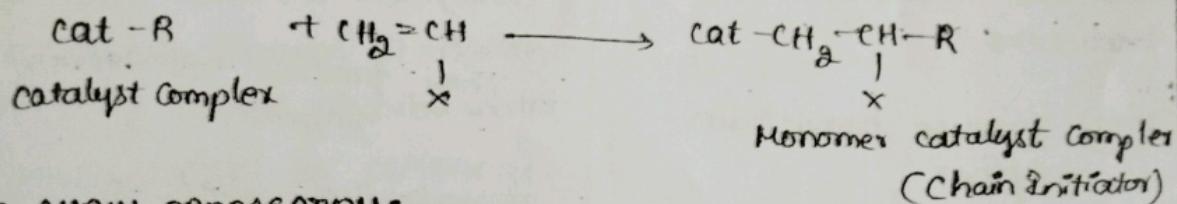


Zeigler-Natta catalyst is represented by "Cat-R"

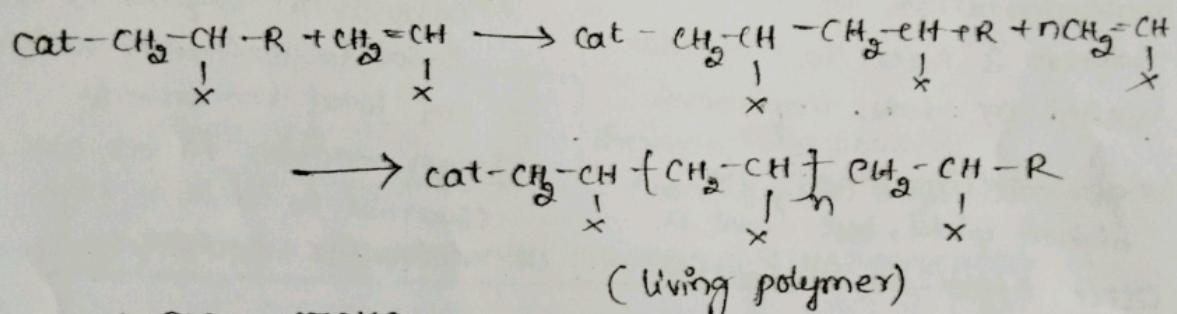
## Mechanism:

It is followed by 3 steps. They are 1. chain initiation  
 2. chain propagation  
 3. chain termination

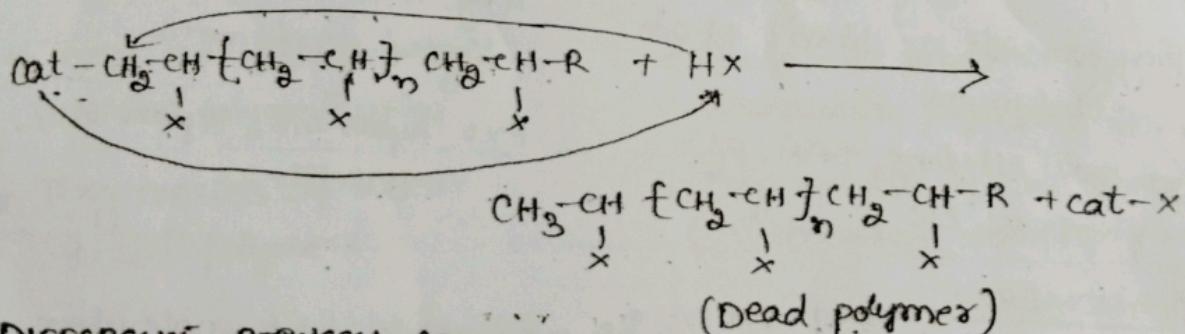
### 1. CHAIN INITIATION:



### 2. CHAIN PROPAGATION:



### 3. CHAIN TERMINATION:



### Difference between Addition & Condensation Polymerisation.

#### A.P

When the large no. of monomers add to give polymers without elimination.

It is chain growth polymerisation.

It takes place in monomer having multiple bonds.

#### C.P

When the large no. of monomers condense to give polymers with elimination.

It is step-wise polymerisation.

It takes place in monomer having only reactive functional group.

It takes place without elimination of simple molecules.

These are thermo plastics producers.

They produce homochain polymer

molecular weight of addition polymers is equal to molecular weight of total monomers.

longer reaction times give higher yield, but have a little effect on molecular weight.

They consists of linear chain polymers.

Ex: poly ethylene, PAN, PS, PTFE etc

It takes place with elimination of simple molecules.

These are thermo setting plastics producers.

They produce heterochain polymer.

molecular weight of condensation polymers is not equal to molecular weight of total monomers.

longer reaction times are essential to obtain high molecular weight.

They consists of cross linked polymers.

Ex: Nylon-6,6, Nylon-6,10, Bakelite

### PLASTOMERS:

Plastomers are inorganic (or) organic high molecular weight polymers which can be moulded into any desired form by the application of heat & pressure in the presence of catalyst.

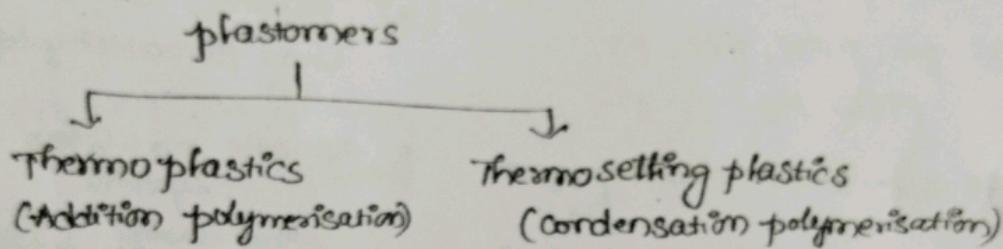
But Resins are basic binding materials and also major part of the plastic so that these two terms are synonyms i.e, (resins & plastics).

Now-a-days they have great importance because of they are having some important properties.

- \* light in weight.
- \* low fabrication cost
- \* low maintenance cost.
- \* high resistant to corrosion.
- \* resistance to abrasion.

- \* Easy moulding
- \* Easy workability
- \* Easy transportation
- \* Good dimensional stability
- \* Good Electrical Insulation
- \* Good thermal insulation
- \* they do not absorb water.

### CLASSIFICATION OF PLASTICS:



### DIFFERENCE B/w THERMO AND THERMOSETTING PLASTICS:

#### Thermo plastics

- \* These are prepared by addition polymerisation
- \* They consists of linear chain polymers
- \* All the polymer chains are held together by weak van der waal forces of attraction.
- \* They are weak, soft and less brittle nature.
- \* They soften on heating and harden on cooling

#### Thermosetting plastics

- \* These are prepared by condensation polymerisation.
- \* They consists of cross-linked 3 dimensional network polymers
- \* All the polymer chains are linked by strong covalent bonds
- \* They are strong, hard and more brittle nature.
- \* They do not soften on heating.
- \* They cannot be remoulded.
- \* They have high molecular weights

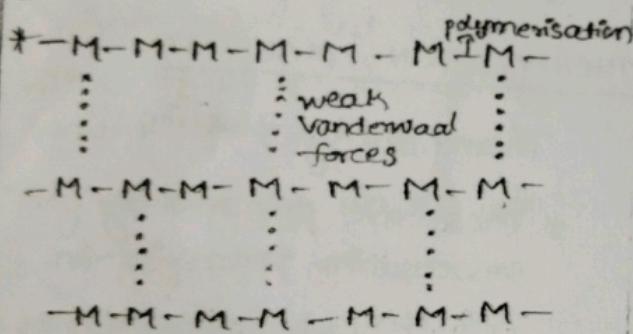
\* They are soluble in organic solvents

\* The resin is synonymous with plastics.

\* They can't change the chemical composition in thermo plastic

\* Ex: PE, PAN, PVC, PS, PTFE etc

\* All are linear chain polymers



\* These are used for the manufacture of comb, heater handles, mugs, jugs etc

\* They can be reclaimed from waste, that is recycling.

#### IMPORTANT PLASTOMERS:

The important plastomers are

1. PVC

2. PTFE

3. Bakelite

4. Nylons

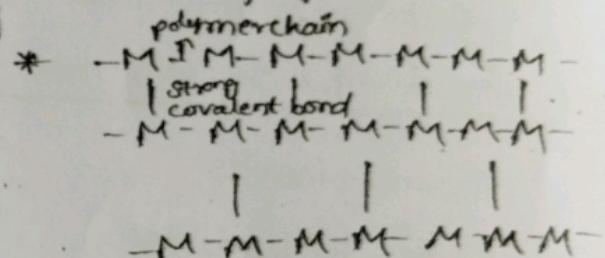
\* They are insoluble in organic solvents.

\* Resin is not synonymous with plastics.

\* They change the chemical composition in thermo setting plastic.

\* Ex: Nylons, Bakelite, Urea formaldehyde etc.

\* All are non-linear chain polymers



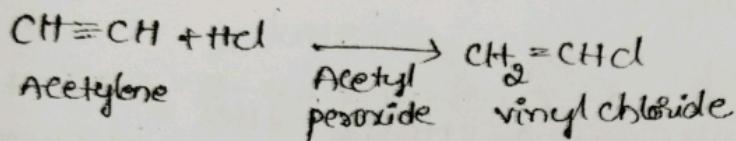
\* These are used for the manufacture of Electrical devices (switches, switchboards)

\* They cannot be reclaimed from waste and cannot be recycling.

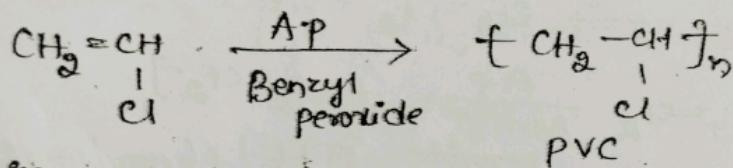
## 1. PVC (poly vinyl chloride)

pvc is a thermo plastic because it is prepared by the addition polymerisation of large no. of vinyl chloride in the presence of catalyst (metal chloride). It is followed by 2 steps.

### Step 1:



### Step 2:



### Properties:

1. pvc is colourless and odourless.
2. It is non-flammable and chemically inert powder.
3. It is resistant to atmospheric oxygen, inorganic acids and alkalis.
4. It is soluble in hot chlorinated hydrocarbons such as Ethyl chloride and Ketones.
5. It is not stable to heat and UV radiation, it undergoes degradation.

### Uses:

1. wire coating, electrical insulation like covering of Electrical cables.
2. The production of pipes, sheets and moulded parts.
3. Tank linings, motor parts and safety helmets.
4. The production of toys, tool handles etc.
5. It is also used in making table cloths, rain coats, jackets and bags etc.

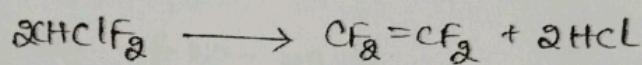
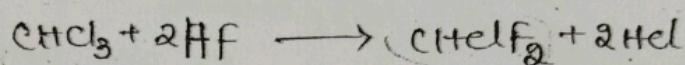
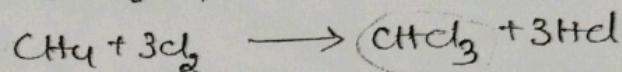
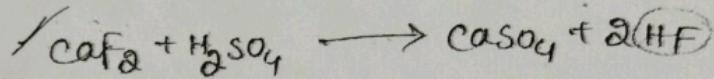
### 2. PTFE / Fluoroflon:

PTFE means poly tetra fluoro Ethylene

PTFE is a thermoplastic because it is prepared by the addition polymerisation of tetrafluoro Ethylene in the presence of Benzyl peroxide.

It is followed by 3 steps.

Step 1:



Step 2:  $n\text{CF}_2=\text{CF}_2 \xrightarrow[\text{peroxide}]{\text{Benzyl}} \text{f}\left[\text{CF}_2-\text{CF}_2\right]_n$

PTFE / fluor / teflon

### PROPERTIES:

1. Teflon is tough and flexible material and also possess high softening point (above 350°C)
2. It possess good electrical and mechanical properties.
3. It is chemically resistant towards all chemicals.
4. It has an excellent thermal stability.

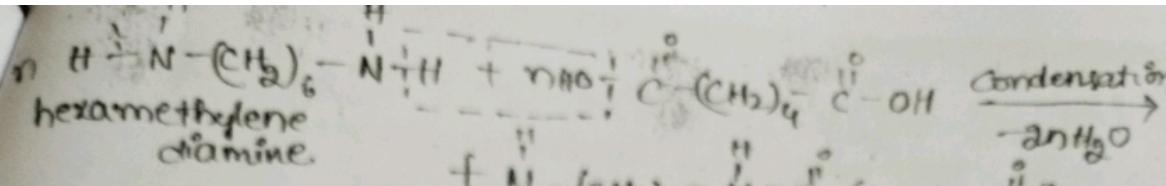
### APPLICATIONS:

1. It is used as a very good Electrical insulating material in motors, cables, transformers & Electrical fittings.
2. It is also used for making gaskets, packings, pump parts, tank linings, etc.
3. It is also used for non-lubricating bearings, chemical carrying pipes etc.
4. It is used in making non-sticking stop cocks for burettes.

### NYLONS:

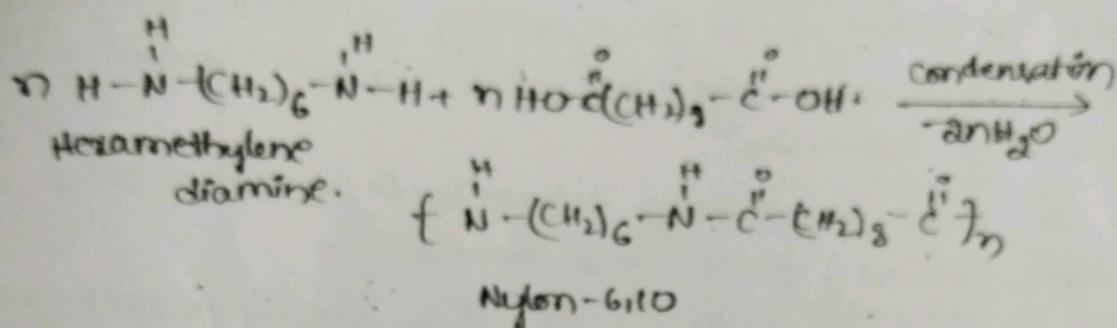
Nylons are poly amides. They are prepared by the condensation polymerisation.

Nylon-6,6: Nylon-6,6 is prepared by condensation polymerisation of hexamethylenediamine and trimethylene dicarboxylic acid.

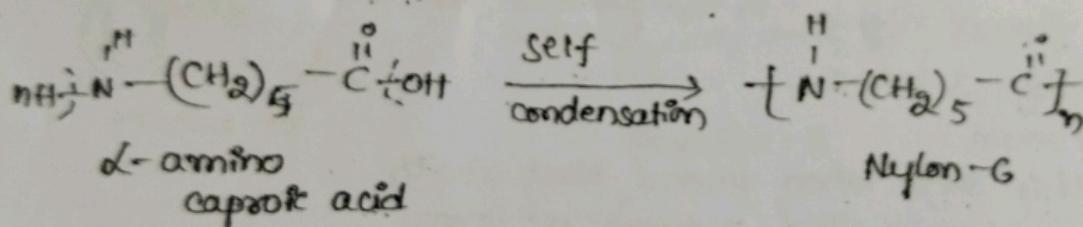


### 2. NYLON-6,10:

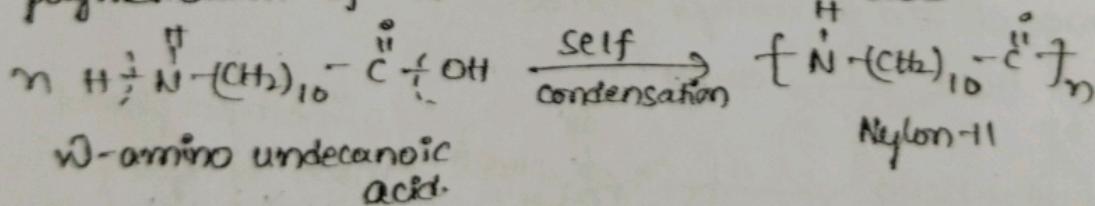
It is prepared by the polymerisation of hexamethylene diamine and octamethylene dicarboxylic acid.



3. NYLON-6: It is prepared by the self condensation polymerisation of  $\alpha$ -amino caproic acid.



4. NYLON-11: It is prepared by the self condensation polymerisation of  $\omega$ -amino undecanoic acid.



### PROPERTIES OF NYLONS:

- \* They behave as plastic as well as fibre.
- \* They are having high melting polymers (points)
- \* They are insoluble in common organic solvents but soluble in phenol-formic acid ( $\text{HCOOH}$ )
- \* They possess good mechanical properties and fairly resistant to moisture.

\* They are characterised by combination of high strength, elasticity, toughness and abrasion resistance.

### APPLICATIONS:

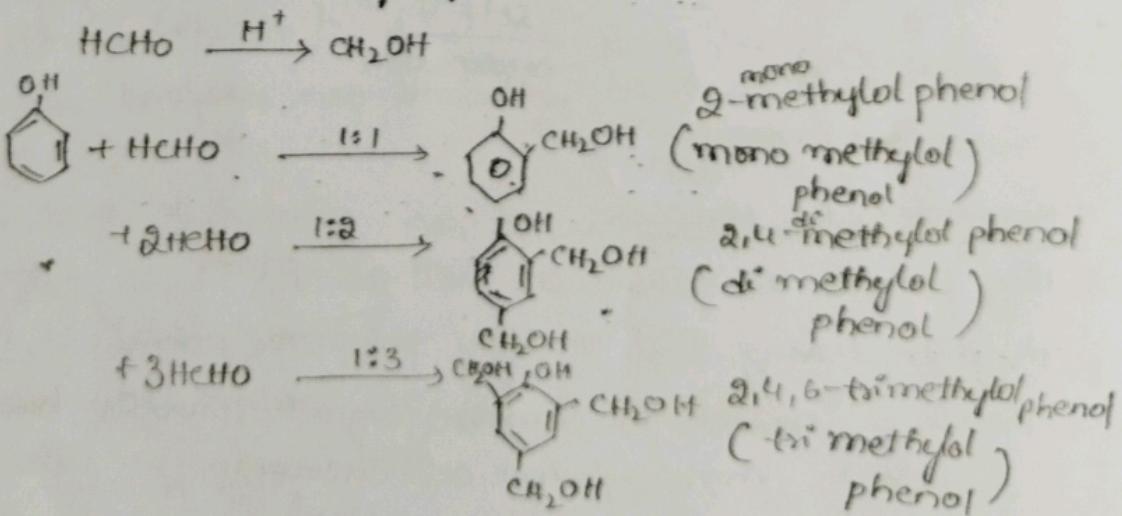
\* Nylon-6,6 is used for fibres, which are used in making socks, lady shoes, dresses & carpets etc.

\* Nylon-6 is mainly used for moulding purposes for gears, bearings, Electrical mountings etc. Nylon bearings work without any lubrication.

\* They are used for making filaments for ropes, bristles for tooth brushes, films and tire-cords.

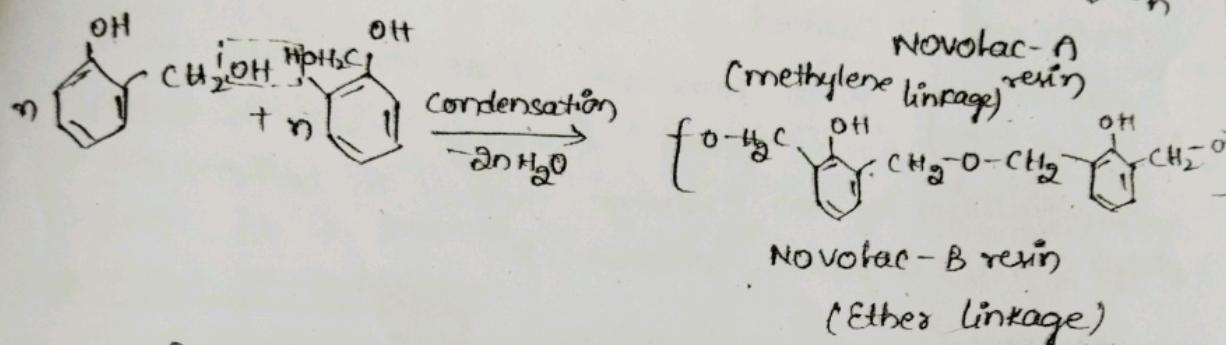
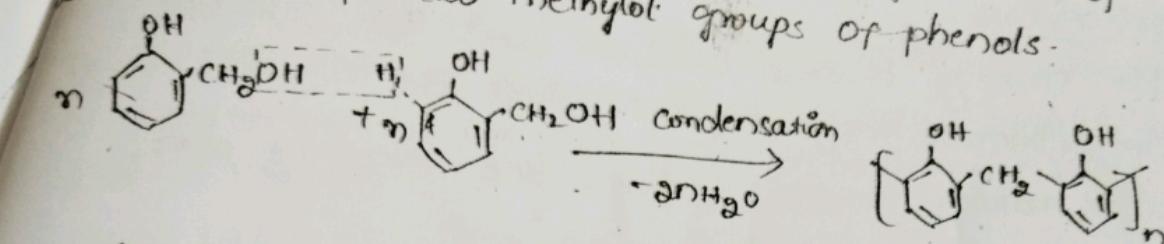
MANUFACTURE OF BAKELITE: It is thermosetting plastic. Bakelite is phenol-formaldehyde resin. It is discovered by Bakelend in 1909 so, that it is also called as Bakelite. It is prepared by the condensation polymerisation of phenol & formaldehyde in the presence of acid medium. It is followed by 3 steps.

Step 1: In this step when phenol react with formaldehyde to produce 3 types of non-polymeric molecules in the presence of acid medium - they are mono, di and tri methyl phenols.

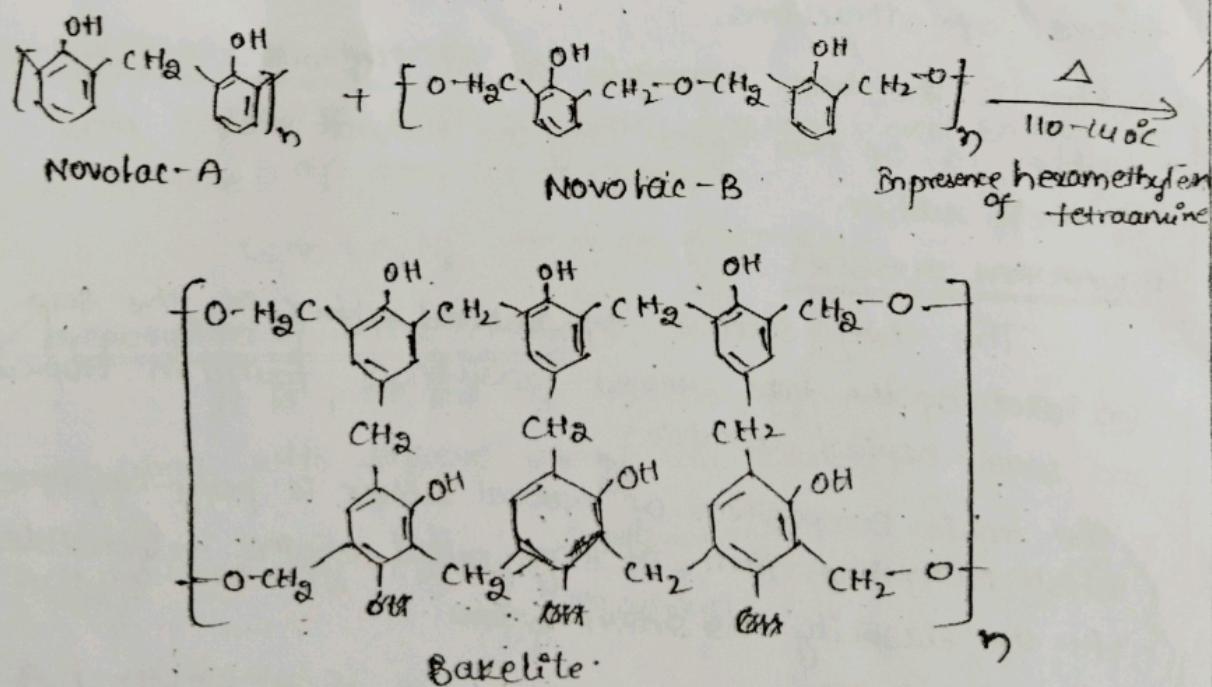


Step 2: In second step any two mono (or) di or tri methylol phenols on condensation to produce Novolac - A resin & novolac-B resin through condensation polymerisation.

Strength takes place b/w methylol group & Hydrogen atom of benzene and b/w two methylol groups of phenols.



Step 3: In this step, take Novolac-A and Novolac-B resins on heating at 110-140°C to develop the cross linkages and produce 3-dimensional Network polymer. It is called phenol formaldehyde resin.



### PROPERTIES:

1. Bakelite is resistant to acids, salts and most organic solvents, but it is attracted by alkalis because of the presence of -OH groups.
2. It possesses excellent electrical insulating property.
3. It possesses excellent thermal insulating property.

## APPLICATIONS:

1. for making Electrical insulators parts like switches, switch boards, heater handles, plugs etc.
2. for making moulded articles like telephone parts, radio and TV cabinets.
3. for making wood laminates, glass laminates.
4. It is used as an anionic Exchange resins in water purification by ion exchange method in boilers.
5. It is used in paints, varnishes etc.

## ELASTOMERS:

Those polymer having elastic property like rubber is known as Elastomer.

They have long flexible chains with weak intermolecular forces of attractions.

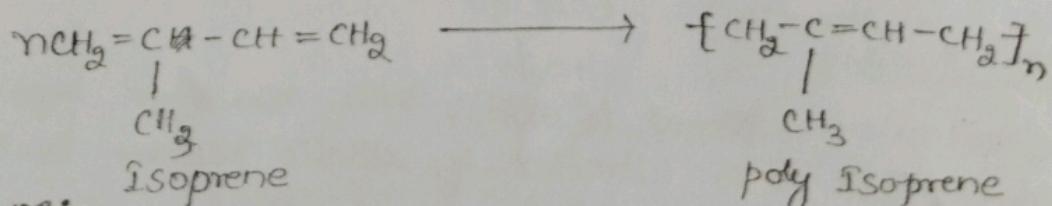
\* Rubber is the best example of an Elastomer.

\* Rubber is of two types. They are Natural rubber and Synthetic rubber.

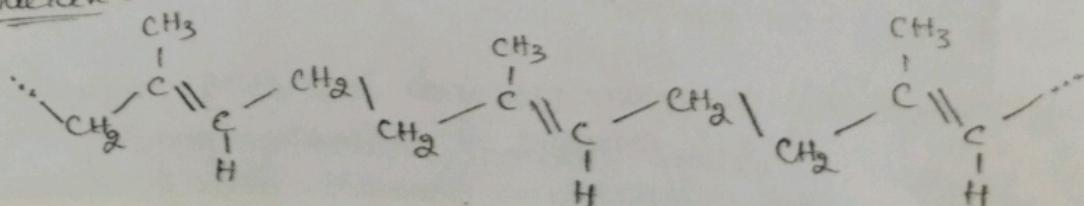
### I. NATURAL RUBBER:

The chief source of Natural rubber is the sap (or latex) of the tree *Hevea brasiliensis* found in tropical and semi-tropical countries.

\* The main composition of natural rubber is poly-isoprene, which is in the form of long coiled chains responsible for the elasticity as shown below:



### Structure:



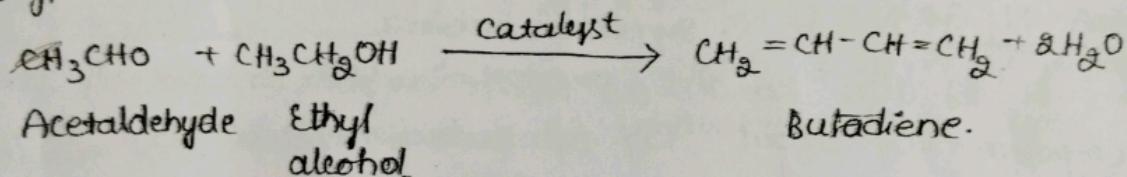
## SYNTHETIC RUBBER:

Those polymers which are prepared in the laboratory by synthetic methods and can be used as a substitute of natural rubber are called as synthetic rubbers (or) artificial rubbers.

BUNA-S/GR-S: It is synthetic rubber. Buna-S is a co-polymer. It is Elastomer. Buna-S is also known as Styrene-butadiene rubber. It is a co-polymer of about 75% of 1,3-Butadiene and 25% of styrene. It is followed by 3 steps. In presence of Na catalyst

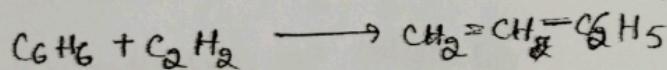
### Synthesis of 1,3-Butadiene:

Butadiene is produced from acetaldehyde and ethyl alcohol.



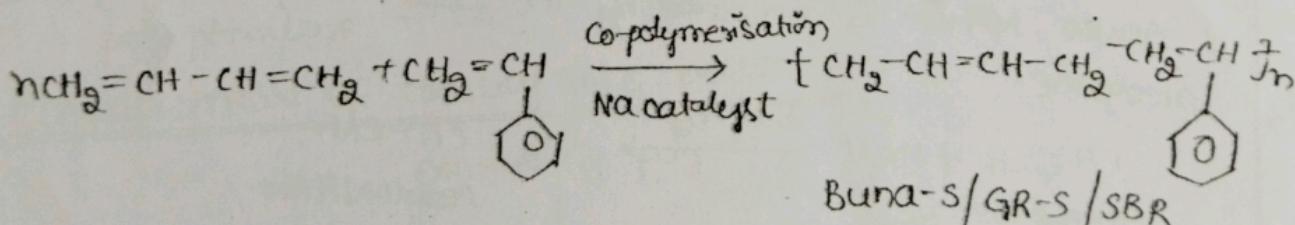
### Synthesis of Styrene:

Styrene is obtained from benzene and Ethylene in the presence of  $\text{AlCl}_3$  as a catalyst.



### Preparation of buna-S rubber:

It is produced by the co-polymerisation of butadiene with styrene using Na catalyst.



### Properties:

1. Styrene rubber is strong and tough.
2. It is vulcanized by sulphur chloride (or) Sulphur.
3. It resembles natural rubber in processing characteristics and quality of finished products.

- 4. It possesses excellent abrasion resistance.
  - 5. It is resistant to chemicals but swells in oils.
  - 6. It possesses high load bearing capacity.

### Uses:

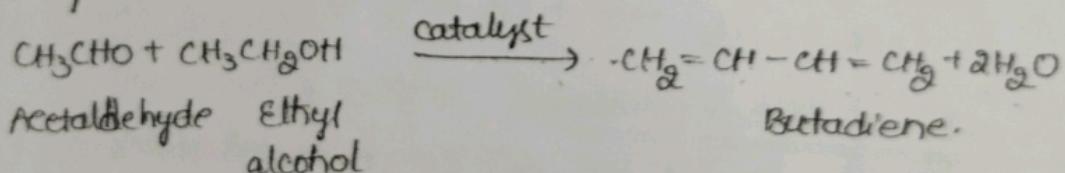
1. Major use of Styrene rubber is in the manufacture of tyres.
  2. It is used in the footwear industries for making shoe soles and footwear components.
  3. It is also used for making wires and cable insulators.
  4. Styrene rubbers are used in the production of floor tiles, tank linings, and chemical industries.

BUNA-N / GR-N: It is synthetic rubber.

Buna-N is also known as Nitrite rubber (or) GR-N. It is a copolymer of about 75% of Butadiene and 25% of Acrylonitrile. It is followed by 3 steps.

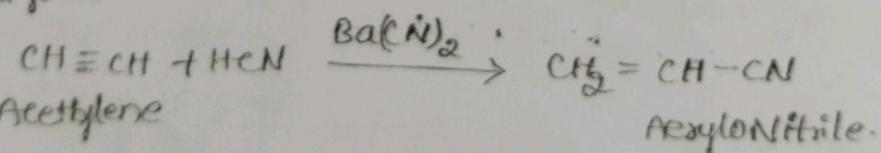
### Synthesis Of $\beta$ , $\beta$ -Butadiene:

Butadiene is produced from acetaldehyde and Ethyl alcohol.



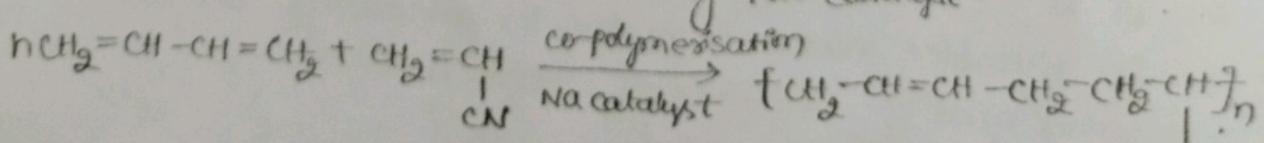
## 8. Synthesis of Acrylo Nitrile:

Acylo Nitrile is prepared by the addition of HCN and acetylene.



3 Preparation of buna-N rubber:

It is produced by the co-polymerisation of butadiene with Acrylo Nitrile using Na catalyst.



## Properties:

1. It is a strong and tough polymer with light weight.
2. It can be vulcanized in the same way as Natural rubber.
3. It has good oil, heat and abrasion resistances.
4. It is attacked by alkalis due to presence of cyano group.

## USES:

Nitrile rubber is used for the making aircraft components, conveyor belts, tank linings, gaskets, printing rollers, automobile parts etc.

## CONDUCTING POLYMERS [Imp \*\*\* 10M]

An organic/inorganic polymer which is having conjugated system or similar to metallic conductivity they are called conducting polymers.

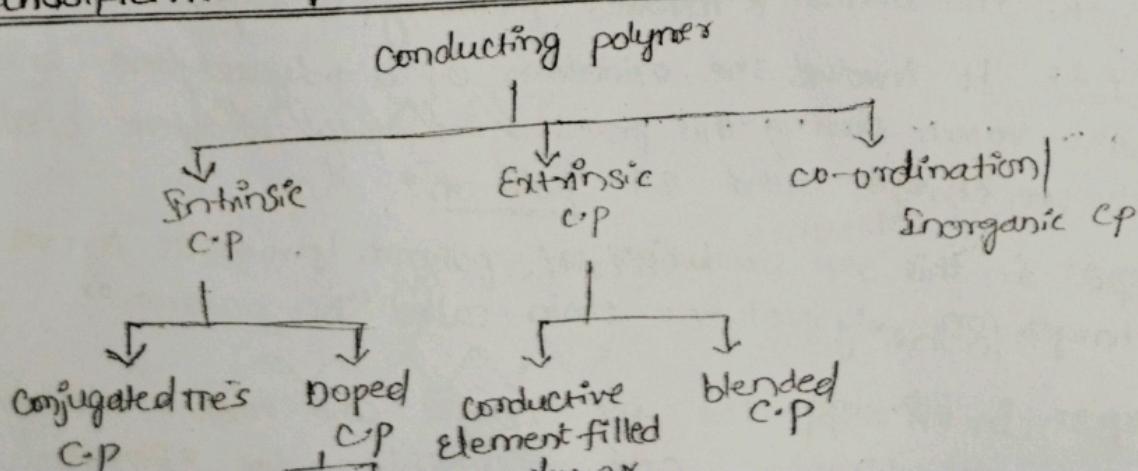
(or)

Those polymers which can conduct the Electricity they are called conducting polymers.

### Reasons for conduction of polymers:

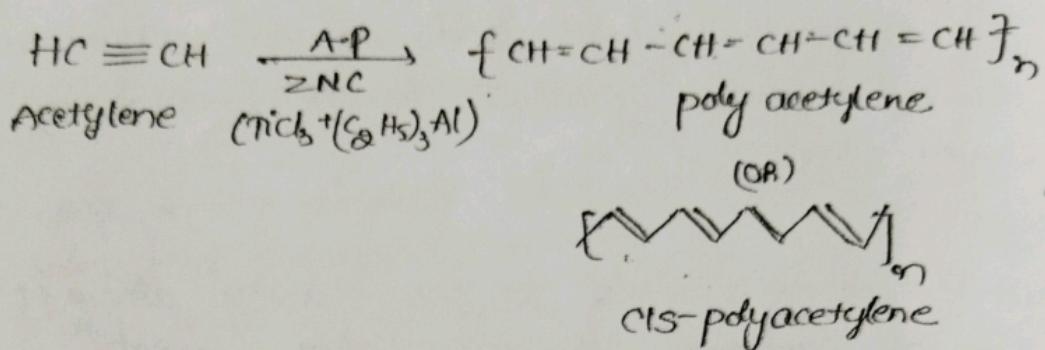
1. conjugated  $\pi e^-$  in the polymer
  2. doping process (removal / addition of  $e^-$  in the polymer)
- Ex: polyacetylene, polyaniline, poly phenylene, poly thiophene, poly phenylene — etc.

## CLASSIFICATION OF CONDUCTING POLYMERS:



## Poly Acetylene [10 M]:

Preparation: It is prepared by addition polymerisation of acetylene in the presence of Ziegler Natta catalyst.



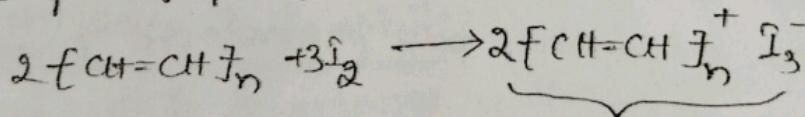
### Mechanism:

The conductivity of cis-form of poly acetylene is less when compared to trans-poly acetylene. So that the conductivity of cis-poly acetylene can be improved by either positive doping (or) negative doping.

#### 1. POSITIVE DOPING: (oxidative doping) p-doping

When poly acetylene is treated with Iodine vapour (Lewis acids (or) halogens) by oxidation takes place then +ve charge creates on poly acetylene chain back bone. They are acting as good conductors of electricity. It is known as p-doping (or) oxidative doping.

Ex: Examples of p-dopants are  $\text{I}_2$ ,  $\text{Br}_2$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$  --- etc



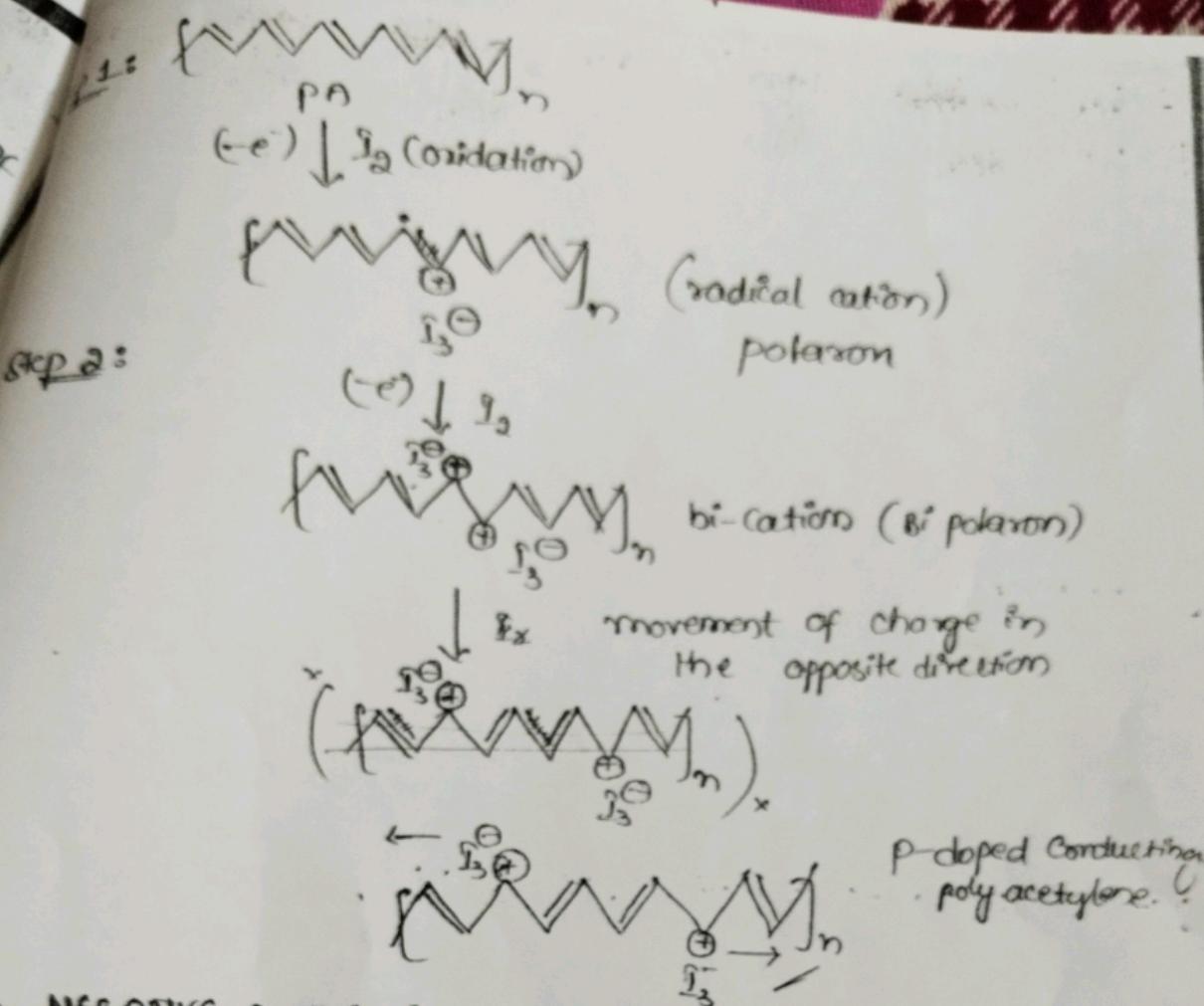
p-doped poly acetylene

In this mechanism it involves following 3 steps.

Step 1: It involves the oxidation of a polyacetylene with Iodine vapour. During this process the poly acetylene chain gets +ve charge called as "polaron".

Step 2: In this step oxidation of polaron produces 2 +ve charges on poly acetylene chain called "bi-polaron".

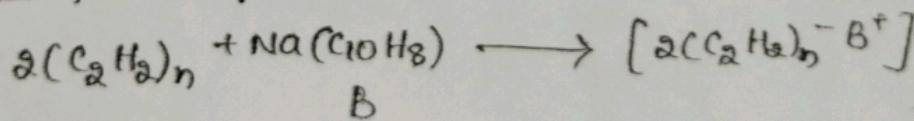
Step 3: In this step the +ve charges are mobile because of delocalization and responsible for electrical



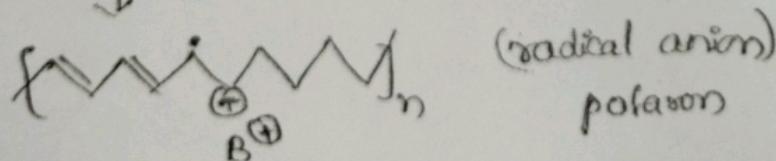
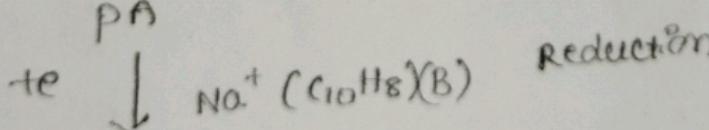
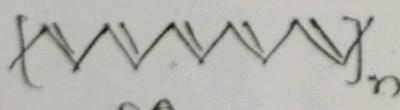
## 2. NEGATIVE DOPING (n-doping):

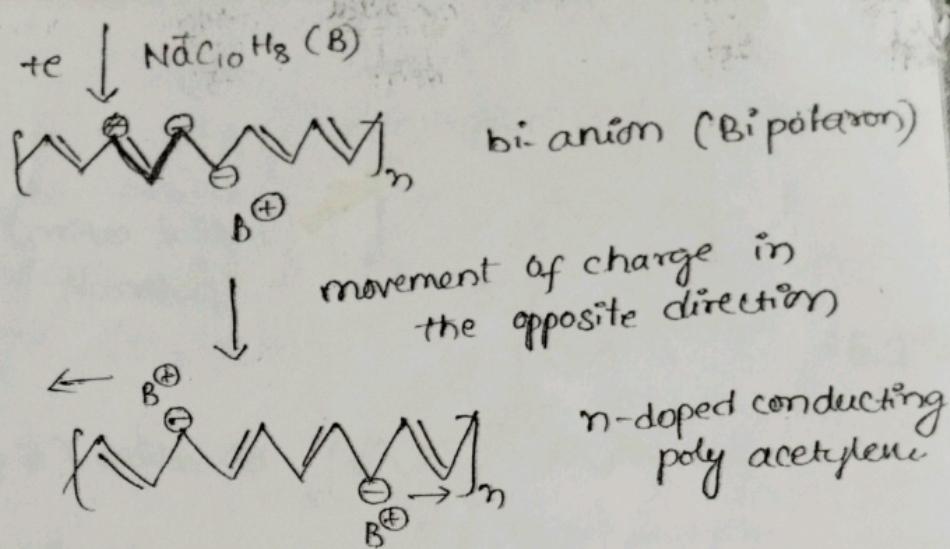
when poly acetylene is treated with Sodium Naphthalide ( $\text{NaC}_{10}\text{H}_8$ ) (Lewis bases (or) Alkali metals) by reduction takes place and creates negative charge on polyacetylene chain backbone. They are acting as good conductor of Electricity. It is called n-doping (or) reductive doping.

Ex: Examples for n-dopants -  $\text{NaK}$ , lithium naphthalides



Step 1:



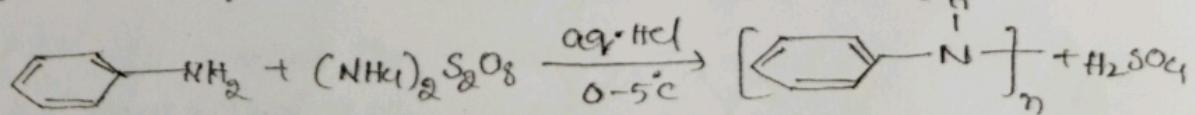


### APPLICATIONS :

- \* It is used in various electronic devices as active and passive electrodes.
- \* The main area of its application are batteries, nonlinear optics and microelectronics.
- \* PA with various conductivities are used for the formation of schottky batteries, p-n transistors, heterojunctions.
- \* It is also used in the development of photovoltaic devices.
- \* It is used as an electrode material of solid state batteries operating at room temperature.

### Poly aniline :

Preparation: It is prepared by the addition of aniline solution with Ammonium persulphate at low temperature  $0-5^\circ\text{C}$  in the presence aq. HCl to produce poly aniline.



It is separated by filtration, which is Emeraldine hydrochloride.

- \* poly aniline is a transparent and stable material. It shows green colour in conducting state. It turns to blue under oxidising condition and red under reducing condition.