UNIT - III POLYMERS

The word polymers is derived from Greek poly - many, mers units or parts.

Polymers are termed as Macromolecules as they are the giant molecules of high molecular weight which are built up up by the linking together of a large no of small molecules called monomers Thus the small molecules which combine with each other to form polymer molecules are termed as monomers and the repeating unit as called "mer" denoted as as n. the no% of repeating units in chain formed in a polymer is known as the "degree of polymerization" (DP)

-A polymer may consists of two different types of monomers

1. If the polymer is made up of identical monomers, they are called homopolymers.

$$-M-M-M-M-M$$

2. If the polymer is made up of monomers of different chemical structure they are called copolymers $-M_1-M_2-M_1-M_2-M_1-M_2-$

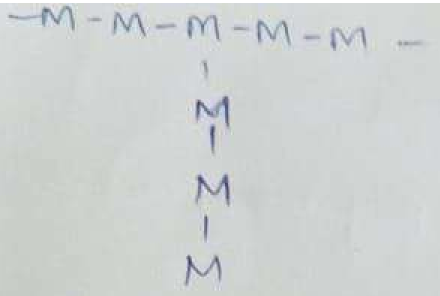
The monomeric unit in a polymer may be present in Linear branced cross Linked (3 dimensional) structure.

$-M-M-M-M-M-$

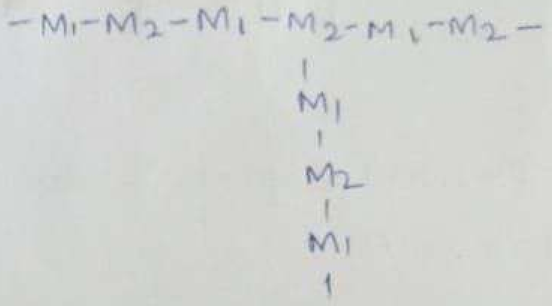
Linear homopolymer

$-M_1-M_2-M_1-M_2-M_1-M_2-$

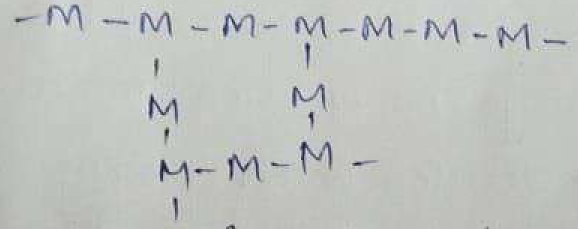
Linear copolymer



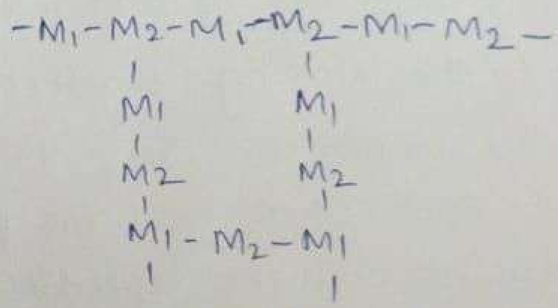
Branched chain homopolymer



Branched copolymer



cross Linked homopolymer



cross Linked copolymer,

If the main chain is made up of same species of atoms the polymer is called homochain polymer & if the main chain is made up of different atoms then it is called hetero chain polymer

$-C-C-C-C-C-C-$

Homo chain polymer

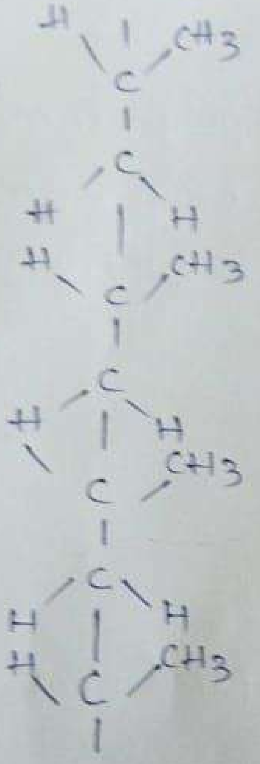
$-C-C-O-C-C-O-$

Hetro chain polymer

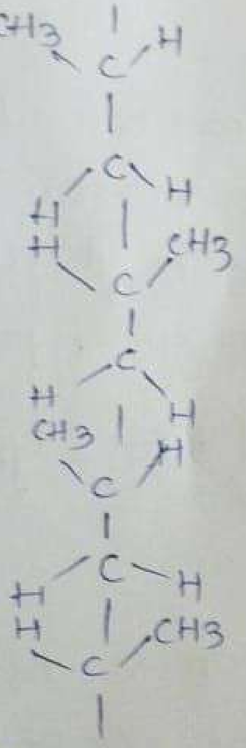
3. Syndwtatic polymer:

If the arrangement of side groups is in alternating fashion it is called syndwtatic polymer

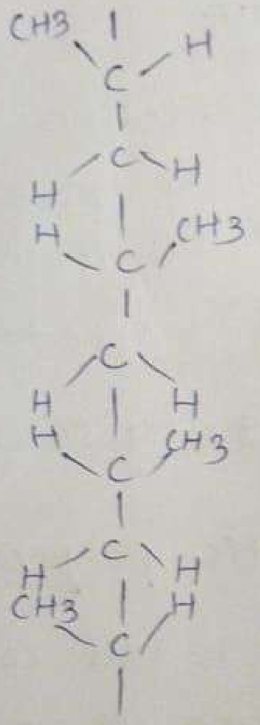
For example:



Isotactic



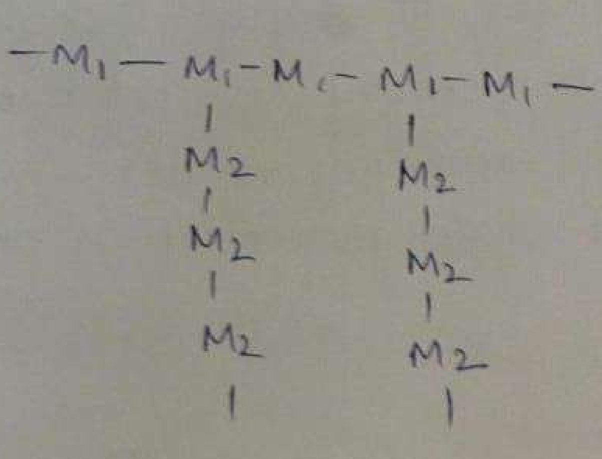
Syndiotactic



Atactic

FUNCTIONALITY

The no. of bonding sites in a monomer is called functionality. For a substance to act as monomer it must have atleast two reactive sites or bonding sites. In an olefine the double bond can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination. Craft copolymers are the branched structures in which the monomer segments differ from the main chain and its branches.



Craft copolymers.

TACTICITY:

The orientation of monomeric units in a polymer molecule can take place in an or disorderly fashion with respect to the main chain. The difference in configuration (tacticity) affect their physical properties

Tacticity is classified into 3 types

1. Isotactic polymer

The head to tail configuration in which the functional groups are all on the same side of the chain is called isotactic polymer

2. Atactic polymer

If the arrangement of functional groups are at random around the main chain, it is called atactic polymer.

$$H_2C=CH_2 \longrightarrow -CH_2-CH_2-$$

ethylene is bifunctional. Thus if the monomer is bifunctional two st reactive groups attach side by side to each other forming a linear or straight chain molecule. Linear polymers have primary covalent bonds, but different chains are held by secondary vander waals force which gives the possibility of chain movement in one direction

-A branched chain molecules results when a trifunctional monomer is mixed in small amounts with a functional monomer and polymerized.

In case of polyfunctional groups, monomer molecules are connected to each other by covalent bonds, resulting in the formation of 3 dimensional network. In such polymeric molecules the movement of individual molecules is prevented by strong cross Links

CLASSIFICATION OF POLYMERS

1) classification on the basis of Source:

i) Natural polymers:

These are the polymers which are found in nature in plants and animals.

egs Starch - polymer of α-D-glucose
Cellulose polymer of β-D-glucose
proteins, nucleic acids, natural Rubber

ii) Synthetic polymers :-

These are the manmade polymers which are synthesized

egs: PE, PP, PS, PVC, etc

2) Classification on the Basis of Structure

i) Linear polymers!

Linear polymers are those in which the monomeric units are joined in the form of long straight chains.

ii) Branched chain Polymers:

These are linear in nature with some branches along the main chain. They have low melting point, density, tensile strength compared to linear polymers due to poor packing of polymer chains in presence of branches. egs LDPE, glycogen, amylopectin.

iii) Three-dimensional network polymers:

These polymers contains monomer molecules connected to each other by only covalent bonds. They are giant molecules in which the movement of individual monomeric units is prevented by strong cross-links. Due to the presence of strong cross-links, they are hard, rigid, brittle and do not melt but burn on strong heating.
egs Bakelite, urea-formaldehyde.

3. Classification on the basis of their Method of Synthesis:

1) ADDITION POLYMERS:

Addition polymers are obtained by addition polymerization, which involves the repeated addition of monomers to give long chains

Their empirical formula is same as that of their monomers. eg PE, PP, PS, PVC.

ii) CONDENSATION POLYMERS:

Condensation polymers are obtained by a series of condensation reaction involving two monomers with the elimination of small molecules like H_2O, HCl, NH_3 etc.
eg Nylon-6, bakelite, Polyester.

4. Classification On the basis of Growth Polymer Chain:

i) Step Growth Polymers:

These polymers are formed by addition of monomeric units to the growing chain which carries a reactive intermediate.

egs PE, PP, PS, PVC etc.

Mechanism:

$$(RCOO)_2 \xrightarrow{\Delta} 2RCOO \longrightarrow 2R^{\cdot} + 2CO_2$$

peroxide (initiator) free radical.

$$R^{\cdot} + CH_2=CH_2 \longrightarrow R-CH_2-\dot{C}H_2 \xrightarrow{CH_2 \pm \dot{C}H_2}$$

$$CH_2^{\cdot} \pm {}^{\cdot}CH_2$$

$$R-CH_2-CH_2-CH_2-\dot{C}H_2 \longrightarrow -(CH_2-CH_2)_n- + R^{\cdot}$$

chain growth polymer.

ii) **Step - Growth Polymers** are also formed thro a series of independent reactions involving bond formation between two different monomers with loss of small molecules like H_2O, HCl, NH_3.

Mechanism:

$$A-X + B-Y \longrightarrow A-B + XY$$

Monomers dimer.

$$A-B + A-B \longrightarrow A-B-A-B \quad \text{or } (A-B)_2$$

tetramer.

$$(A-B)_4 \xrightarrow{\text{Polymerization}} (A-B)_n$$

5) Classification Based on Molecular forces:

Based on the intermolecular forces, the polymers are classified into 4 categories:

i) Thermoplastic Polymers:

These polymers are linear long chain polymers which get softened on heating and hardened on cooling reversibly. Their hardness is a temporary property which changes with rise or fall in temperature. Thus, they can be processed and moulded again.

eg PE, PP, PVC, PS, nylons, Teflon etc.

ii) Thermosetting Polymers (or) Thermosets:

These are the polymers which get hardened on heating and once they have solidified, they cannot be softened. Thus, a thermosetting polymer once moulded cannot be reprocessed

eqs: polyester, bakelite, urea formaldehyde resins.

iii) Elastomers:

These are rubber like elastic polymers, which can be streched to atleast thrice its length but returns to its original shape and dimensions as soon as the stress is released.

iv) Fibres:

These are the polymers whose chains are held by strong intermolecular forces like H-bonding. They are crystalline in nature and of high tensile strength.

eqs: nylon, polyester etc.

TYPES OF POLYMERISATION:

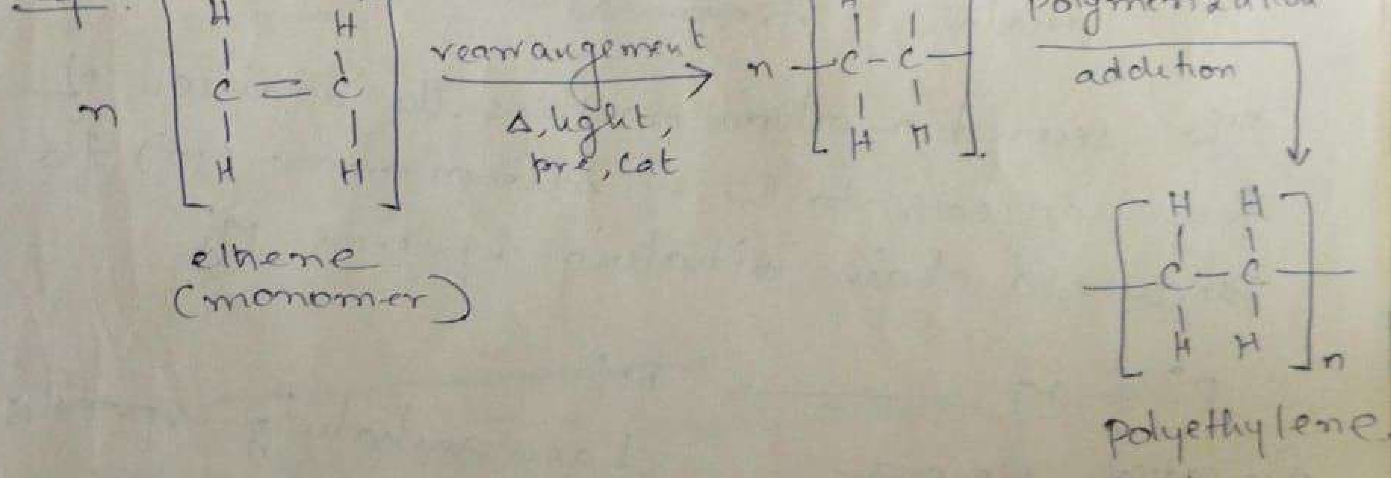
1. ADDITION (or) CHAIN POLYMERISATION:

Polymerization reaction involves the

combination of two or more small molecules to form single large molecule called Polymer.

Addition polymerization involves the addition of monomeric units to form a product of exact multiple of original monomeric molecule. This can be brought about by heat, light, pressure, catalyst.

eg.



Polymerization of ethylene & its substituted compound, $CH_2 = CHX$ can be carried out by using 3 mechanisms.

1. Free Radical Polymerization
2. Cataionic Mechanism of Polymerization
3. Anionic Mechanism of Polymerization

1. Free Radical Polymerization:

This polymerization involves 3 Steps

1) Initiation Step 2) Propagation Step 3) Termination Step

i) Initiation Step:

Initiation step involves two reactions:
The first reaction is the production of free radicals, by homolytic dissociation of an initiator or Catalyst to yield a pair of radicals $R^{\cdot}$

$$\underset{\text{initiator}}{I} \longrightarrow \underset{\text{free radicals}}{2R^{\cdot}}$$

The second reaction involves the addition of free radicals to the first monomer (M) to produce a chain initiating species M_i

$$\underset{\text{free radical}}{R^{\circ}} + \underset{\text{Monomer}}{M} \longrightarrow \underset{\text{chain initiating species}}{M_i^{\cdot}}$$

$$R^{\circ} + \dot{C}H_2 = \dot{C}HY \longrightarrow R-CH_2-\dot{C}HY$$

initiator radical or primary radical.

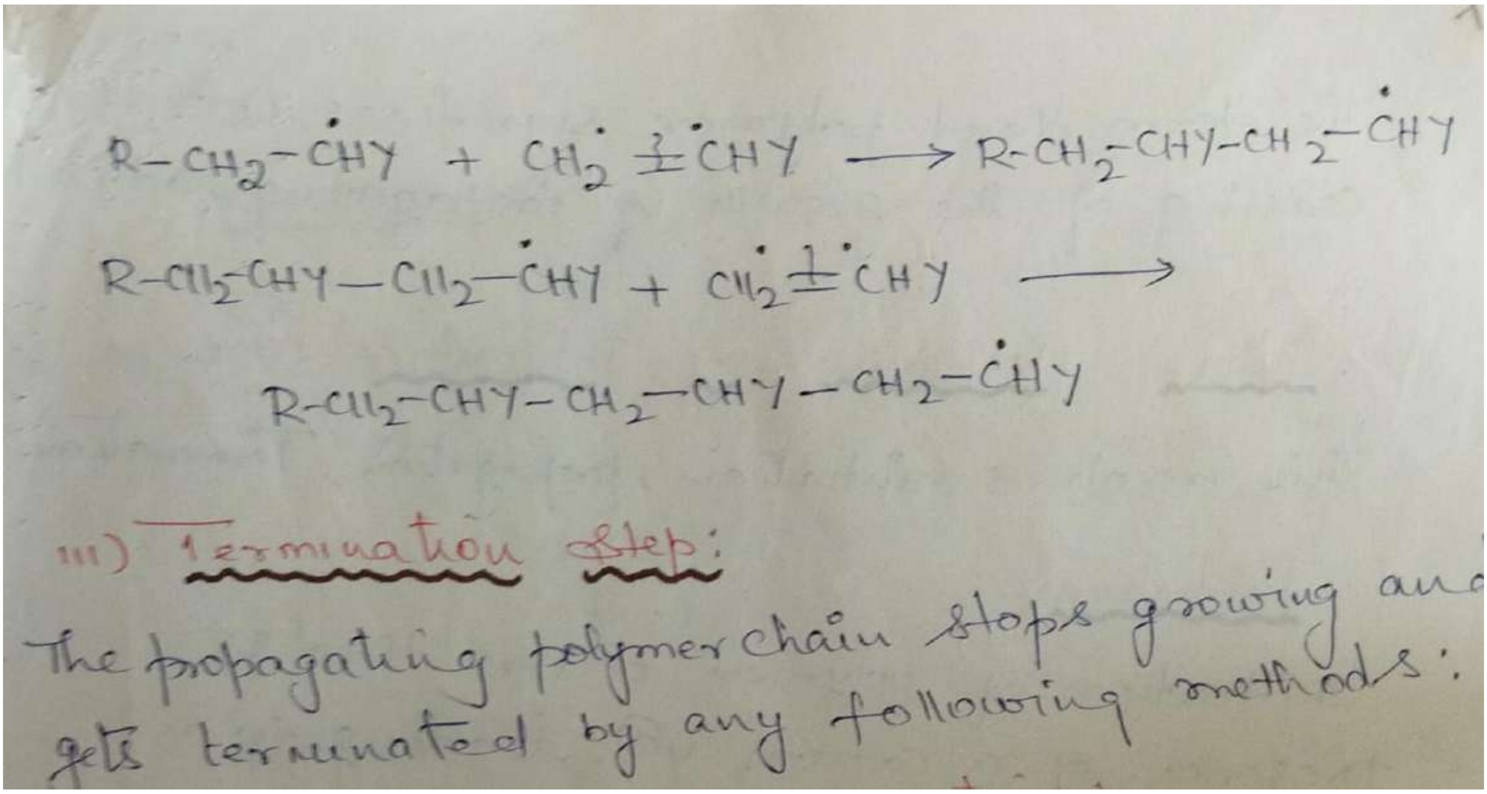
chain initiating species.

ii) Propagation Step:

Propagation step involves the propagation of chain initiating species by addition of large no. of monomers. Thus.

$M_1^{\circ} + M \rightarrow M_2^{\cdot}$ $M_2^{\cdot} + M \rightarrow M_3^{\cdot}$ & so on.

$$M_n^{\cdot} + M \longrightarrow M^{\circ}_{n+1}$$



$$R-CH_2-\dot{C}HY + \dot{C}H_2 \overset{\uparrow}{=} \dot{C}HY \longrightarrow R-CH_2-CHY-CH_2-\dot{C}HY$$

$$R-CH_2-CHY-CH_2-\dot{C}HY + \dot{C}H_2 \overset{\uparrow}{=} \dot{C}HY \longrightarrow$$

$$R-CH_2-CHY-CH_2-CHY-CH_2-\dot{C}HY$$

iii) **Termination Step:**

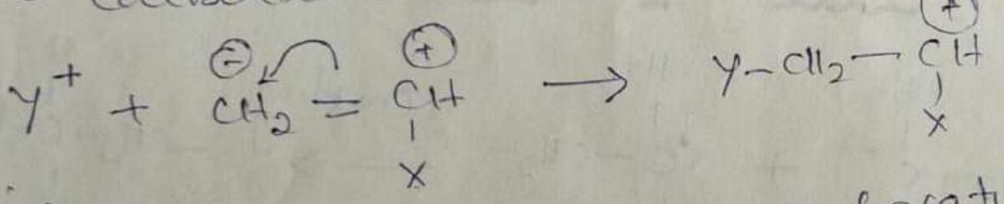
The propagating polymer chain stops growing an
gets terminated by any following methods:

2) Cationic Mechanism of Polymerization:

This involves intiation, propagation, Termination

i) Initiation:

Initiation of polymer occurs thro the presence of a cation $Y^{\oplus}$ leading to a new carbocation.

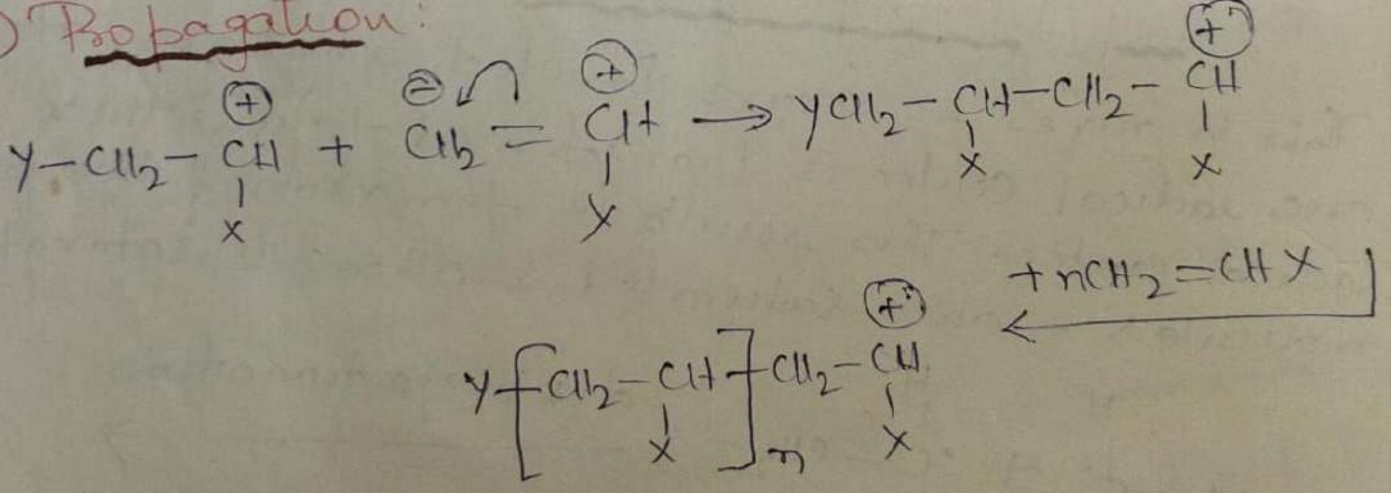


$$\underset{\text{Cation (acid)}}{Y^{+}} + \overset{\ominus}{C}H_2 = \underset{\substack{| \\ X}}{\overset{\oplus}{C}H} \longrightarrow \underset{\text{Carbocation}}{Y-CH_2-\underset{\substack{| \\ X}}{\overset{\oplus}{C}H}}$$

Cation
(acid)

Carbocation

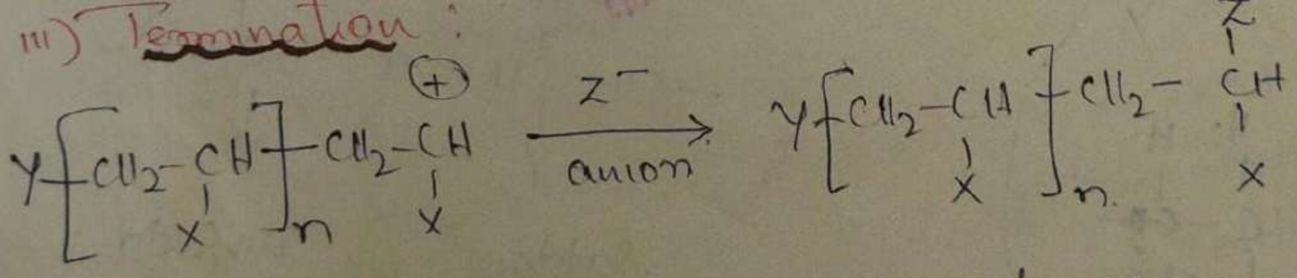
ii) Propagation:



$$Y-CH_2-\underset{\substack{| \\ X}}{\overset{\oplus}{C}H} + \overset{\ominus}{C}H_2 = \underset{\substack{| \\ X}}{\overset{\oplus}{C}H} \longrightarrow YCH_2-\underset{\substack{| \\ X}}{CH}-CH_2-\underset{\substack{| \\ X}}{\overset{\oplus}{C}H}$$

$$\xrightarrow{+\,nCH_2=CHX} Y\left[CH_2-\underset{\substack{| \\ X}}{CH}\right]_n CH_2-\underset{\substack{| \\ X}}{\overset{\oplus}{C}H}$$

iii) Termination:

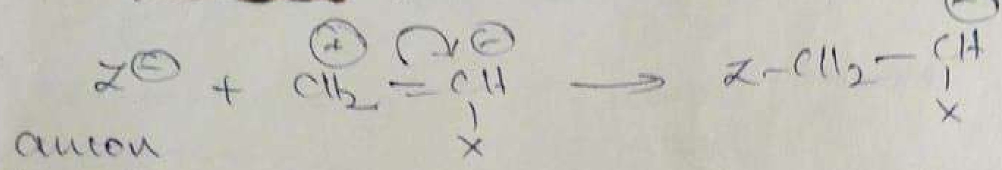


$$Y\left[CH_2-\underset{\substack{| \\ X}}{CH}\right]_n CH_2-\underset{\substack{| \\ X}}{\overset{\oplus}{C}H} \xrightarrow[\text{anion}]{Z^{-}} Y\left[CH_2-\underset{\substack{| \\ X}}{CH}\right]_n CH_2-\underset{\substack{| \\ X}}{\overset{\substack{Z \\ |}}{C}H}$$

polymer.

3) Anionic Mechanism of Polymerization :

i) Initiation :

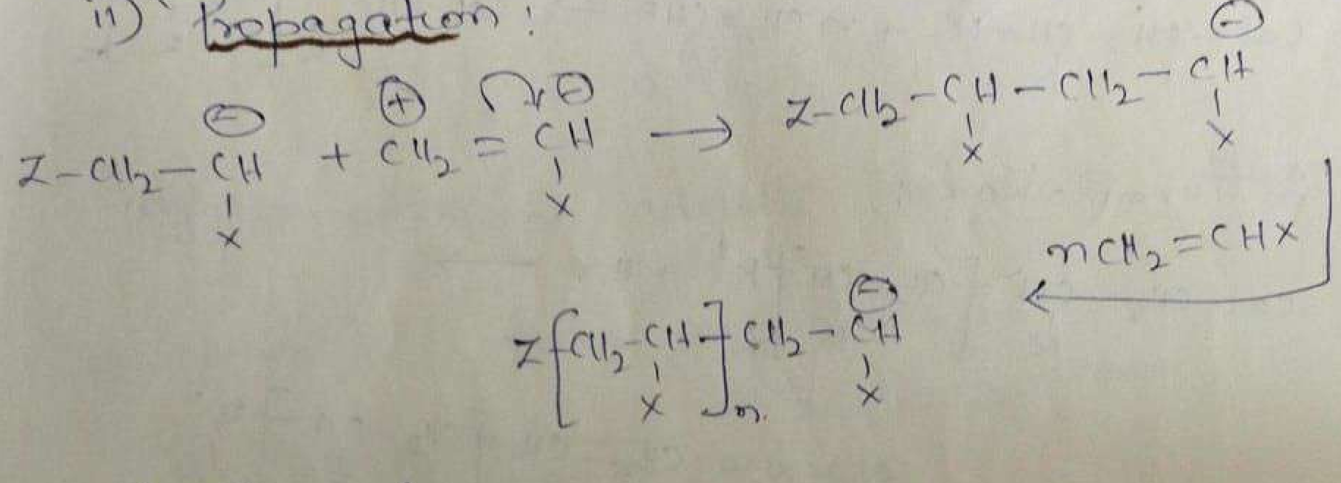


$$\underset{\text{anion (base)}}{Z^{\ominus}} + \overset{\oplus}{C}H_2 = \underset{X}{\overset{\ominus}{C}H} \longrightarrow Z-CH_2-\underset{X}{\overset{\ominus}{C}H}$$

anion
(base)

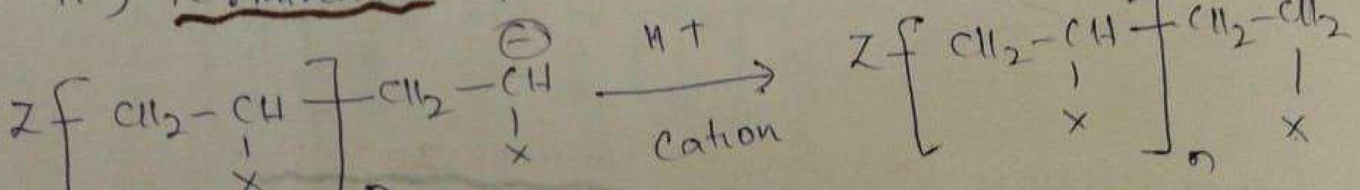
Carbanion

ii) Propagation :



$$Z-CH_2-\underset{X}{\overset{\ominus}{C}H} + \overset{\oplus}{C}H_2 = \underset{X}{\overset{\ominus}{C}H} \longrightarrow Z-CH_2-\underset{X}{CH}-CH_2-\underset{X}{\overset{\ominus}{C}H} \xrightarrow{nCH_2=CHX} Z\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{\overset{\ominus}{C}H}$$

iii) Termination :



$$Z\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{\overset{\ominus}{C}H} \xrightarrow[\text{cation}]{H^+} Z\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{CH_2}$$

polymer.

4) Coordination or Ziegler - Natta Polymerization

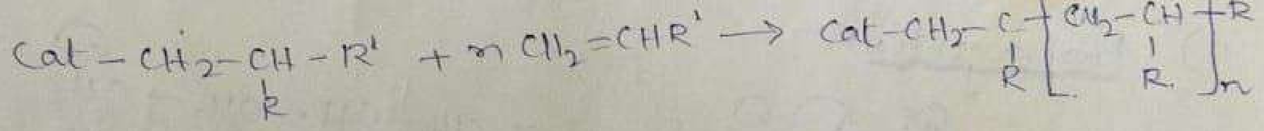
The cordination polymerization is carried out in presence of transition metal halides like $TiCl_4$ $TiCl_3$, $ZrBr_3$ with organo-metallic compounds like triethyl aluminium, trimethyl aluminium, Steriospecific polymerization can be obtained.

The Mechanism involves 3 steps as follows :

1. Initiation :

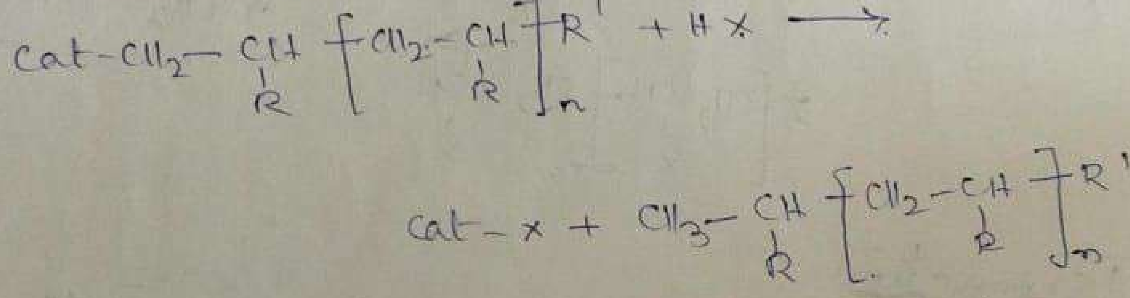
$$\underset{\text{Complex catalyst}}{Cat-R'} + \underset{\text{Monomer}}{CH_2=CHR} \longrightarrow Cat-CH_2CH(R)R'$$

2. Propagation :



$$Cat-CH_2-\underset{R}{CH}-R' + n\,CH_2=CHR' \longrightarrow Cat-CH_2-\underset{R}{C}-\left[CH_2-\underset{R}{CH}\right]_n R'$$

3. Termination ;



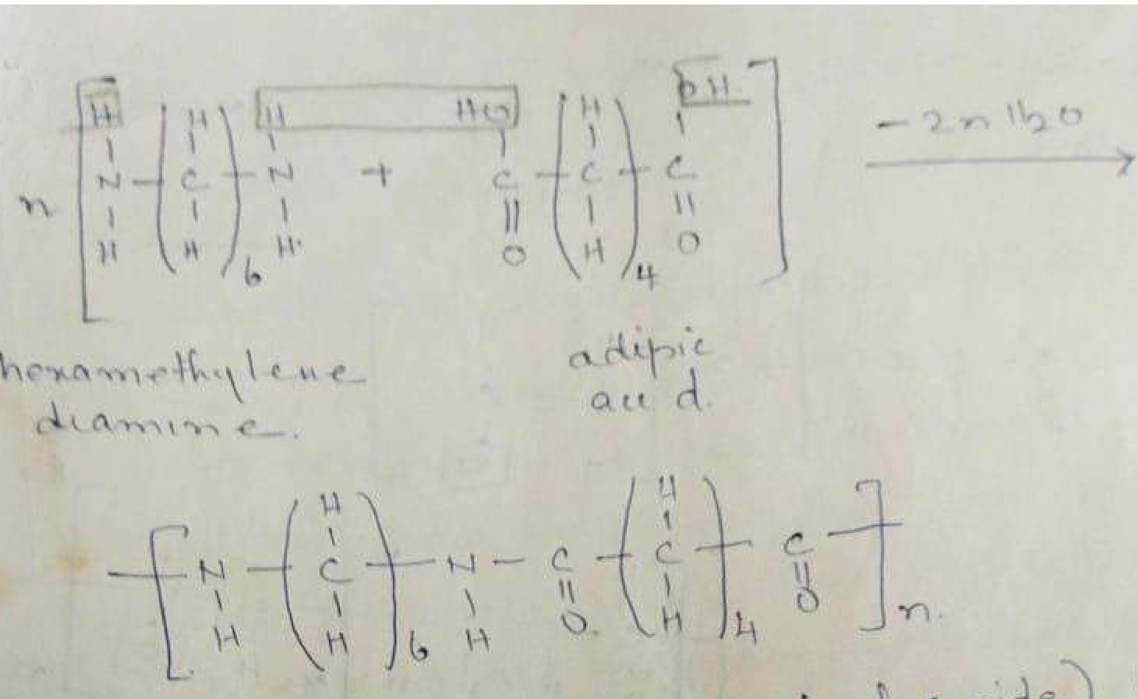
$$Cat-CH_2-\underset{R}{CH}\left[CH_2-\underset{R}{CH}\right]_n R' + HX \longrightarrow$$

$$Cat-X + CH_3-\underset{R}{CH}\left[CH_2-\underset{R}{CH}\right]_n R'$$

CONDENSATION (or) STEP-POLYMERIZATION :

This is the reaction between simple polar-group containing monomers with the formation of polymer and elimination of small molecules like water, HCl etc.

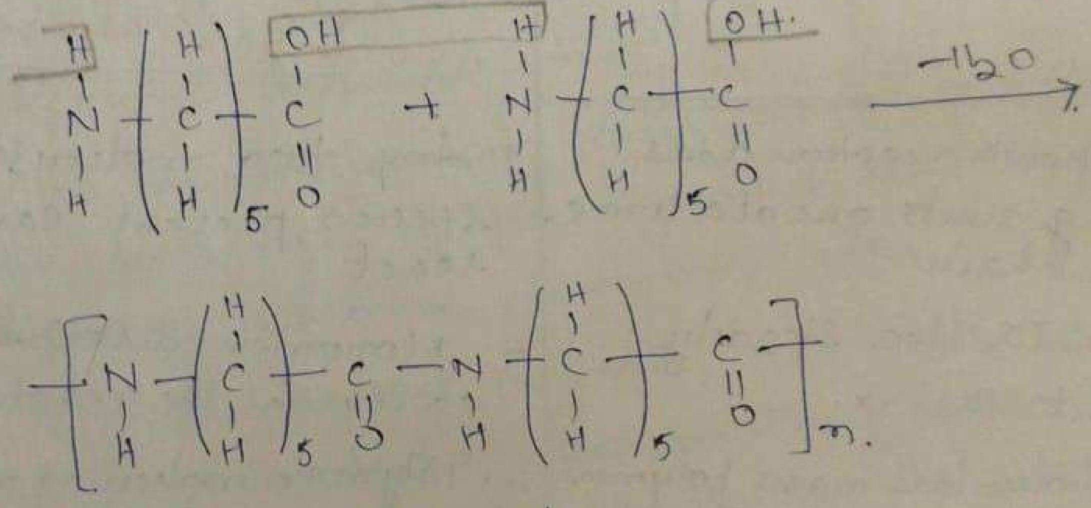
eg Nylon 6,6 is obtained by the polymerization of hexamethylene diamine and adipic acid with elimination of H_2O molecule.



$$n\left[H-NH-(CH_2)_6-NH-H + HO-\underset{O}{\overset{}{C}}-(CH_2)_4-\underset{O}{C}-OH\right] \xrightarrow{-2nH_2O} \left[-NH-(CH_2)_6-NH-\underset{O}{C}-(CH_2)_4-\underset{O}{C}-\right]_n$$

polyhexamethylene adipate (polyamide) Nylon 6:6

eg Nylon-6 from amino-Caproic acid $NH_2-(CH_2)_5-COOH$



$$H-NH-(CH_2)_5-\underset{O}{C}-OH + H-NH-(CH_2)_5-\underset{O}{C}-OH \xrightarrow{-H_2O} \left[-NH-(CH_2)_5-\underset{O}{C}-NH-(CH_2)_5-\underset{O}{C}-\right]_n$$

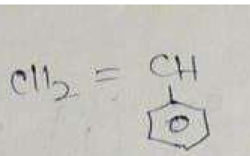
Nylon 6.

3) Co-polymerization :

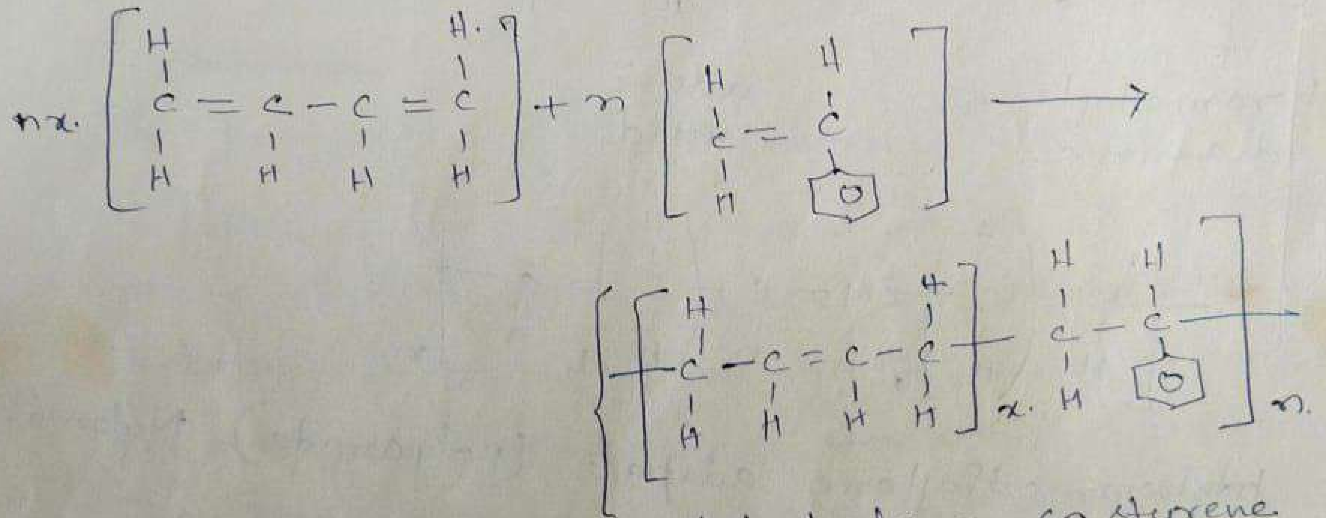
copolymerization is the joint polymerization of two or more monomer species. High molecular weight compounds obtained by copolymerization are called copolymers.

$CH_2=CH-CH=CH_2$

butadiene



Styrene



polybutadiene-co styrene
(Styrene-butadiene rubber)

Addition Polymerization	Condensation Polymerization
1. Only growth reaction adds repeating units one at a time to the chain	1. Any two molecular species present can react
2. No. of units dec steadily throout the rx.	2. Monomer disappears early in the reaction
3. High molecular mass polymer is formed at once	3. Polymer molecular mass or DP rises steadily
4. Longer rx times have a little effect on molecular - wt but gives higher yields	4. To obtain high molecular wt, longer rx time is essential.
5. The rx mixture contains only monomers, high polymers & about [illegible]	5. All types of molecular species are present at any stage.

PLASTICS:

Plastics are the organic materials of high mol.wt which can be moulded into any desired form, when subjected to heat & pressure in presence of a catalyst. Resin form the major part of the plastics which acts as binding material that undergoes polymerization during the preparation.

Importance of plastics:

1. Light in weight and good thermal & electrical insulator. They are highly resistant to corrosion
2. Plastic adhesives produce a very thin film which are quite strong & durable
3. They have low fabrication cost, easy moulding and good decorative surface effect. They are chemically inert to action of light, oils and acids.
4. They are highly transparent, translucent and can be ground and used as optical lenses. They have low maintenance cost, good shock absorption capacity, good strength, toughness and has high resistance to abrasion.

USES OF PLASTICS:

1. For making electrical goods and in furniture
2. For making handles for tools & covers of machines and in making paints, floor and wall linings, table-tops, wind screens,
3. Electrical appliances such as plugs. switches, holders, radio, T.V cabinets.
4. For heat & sound insulation in cold storage, refrigeration, air conditioning buildings, theaters. auditoriums etc.
5. For making hoses, H_2O tubes, electrical cables, floor tiles, pulleys, telephone parts, packing bags seat covers, boxes to hold the storage batteries of automobiles, safety glass, tank linings etc.
6. For preparing decorative laminates, films for H_2O-proofing, damp proofing, household articles like combs, toys, trays, toilet goods, lenses, films, tooth brush bristles, syringes etc.
7. For making synthetic fibres like terylene, nylon, and adhesives and water softening agents.

TYPES OF PLASTICS:

Plastics are classified into Two basic types

1. Thermo Plastic Resins
2. Thermo Setting Resins

THERMOPLASTIC RESINS

Thermoplastics get soften or melted when heated and hard on cooling. On reheating, they again soften and can be moulded into any desired shape. A Resin is a pure polymer and a plastic is a compounded resin Thus these plastics are repeatedly heated and cooled without decomposing, to get back same chemical properties with change in physical property. These are linear polymers with low molecular weight than thermosetting polymers. Thermoplastics have weak intermolecular forces & thus swell or dissolve in suitable solvents.

Based on the raw materials used, the thermoplastics may be sub-divided into:

1) Cellulose Resins
2) Non-Cellulose Resins

THERMO SETTING RESINS:

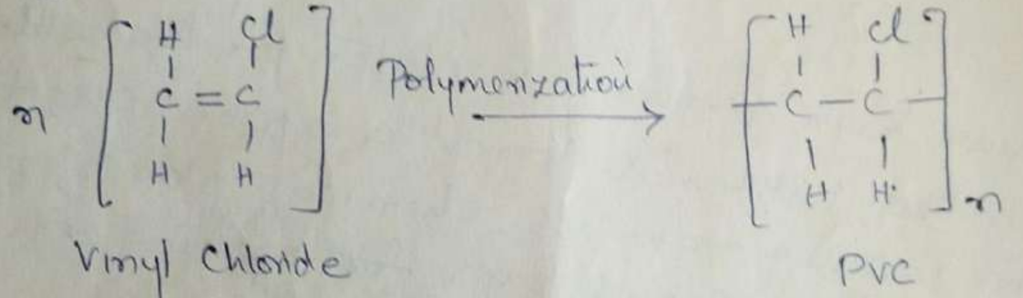
These are the polymers which get hardened on moulding and once solidified, they cant be softened ∴ they are permanent setting polymers.

Thermoplastic vs Thermosetting Polymers:

THERMOPLASTICS	THERMOSETTING -
1. They soften on heating	1. They dont soften on heating but they burn
2. They consist of long-chain linear macromolecules	2. They have 3-D structures joined by Covalent bonds
3. They are formed by addition polyzn.	3. They are formed by condensation polyzn.
4. By reheating, they can be softened, reshaped & thus reused.	4. They retain their shape & structure even on heating. ∴ they cant be reshaped & reused.
5. They are soft, weak & less brittle	5. They are hard, strong & more brittle
6. These can be reclaimed from waste	6. These cannot be reclaimed.
7. They are soluble in organic solvents	7. Due to strong bonds & cross linking, they are insoluble in all organic solvents.

4. Polyvinyl chloride PVC :

PVC is obtained by heating a water emulsion of vinyl chloride in presence of benzylperoxide or H_2O_2.



$$n\begin{bmatrix} H & & Cl \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{bmatrix} \xrightarrow{\text{Polymerization}} \left[\begin{array}{ccccc} & H & & Cl & \\ & | & & | & \\ - & C & - & C & - \\ & | & & | & \\ & H & & H & \end{array}\right]_n$$

Properties :

PVC is colourless, odourless, non inflammable and chemically inert powder, resistant to light, inorganic acids and alkalis. Pure resin posses high softening point and greater stiffness compared to PE but is brittle.

Uses :

1) Rigid PVC or unplasticized PVC have good chemical resistance & high rigidity and is brittle. It is used for making sheets used for tank linings, light fittings, safety helmets, refrigerator components, tyres, cycle mudguards.

Uses

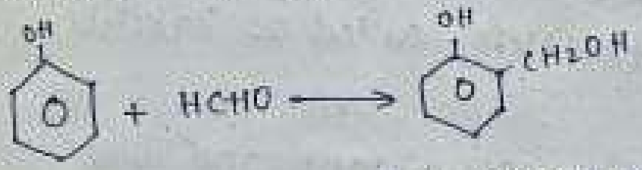
2) Plasticized PVC is used for continuous sheets, packing raincoats, table cloths, curtains electrical insulation like electric cables, injection moulding of articles like toys, tool-handles, radio-components, plastic coated cloth, chemical containers, conveyor belts etc.

- Thermosetting plastics:

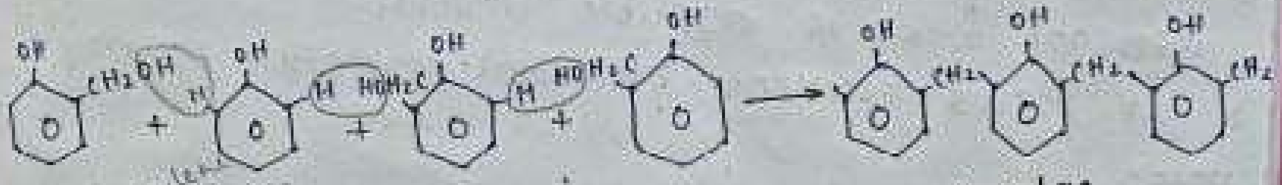
These are the plastics which do not become soft on heating but they get burnt. They posses High tensile strength, stiffness, Hardness, and They are very tough and Brittle.

*** Ex: Bakelite - phenolic Resins (or) phenol- formaldehyde resins (or) phenoplasts.

Monomer: phenol and formaldehyde

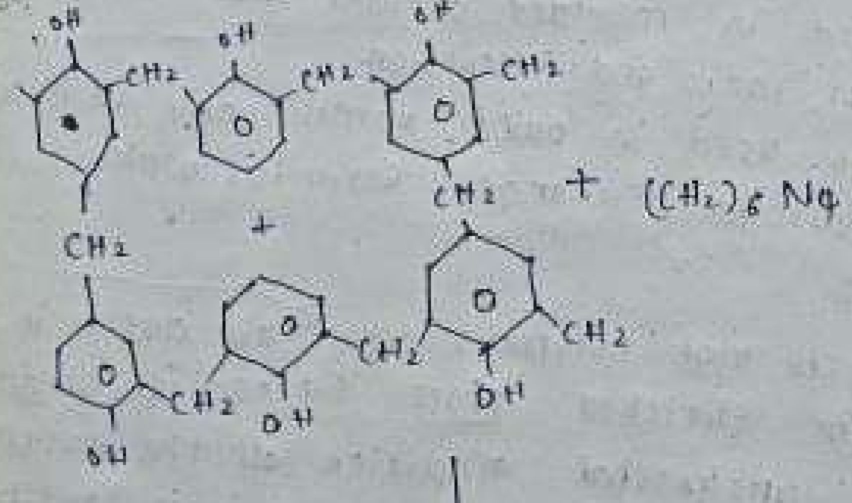


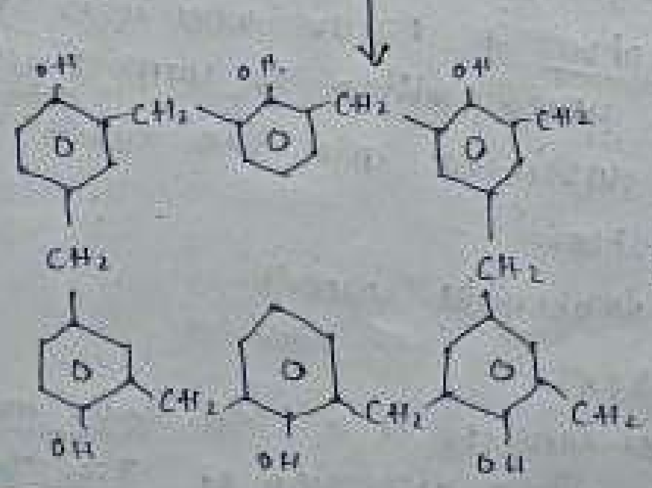
o- hydroxy methyl phenol



Novalac

hexamethylene tetramine $(CH_2)_6 N_4$





Bakelite.

Rachana Ga

20/03/24

Bakelite is a phenol formaldehyde Resin which is
synthesised by phenol and formal dehyde in presence
of an acid catalyst it produces o-hydroxy methyl
phenol which undergoes further polymerisation to
form soluble Novalac structure.
The Novalac is Moulded in presence of Hexamethylene
tetramine $(CH_2)_6 N_4$ where it give raise to insoluble
cross linked complex structure called as Bakelite

Properties:
1. It is very hard rigid scratch resistant and water
resistant which is insoluble in acids.
2. It posses Excellent Electrical insulating property.

Uses:
1. It is used in Making insulating parts like switches,
electrical plugs, switch boards and heater handles.
2. It is used in moulded articles like telephone parts
cabinets for radio and Television.
It is also used in paint varnish and it is also
used as Hydrogen Exchanger Resin for water softening.

2) Synthetic fibres :

Synthetic fibres can be produced and are Cheaper than natural fibers.
eg PVC, nylons, polyesters, PE, etc.

Reinforced Plastics :

In general, pure polymers are soft & compounded polymers with plasticizers are hard, elastic & largely used. The combination of plastic with solid fillers give hard plastic with good mechanical strength known as reinforced plastic. The fibre polymer with fillers gives hardness without loosing plasticity are known as fibre reinforced plastic FRP. The various fillers used for FRP are: Carborundum, mica, quartz, asbestos, wood floor, sawdust paper pulp, cotton fibres, china clay, metal oxides. Both thermoplastic & thermosetting plastics are used for FRP eg PE, PP, Nylon6, polyester, PS etc

A variety of FRP with solid fillers impart a specific property like :

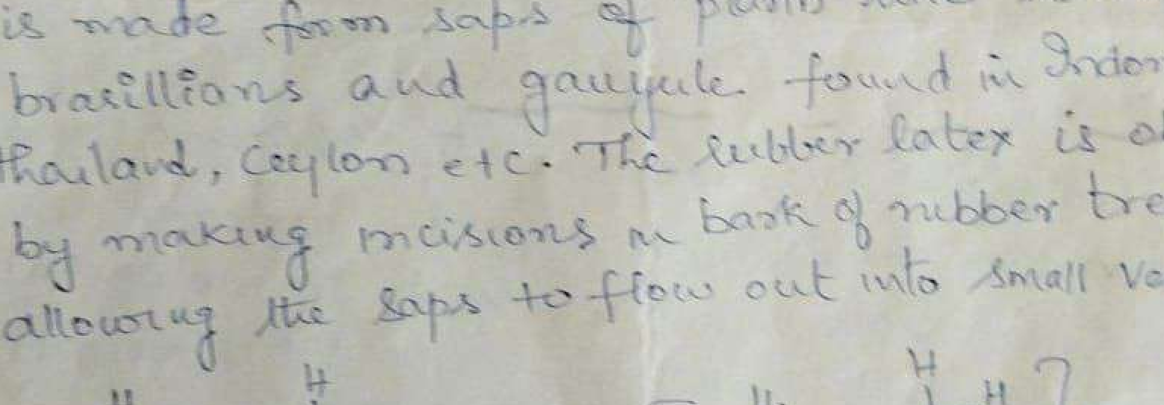
1) Addition of carbon black to natural rubber which increase tensile strength of rubber & used in tyres.

2) Addition of china clay improves insulation property of polymers like PVC, Teflon.

Rubbers - Elastomers:

Rubbers are high polymers which have elastic properties which can be streched 3 times of its original length. In unstressed condition, an elastomer molecule is not straight chain but in form of a coil existing in amorphous state. In streched condition, the molecules align causing cystalization & stiffening of molecule due to increased attractive forces.

Natural rubber consists of basic material latex which is a dispersion of isoprene. These isoprene molecules polymerize to form long coiled chains of cis-polyisoprene. In general, natural rubber is made from saps of plants like havea brasillions and gauyule found in Indonesia, thailand, Ceylon etc. The rubber latex is obtained by making incisions in bark of rubber trees & allowing the saps to flow out into small vessels.

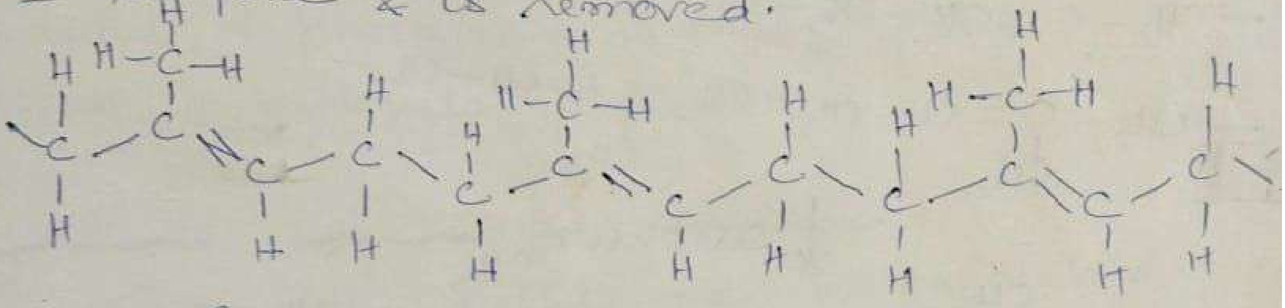


isoprene   cis polyisoprene.

Gutta percha is obtained from the mature leaves of dichopsis gutta and palagum gutta trees, grown in Malaya, Sumatra. Gutta Percha may

LCD drawbacks — ① problems with viewing angle
② Contrast ratio
③ response time.

~~be~~ recovered by solvent extraction, when insoluble resins and gums are separated. The mature leaves can also be ground carefully and treated with H_2O at 70°C for 30 mts & then poured into cold H_2O when gutta percha floats on H_2O surface & is removed.



Structure of Gutta Percha.

Properties:

Gutta Percha is horny & tough but it softens & it is soluble in aliphatic hydrocarbons but insoluble in aromatic and chlorinated hydrocarbons.

uses It is used in manufacture of golf ball covers, submarine cables, adhesives etc.

VULCANIZATION OF RUBBER:

This was discovered by Charles Goodyear in 1839. To improve the properties of rubber, it is compounded with some chemical like S, H_2S, benzoyl chloride etc. This process consists in heating raw rubber with sulphur to 100–140°C. The added sulphur combines chemically at double bonds of different rubber springs. vulcanization serves to stiffen the material

3. It is non-resistant to non polar solvent and is attacked by oxidising agent.

4. It perishes due to oxidation in air and swells in organic solvents.

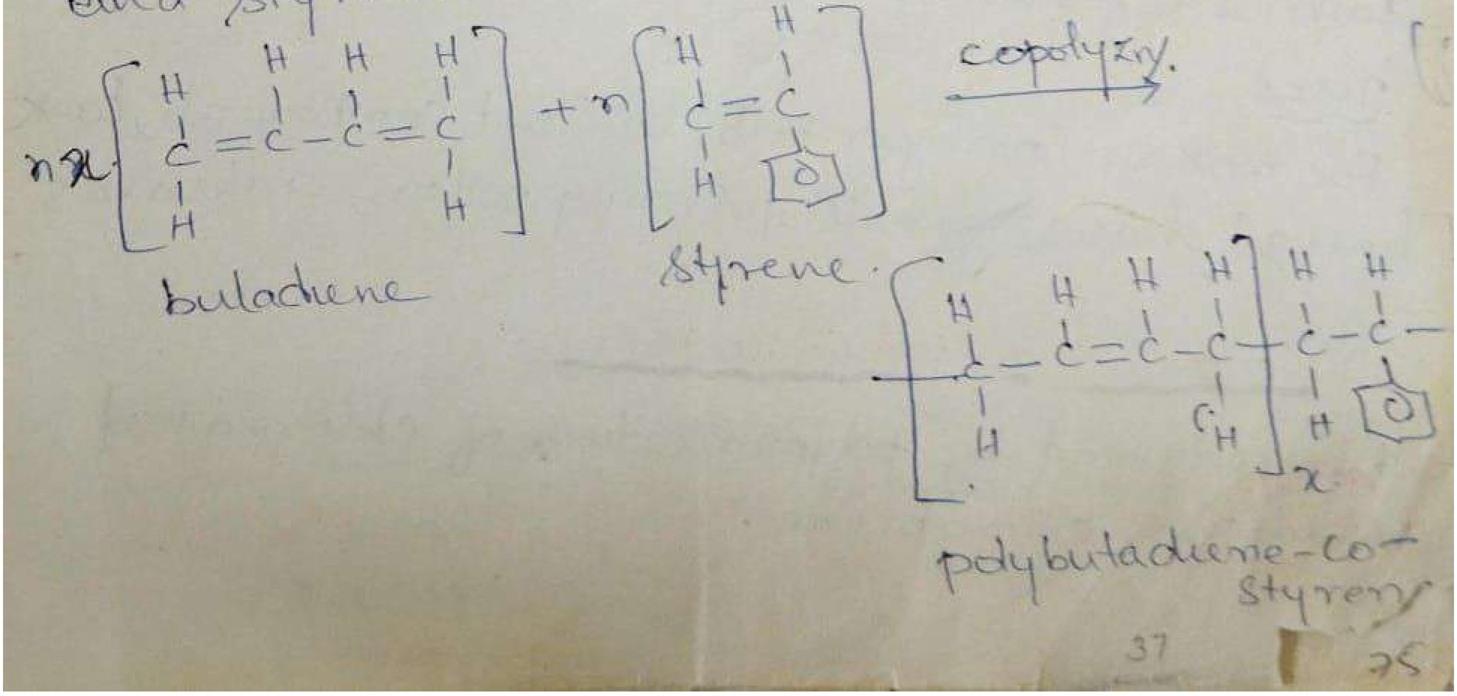
5. When streched to a great extent, it suffer permanent deformation due to sliding or slippage of molecular chains.

Synthetic Rubbers or elastomers :

These are vulcanisable man-made rubber like polymer which can be streched twice its length but returns to original shape and dimensions as soon as the stress is realeased. It is also called as misnomer as it is not chemically identical with natural rubber. Thus it is called as artificial rubber.

1. Styrene rubber - Buna-S :

This is produced by copolymerization of butadiene, and styrene.



Properties

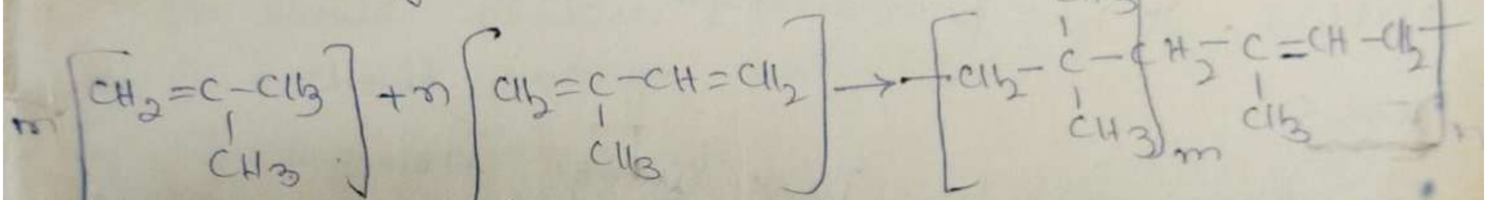
Styrene rubber posses high abrasion resistance, high load bearing capacity. It gets oxidised in air & swells in solvents.

Uses

Manufacture of motor tyres, floor tiles, shoe soles, gaskets, foot wear components, wire & cable insulation, Carpet backing, adhesives etc.

4. Butyl rubber:

It is made by copolymzn/. of isobutene & isoprene.



$$n\left[CH_2=\underset{\substack{|\\CH_3}}{C}-CH_3\right] + n\left[CH_2=\underset{\substack{|\\CH_3}}{C}-CH=CH_2\right] \longrightarrow -\left[CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}\right]_m-\left[CH_2-\underset{\substack{|\\CH_3}}{C}=CH-CH_2\right]_n-$$

isobutene

isoprene

poly isobutene-co-isoprene

butyl rubber.

Properties:

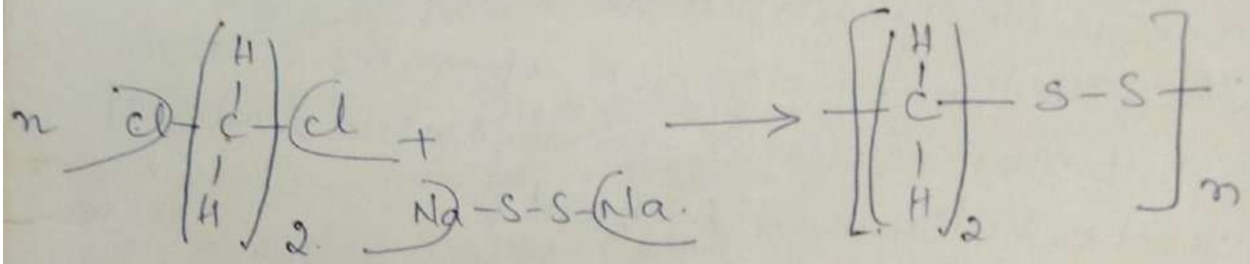
It posses low permeability to air & other gases and is resistance to heat, abrasion, chemical, polar solvents but soluble in hydrocarbon solvents like C_6H_6. It is resistant to ozone & has electrical insulating properties.

uses

For making cycle, automobiles tubes, [illegible]; hoses, Conveyor belts for food & tank linings' etc.

5) Polysulphide rubber or Thiokol :

This is obtained by reacting sodium polysulphide Na_2S_2 and ethylene dichloride.



1,2 dichloro ethylene. sodium polysulphide. thiocol or thiokol rubber.

Properties :

It has good resistance to mineral oils, fuels, solvents, oxygen, ozone and it is impermeable to gases. It cant be vulcanised & thus dont form hard rubber. It has poor strength & abrasion resistance.

uses.

For making hosepipe, tank linings etc.

Bio degradable polymers

Generally polymers are not attacked by the environmental conditions. But they undergo slow degradation by oxidation, ozone attack, sunlight but not by micro-organisms like fungi & bacteria. This property creates problem in disposing the polymer waste in the environment

The usage of biodegradable substance started from the times of Roman. They used a strong cord (wire) for sutures made out of intestine of animals (stiches) which slowly degrades as the wound heals.

Definition :- Biodegradable polymers are polymers which undergo degradation by the naturally occuring micro-organisms like algae, fungi & bacteria

Requirement of bio degradable polymers.

1. It should produce non-toxic substance
2. It should undergo controlled rate of biodegradation
3. It should be capable of maintaining good mechanical integrity until degradation.

Factors affecting degradation :-

1. Molecular wt. of polymer.
2. Amount of crystallinity of polymer.
3. Hydrophobicity of polymer.
4. The environment which surrounds the polymer

Types of biodegradable polymers :-

They are classified in to two types.

1. Natural biodegradable polymers.
2. Synthetic biodegradable polymers.

Natural Biodegradable polymers:-

These types of polymers produced in nature by all living organisms. The rate of degradation depends on the structural complexity of the polymer and the environmental condition. There is belief that anything that comes from nature goes back to nature means all natural polymers are biodegradable polymers.

The natural bio-degradable polymers are grouped in to 4 types.

1. **Poly saccharides** (carbohydrates)
   eg Starch + cellulose.
2. **Proteins** : eg. Gelatin, casein, silk, wool.
3. **Aliphatic polyesters** ; Poly hydroxy alkanoates.
4. **Others** :- lignin, shellac, natural rubber.

These polymers undergo biodegradation by enzyme - catalyzed reaction in aqueous media.

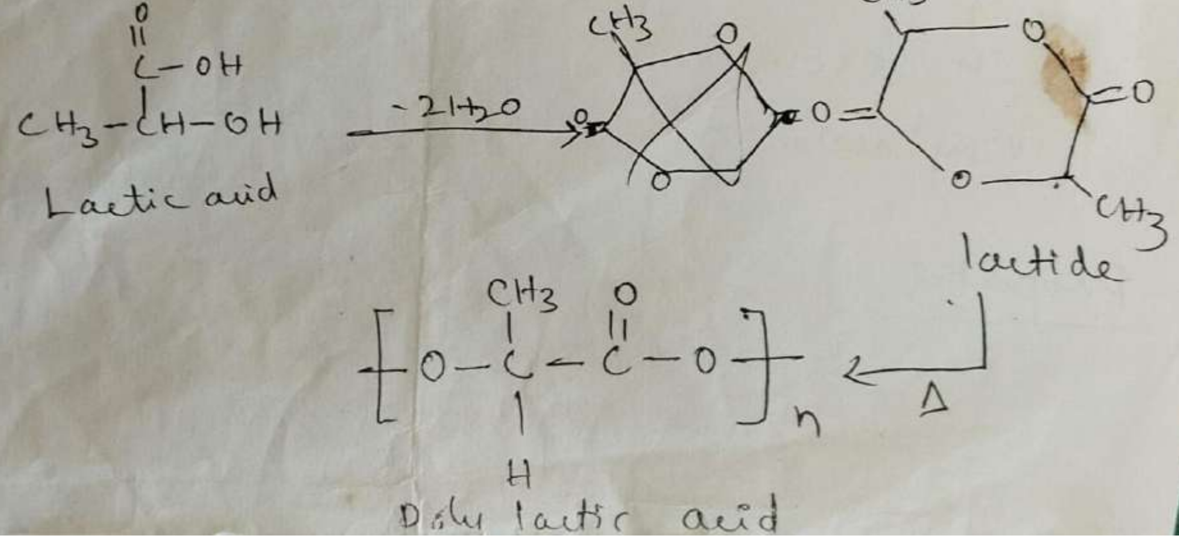
2. Synthetic biodegradable Polymers

~~These~~ ~~poly~~ Synthetic biodegradable polymers are man made biodegradable polymers.
These polymers are produced from chemical or biological sources that are biodegradable.
These polymers are also undergo biodegradation by enzyme-catalyzed reaction in aqueous media

2. Poly Lactic Acid (PLA).

Poly lactic acid is a biodegradable aliphatic thermoplastic polymer. It is derived from renewable sources such as starch, sugarcane etc

Preparation :- It is prepared by the catalytic dimerisation of lactic acid resulting in the formation of lactide monomers.



Poly lactic acid

Polymerization of lactide monomer in presence of stannous octate, to give polylactic acid.

properties :-

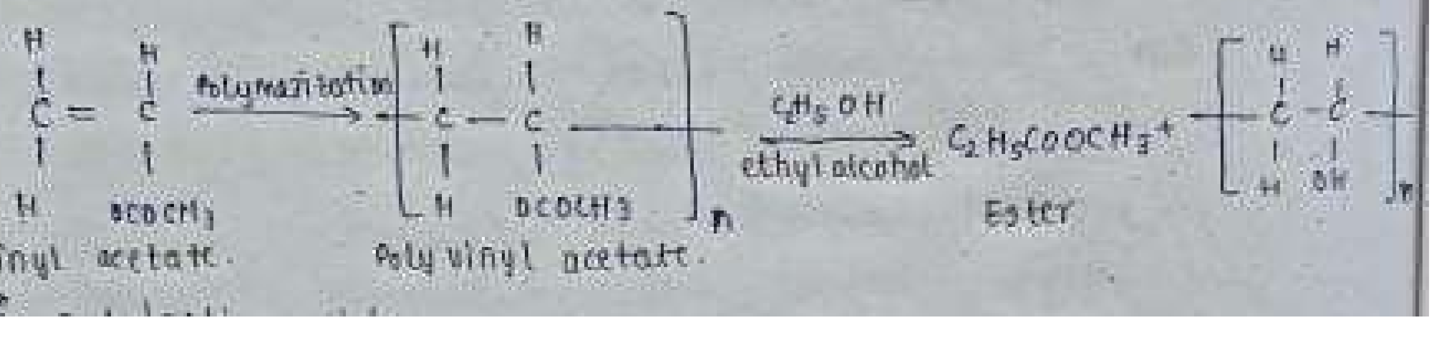
1. PLA posses good bio-compatibility, processability, high strength.
2. D-isomer of PLA is crystalline & L-isomer is amorphous
3. Bio degradation of D-isomer is slower than L-isomer.

Applications.

1. PLA is used for making medical implants like screws, pins, anchors etc.
2. It is used in a number of biomedical applications like drug delivery devices and dialysis media.
3. It is used in the preparation of bioplastics for packing food & disposable tableware
4. It is also used for making composatable packing materials, food packing etc.

1) Poly vinyl alcohol :-

PVA



$$\underset{H}{\overset{H}{C}} = \underset{OCOCH_3}{\overset{H}{C}} \xrightarrow{\text{Polymerization}} \left[-\underset{H}{\overset{H}{C}} - \underset{OCOCH_3}{\overset{H}{C}} - \right]_n \xrightarrow[\text{ethyl alcohol}]{C_2H_5OH} C_2H_5COOCH_3 + \left[-\underset{H}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - \right]_n$$

Vinyl acetate. Poly vinyl acetate. Ester

CONDUCTING POLYMERS:

Most polymers are poor conductor of electricity, because of non-availability of large no. of free electrons in the conduction process. So polymeric materials are synthesized which passes electrical conductivities are called as conducting ~~[illegible]~~ polymers. Conductivities of $1.5 \times 10^{7}\ \Omega^{-1} m^{-1}$ are present in these polymers.

Types of Conducting Polymers:

1. Intrinsically Conducting Polymer ICP or Conjugated π-electrons conducting Polymer:

These are the polymers in which the associated groups consists of delocalized electron pair or residual charge ie they have Conjugated π electrons which are responsible for electric charge. In presence of electric field, the conjugated π electrons get excited, thereby can be transported thro solid polymeric material. Overlapping of conjugated π e^- results in valence & conduction bands.

eqs polyacetylene, poly-p-phenylene, poly aniline, poly pyrrole, poly thiophene etc.

2. Doped Conducting Polymer:

These polymers are obtained by exposing a polymer to a charged transfer agent in solution In general, ICP posses low Conductance, low ionization potential & high e^- affinities, so these can be easily oxidised or reduced. Thus, the conductivity of ICP can be increased by Creating a +ve or -ve charge on the polymer by oxidation or reduction. This process is called doping.

Doping is of two types: ① P- & ② N- doping

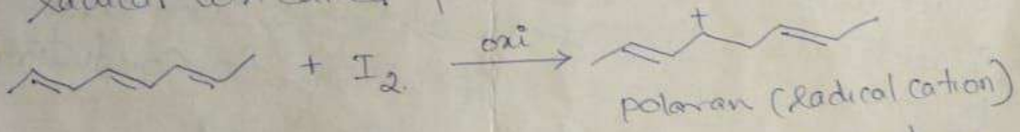
i) P- DOPING :

Creating a positive charge on polymer backbone is called p-doping. This is done by oxidation of a conducting polymer like polyacetylene with a Lewis acid or I_2 vapour. This is called oxidative doping

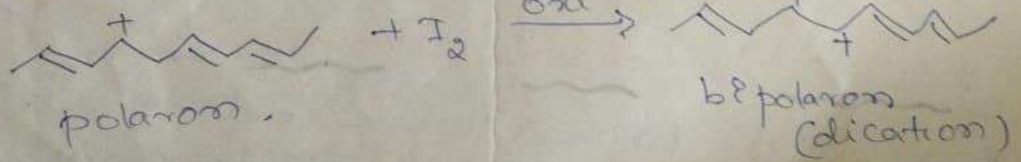
$$-\!\left[CH=CH\right]_n + 2FeCl_3 \longrightarrow \left[CH=CH\right]_n^{+} FeCl_4^{-} + FeCl_2$$

$$\left[CH=CH\right]_n + 3I_2 \longrightarrow 2\left[CH=CH\right]^{+} I_3^{-}$$

During oxidation process, the removal of π-electron from the polymer lead to delocalised radical ion called polaran



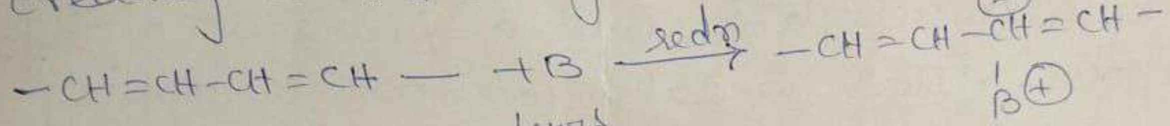
The oxidation of polaron results in 2 +ve charge carriers in each chain called bipolaron, which are mobile because of delocalisation. These delocalised charge carriers are responsible for conductance when placed in electric field.



Some of the P- dopants are I_2, Br_2, PF_6 etc.

2) N-DOPING:

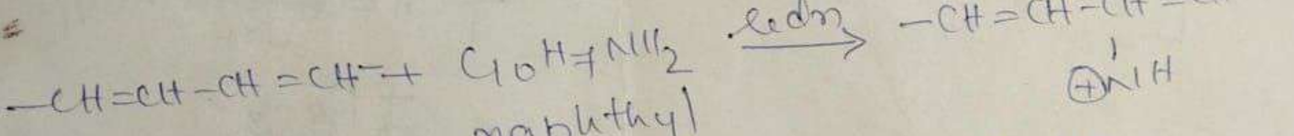
N-doping is done by exposing an ICP to a lewis base thereby reduction occurs, creating a -ve charge on the polymer.



$-CH=CH-CH=CH- + B \xrightarrow{redn} -CH=CH-\underset{B^{\oplus}}{\overset{\ominus}{C}H}=CH-$

polyacetylene

Lewis base



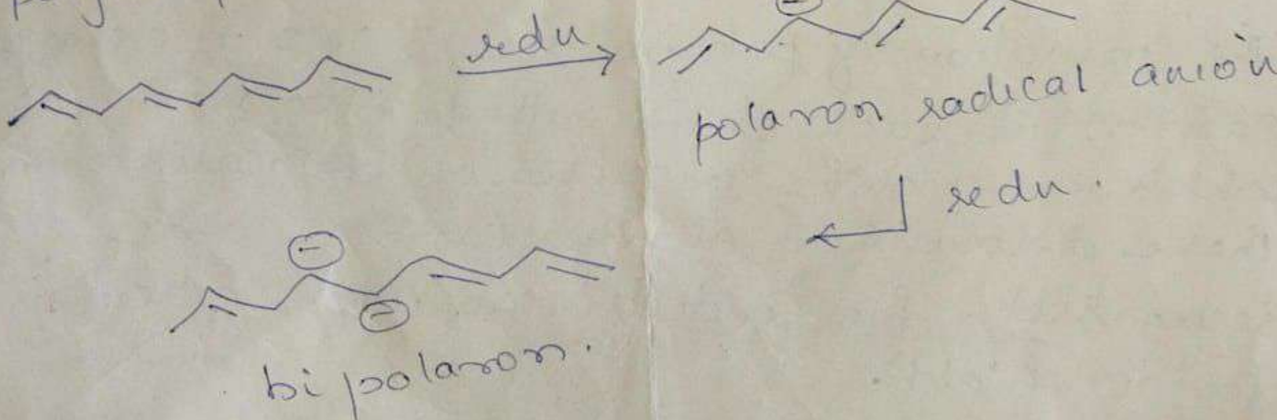
$-CH=CH-CH=CH- + C_{10}H_7NH_2 \xrightarrow{redn} -CH=CH-\underset{\oplus NH}{\overset{\ominus}{C}H}=CH- + C_{10}H_8$

naphthyl amine.

Lewis base.

naphthalene

Common N-dopants are Li, Na, Ca, $FeCl_3$ etc. Thus formation of polaron, bipolaron takes place in 2 steps, followed by recombination of radicals which yield 2 charge carriers on polyacetylene chain responsible for conduction



3. Extrinsically Conducting Polymers:

These are the polymers whose conductance is due to presence of externally added ingredients.
These are of 2-types:

i) Conductive element-filled Polymers :

These polymers are filled with conducting elements such as carbon black, metallic fibres, metal oxides etc. The polymer acts as a binder to hold the conducting elements together. These have good conductivity with light weight, durable and low cost.

ii) Blended Conducting Polymer :

These polymers are obtained by blending a conventional polymer with conducting polymer by physical or chemical change.

eg 40% polypyrrole in a conventional polymer give higher impact strength. These are used in electromagnetic shielding.

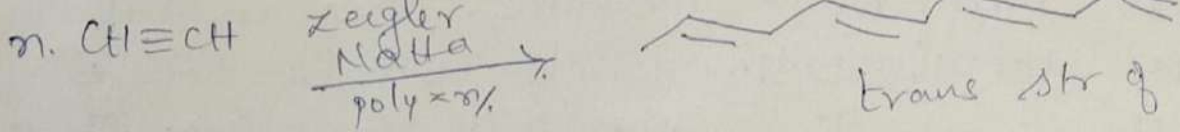
(Inorganic)

Preparation of Conductive Polymers:

1. **Polyacetylene:**

Polymerization of acetylene over Ziegler-Natta catalyst give polyacetylene in cis form.

On increasing temperature, it gives more stable trans form.



trans str of poly acetylene

Applications:

Group I 'Conductivity applications:

Electrostatic materials, antistatic clothing, conducting adhesives, electromagnetic shielding, printed circuit boards, active electronic, diodes, transistors, aircraft structures are some of the conductive applications of conducting polymers.

1) Sudden discharge of static electricity can damage micro circuits. ∴ by coating an insulating surface ~~by~~ with conducting polymer, it is possible to prevent the static circuit and thus prevent damage.

2) By placing a monomer between two joints & allowing it to polymerize, it is possible to stick them together. Thus it acts as conducting adhesive by eliminating the formation of metal oxides.

3) Normal plastic cases are transparent to electromagnetic radiations emitted by computers & cell phones which may further leads to malfunctioning of neighbouring electrical devices. Therefore conducting polymer coatings readily absorb these radiations preventing the damage.

4. Conductive polymer coating on a polymer sheet has a good adhesion. Biocompatible conducting polymers are used to transport small electrical signals through the body ie they may act as artificial nerves.