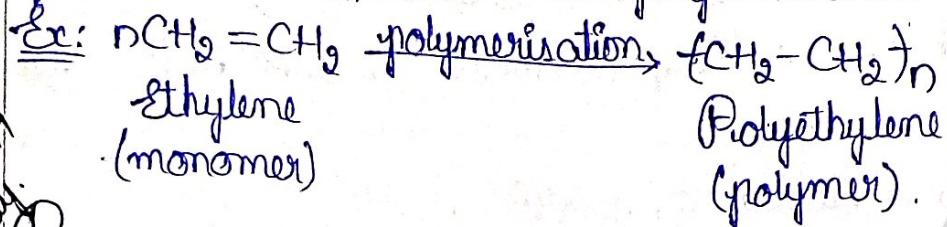


Polymer Technology

82-08-19
Thursday

Polymer: Polymer is a large molecule having high molecular weight which is formed by combination of smaller units (monomers). Process of formation of polymer from monomers, known as polymerisation.



26-08-19
Monday

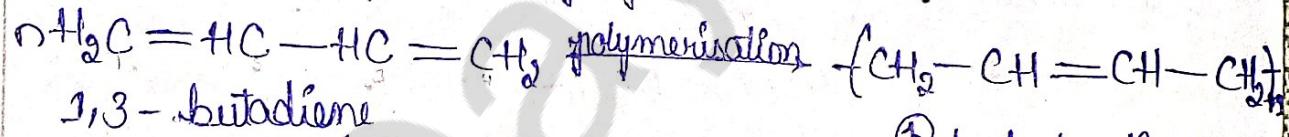
Range of polymer: 5000 - 200,000 amu

Polymer also known as "macro molecules"

Polymer is a Greek word, which contains two parts.

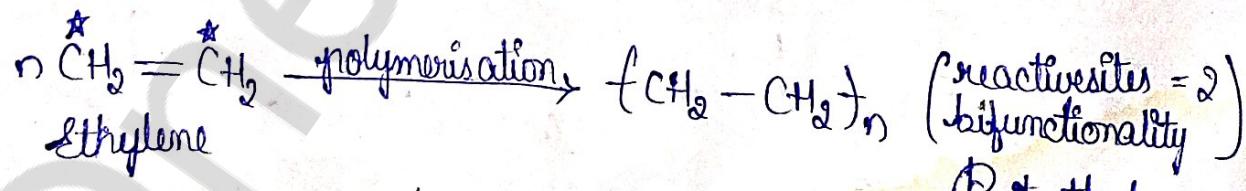
- (1) Poly = many
(2) Meru = units or parts.

Degree of polymerisation: No. of repeating monomeric units in that chain formed in a polymer is known as degree of polymerisation.

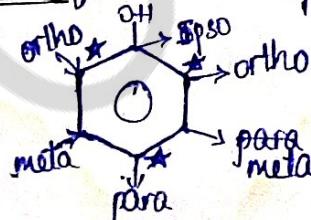


Functionality: The no. of reactive sites in a monomer, where $n=4000$; n' is degree of polymerisation.

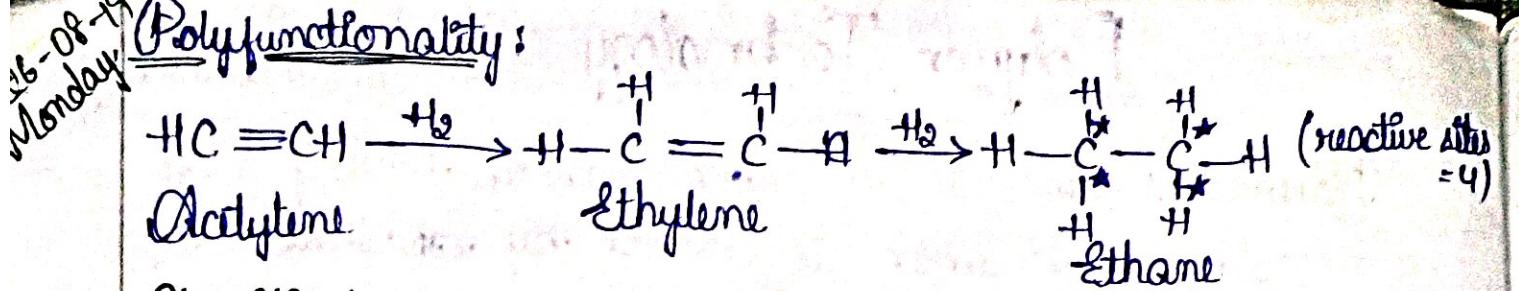
Bifunctionality:



Trifunctionality



(Phenol is ortho, meta, para - deactivating group which contains '3' reactive sites (resonance structure))



Classification of polymer:

* Classification based on occurrence:

Natural Polymer: Polymer which is isolated from nature.

Ex: Silk, Starch, cellulose, proteins...

Synthetic Polymer: Polymer which is derived from low molecular weight.

Ex: PE (poly ethylene), PVC, nylon-6,6, Teflon, Bakelite.

* Classification based on chain structure:

Linear Polymer: Monomers are linked in linear way.

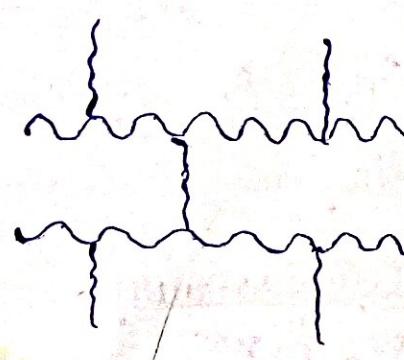
Ex: $\text{---A---A---A---A---}$ (or)

Branched Polymer: Two linear polymers are linked in branched way.

Ex: $\text{---A---A---A---A---A---}$ (or)

Cross linked Polymer: Two or more linear polymers are linked in crossed way.

Ex: $\begin{array}{c} \text{A} \\ | \\ \text{---A---A---A---A---A---} \\ | \\ \text{A} \\ | \\ \text{---A---A---A---A---A---} \end{array}$ (or)



(cross linked - many atoms, little al. bond)
(crossed branched) without & without depth.)

Classification based on monomeric unit:

(1) Homopolymer: Polymers which contains identical monomers.

Ex: Polyethylene, PVC, Teflon, Polystyrene. . . —A—A—A—A—

(2) Co-Polymer: Polymer which contains different monomers.

Ex: Nylon-6,6, Buna-N, Buna-S, Bakelite -A-A-B-B-A-

Co-polymer divided into two types:

(1) Random co-polymer: -A-A-B-A-B-A-A-

(2) Blocked co-polymer: -A-A-A-B-B-B-A-A-A-

(3) Graft co-polymer :- A - A - A - A - A - B - B

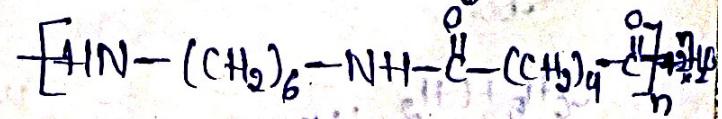
4) Alternate co-polymer: -A-B-A-B-A-B-A-B-

Classification based on synthesis

(1) Addition Polymerisation: Repeating units of monomers combined to form polymers without elimination of byproducts and monomer having double, and triple bonds.

$$\text{Ex: } n\text{CH}_2=\text{CH}_2 \xrightarrow{\text{polymerisation}} \left\{ \text{CH}_2-\text{CH}_2 \right\}_n$$

(2) Condensation Polymers: Repeating units of monomers combined to form polymers with elimination of smaller molecules like H_2O , NH_3 , $-\text{OH}\dots$ and monomer having functional groups.



Bakelite (phenol-formaldehyde resin), nylon - 6,6.

Urea formaldehyde resin.

Classification based on Intermolecular forces:

Elastomers: Polymer in which chain held together by weak or van der waal forces or weak intermolecular forces when stress is released regain its original shape.

Ex: Natural rubber, Buna-S, silicone rubber.

Fibres: Polymer in which chain held together by strong van der waal forces or strong intermolecular forces as hydrogen bond.

Ex: Nylon - 6,6, Nylon - 2,2, Nylon - 2,4...

Plastics: Intermolecular forces lie between elastomers and fibres.

Ex: PVC, Polystyrene...

Thermoplastics: Soft on heating. Hard on cooling. They can be reused.

Ex: PE, PVC, polystyrene...

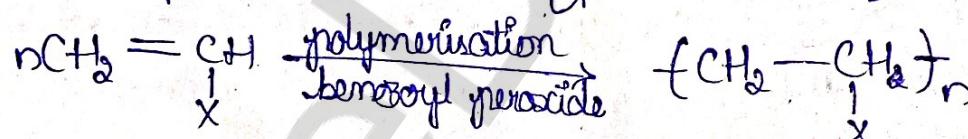
Thermosetting plastics: Insoluble or infusible product on heating. They can not be reused.

Ex: Bakelite,

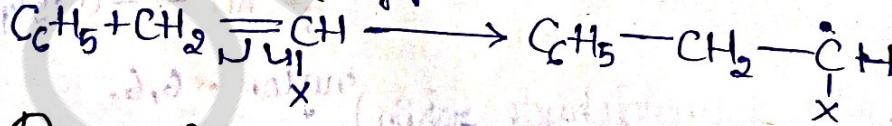
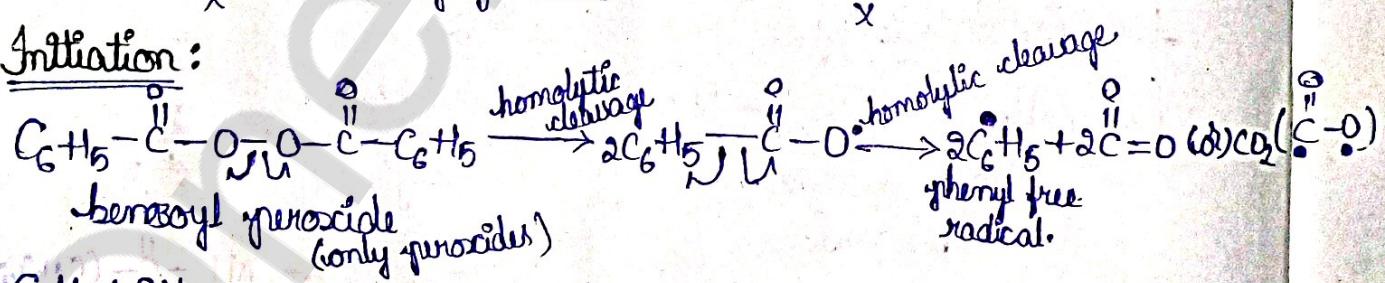
Free radical mechanism:

Homolytic cleavage: $A-B \xrightarrow{\text{sharing of bond}} A^+ + B^-$

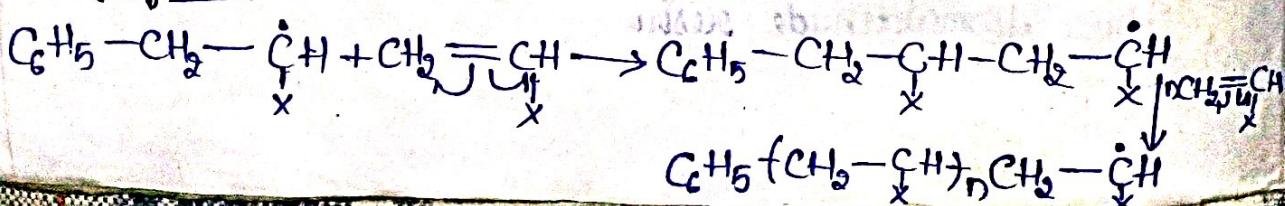
Heterolytic cleavage: $A-B \xrightarrow{\text{transfered from } A \text{ to } B} \text{cation} + \text{anion}$



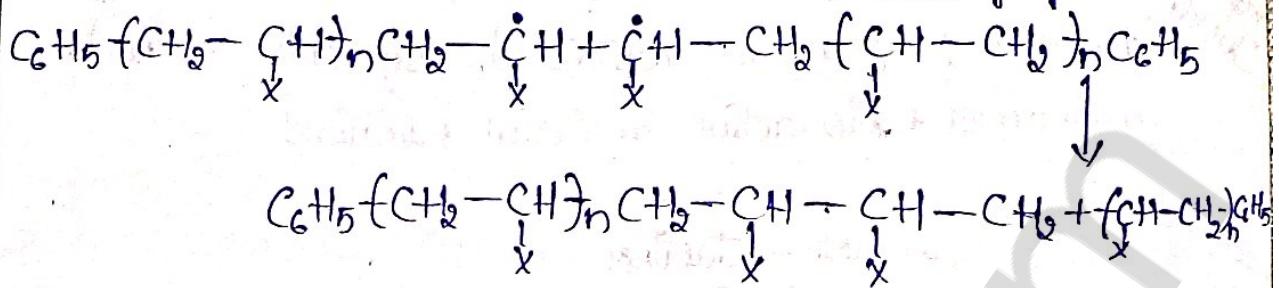
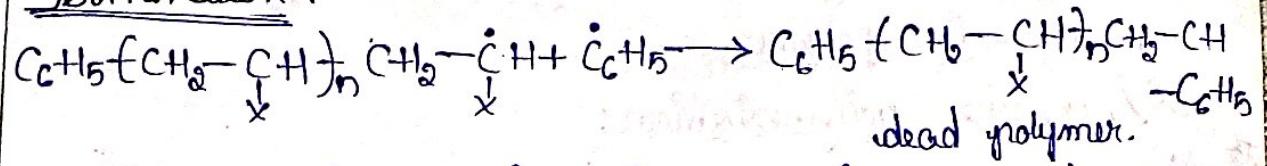
Initiation:



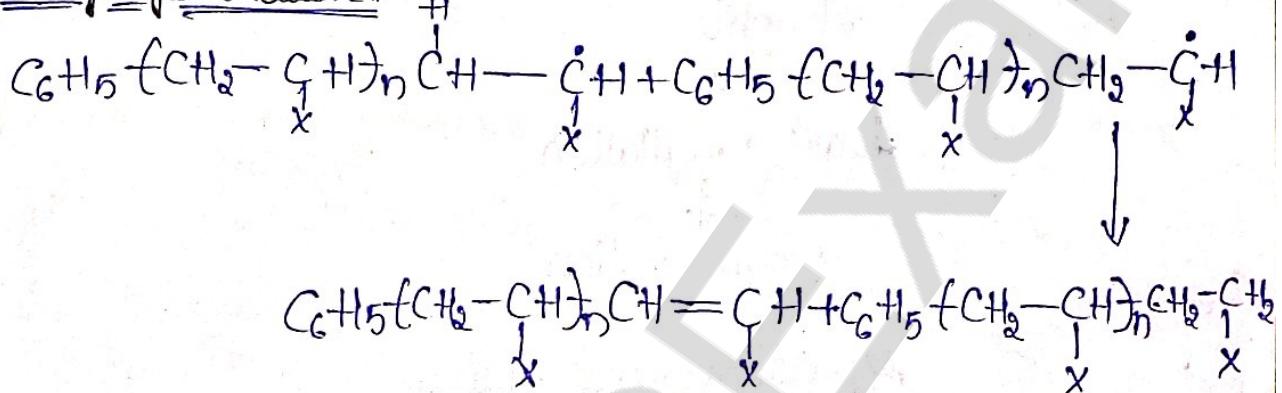
Propagation:



Termination:



Disproportionation:



* Methods of Polymerisation:

1. Emulsion Polymerisation:

Aqueous monomer $\xrightarrow{\text{emulsifying agent}}$ Polymer
 + Initiator

Rubber: Buna-S,
 poly butadiene

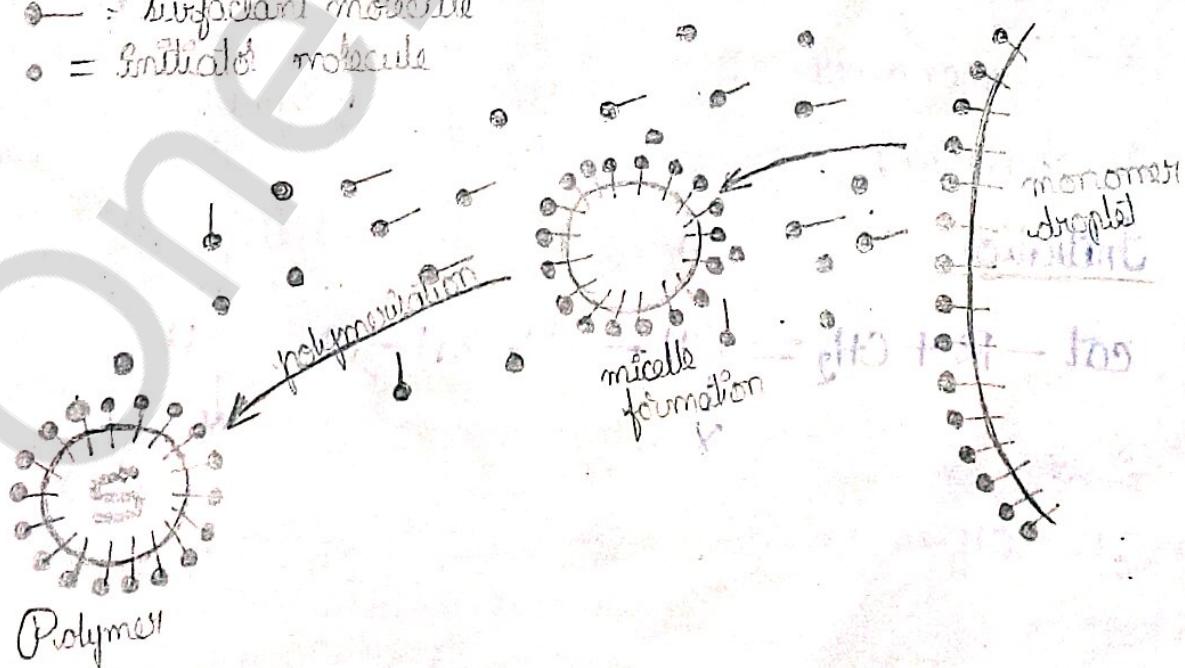
Plastic: (PVC, Polystyrene...)

(high M.Wt. polymer)

Emulsifying agent (OH) surfactant: sodium lauryl sulphate

Initiator: H_2O_2 / Fe

- = surfactant molecule
- = initiator molecule



Drawback: Typical cleaning of emulsifying agent along with polymer.

Suspension polymerisation:

Insoluble polymer is obtained by this method.

monomer + bio active material + initiator



water + stabiliser



droplets



heat + agitation



polymerisation

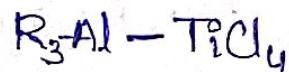


separation and drying

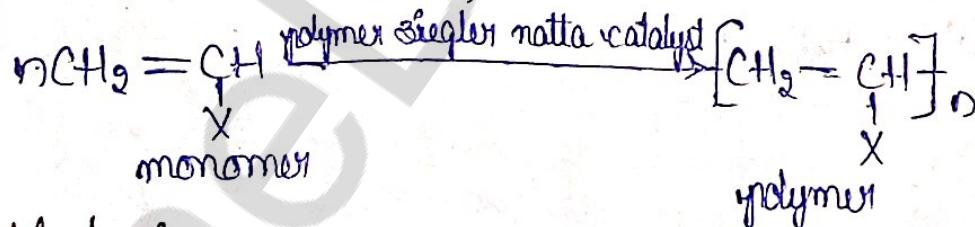
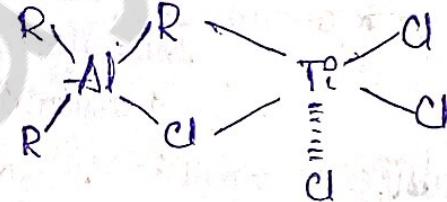


polymer beads (or) pearls.

Co-ordination polymerisation (or) Ziegler - natta polymerisation :

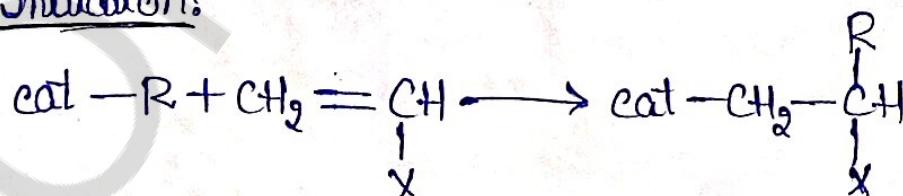


(Tri alkyl aluminium
Titanium tetrachloride)

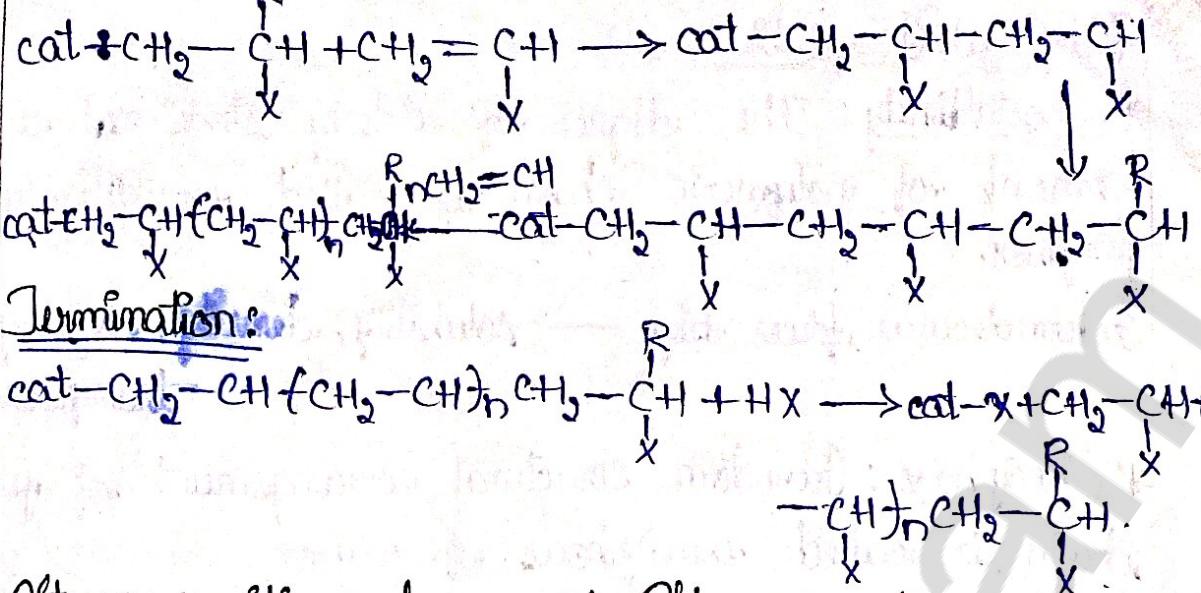


Mechanism:

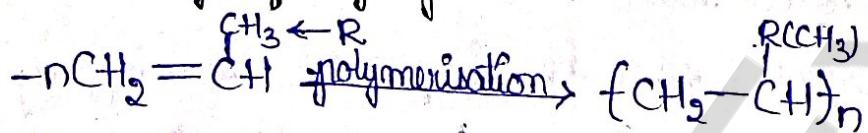
Initiation:



Propagation:



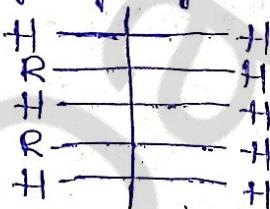
Stereo specific polymers (or) Stereo regular polymers:



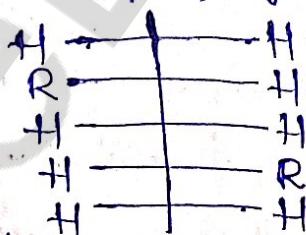
The orientation of monomeric units in polymer chain can express orderly or disorderly fashion with respect to main chain is called tacticity. This process is called stereospecific polymer.

Based on orientation there are 3 types.

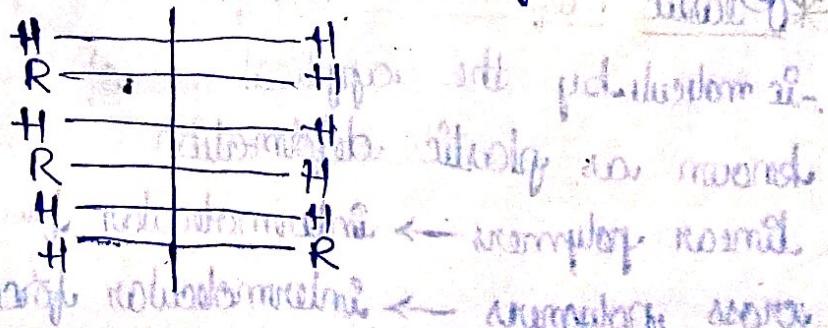
1) Isotactic: Alkyl groups are arranged in same side.



(2) Syndiotactic : Alkyl groups are arranged in opposite way



(3) Deltatic: Alkyl groups are arranged in random way.



5-09-19 Jhunhy Physical and ^{Mechanical} Chemical properties of Polymers:

Physical Properties:

* Crystallinity: The degree of orderly structural arrangement of polymeric chain is called crystallinity of polymer.

Intermolecular forces high \rightarrow solubility, density, rigidity and transparency.

* Amorphous: Random structural arrangement of polymeric chain is called amorphous of polymer.

Intermolecular forces low

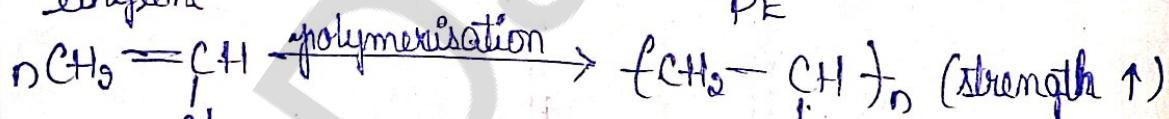
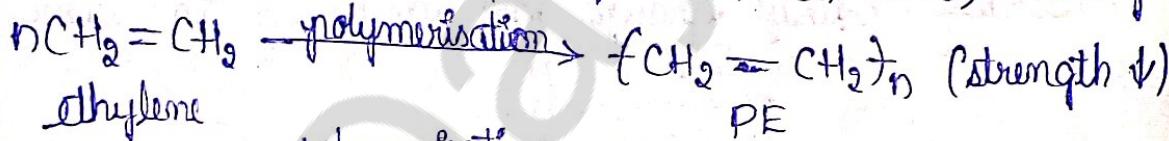
Amorphous polymers can be improved by adding with crystallinity of polymers (mainly flexibility).

Mechanical Properties:

* Strength: Intermolecular forces high, strength high.

Chainlength increases, strength increases.

Functional groups ($-OH$, $-Cl$, $-CHO$) \rightarrow strength ↑



PVC Cl "Cl" is bulky group.

* Elastomeric property: Recovery of original shape after removing of stress is called elastomeric property of polymer. Intermolecular forces weak.

* Plastic deformation: Shaping of particle from polymer molecule by the application of heat and pressure known as plastic deformation

Linear polymers \rightarrow intermolecular forces ↓, plastic deformation ↑

Cross polymers \rightarrow intermolecular forces ↑, plastic deformation ↓

Plastics: Plastic is a solid material which can be mould into decide shape by the application of heat and pressures.

Advantages:

- 1) These are used as
- 2) Corrosion resistance.
- 3) Easily carriable.
- 4) Low cost or low expensive.

Disadvantages:

- 1) Non bio-degradable.
- 2) Combustible and then gives toxic chemicals.
- 3) Easily react with heat.

07-09-19
Saturday

Thermoplastics

- 1) Soft on heating.
- 2) Hard on cooling.
- 3) These are formed by addition polymerisation.
- 4) Monomers having $=$, \equiv
- 5) Adjacent C-C having weak van der waals forces.
- 6) Linear polymers.
- 7) Reclamation from waste.
- 8) Recycle, Reuse.
- 9) Plasticisers are used in moulding.
- 10) PE, PVC, Teflon, polyethylene, cellulose derivatives, polystyrene

Thermosetting plastics

- 1) Infusible product formed on heating.
- 2) These are formed by condensation polymerisation.
- 3) Monomers having functional groups ($-OH$, $-CHO$, $-C=O$).
- 4) Strong van der waals forces exists.
- 5) Cross linked polymers.
- 6) Can't be reclamation from waste.
- 7) Can't be recycled.
- 8) Transfer moulding.
- 9) Fillers are used in moulding.
- 10) Bakelite, urea, formaldehyde Resin, polyesters, silicones.

Compounding of Plastics:
Process of mechanical mixing of various additives for a polymer known as compounding of plastics. In this process, 4-10 ingredients are used.

Resin: Hold (binder) together by different ingredients.

Linear polymers (infusible) $\xrightarrow{\text{catalyst}}$ cross linked polymer (infusible).

Plasticizer: To improve flexibility and plasticity.

To reduce intermolecular forces, strength, brittleness.

Ex: Vegetable oils, camphor, esters, sterates and phosphate.

Fillers: To improve tensile strength, workability, finishing work. To reduce cost, brittleness.

Ex: Carbon black; gypsum, talc, saw dust, corn husk, metal oxides, metal chlorides, ash.

Reinforced fillers: To enhance mechanical property.

Ex: Natural rubber quality 40% improved by carbon black.

Lubricants: Reduce friction.

Ex: Oils, grease, soap.

Accelerators or catalysts:

Rate of reaction increases.

Ex: H_2O_2 , benzoyl peroxide, Ag , Cu , Pb .

Stabilizers:

To maintain stability.

Ex: White lead, red lead, sterates of Pb , Cd , Ba .

Colouring Agent:

Article is attracted by colour.

carbon black - black

ZnO - white

Antimony oxide - crimson red.

Tin oxide - red.

chromic oxide - green.

Anti oxidants:

To prevent oxidation (corrosion).

Ex: Phenyl B-naphthyl amine.

09-09-19
Monday

Fabrication of Plastics (or) Moulding Techniques of plastics

Shaping of particle from polymeric material by the application of heat and pressure in a closed chamber is known as

Fabrication of Plastics. These are 4 types

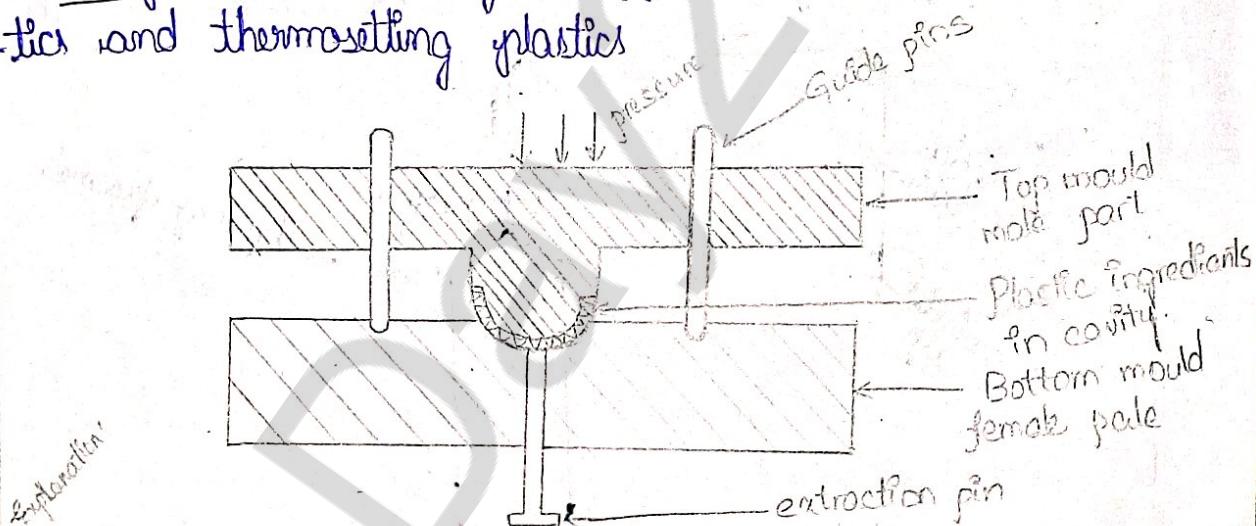
i, Compression moulding.

ii, Injection moulding.

iii, Extrusion moulding.

iv, Blow film moulding.

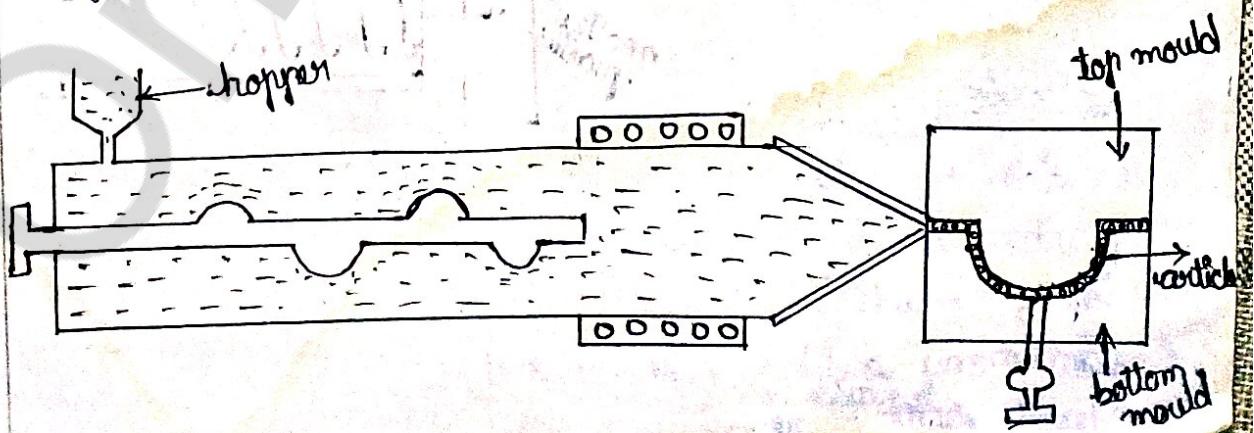
i, Compression moulding: Applicable for both thermoplastic and thermosetting plastics



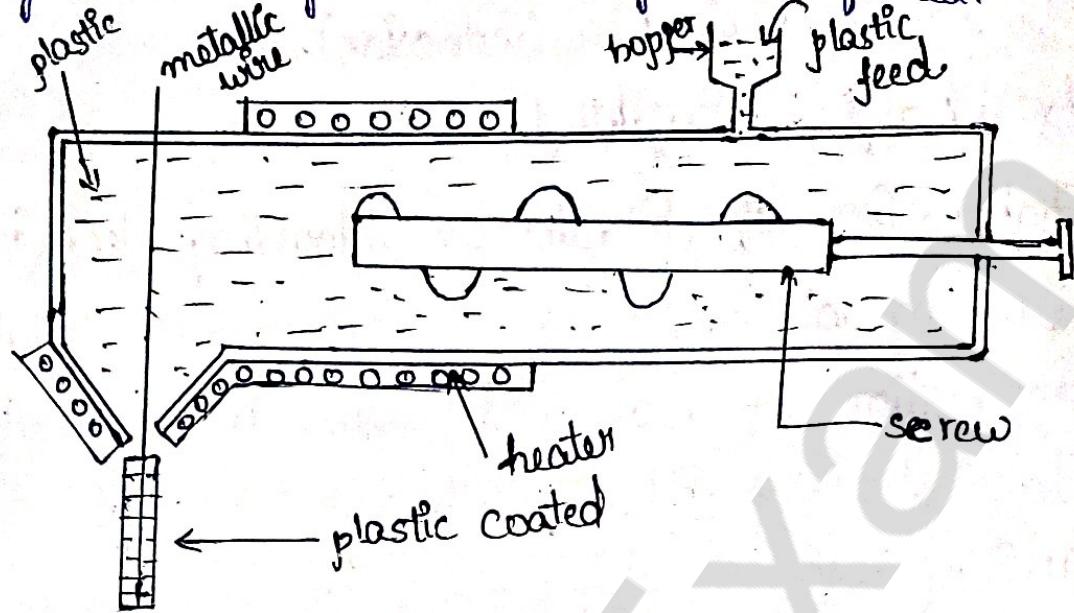
Heating - thermosetting plastics

Cooling - thermoplastics.

ii, Injection moulding: Only applicable for thermoplastics.



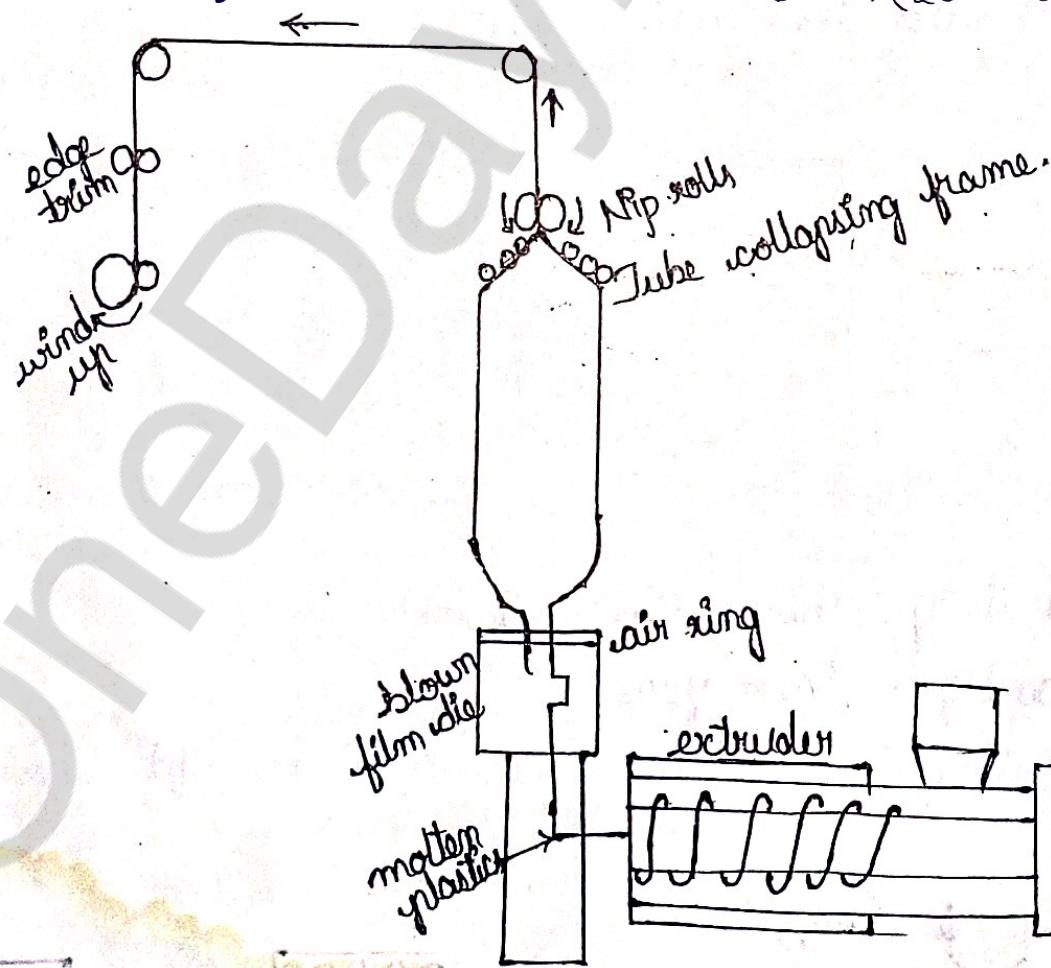
iii) Extrusion moulding: Similar process of injection moulding. In this process thermoplastics formed.



iv) Blow film moulding: Blow film is another method of extrusion process. In this thermoplastics are obtained.

Normal films range - 0.254 mm (10 mill)

In blow film, films are obtained - 0.5 mm (20 mill).



* Poly Vinyl Chloride (PVC):

12-07-19
Thursday
1) Vinyl Chloride when polymerises in the presence of H_2O_2 to form poly vinyl chloride (PVC).



Vinyl chloride. poly vinyl chloride (PVC).

Properties: Colourless, Odourless, non-flammable, chemically inert, soluble in ethyl chloride.

Resistant to light, atmospheric oxygen, inorganic acids and alkalis.

Softening point (148°C).

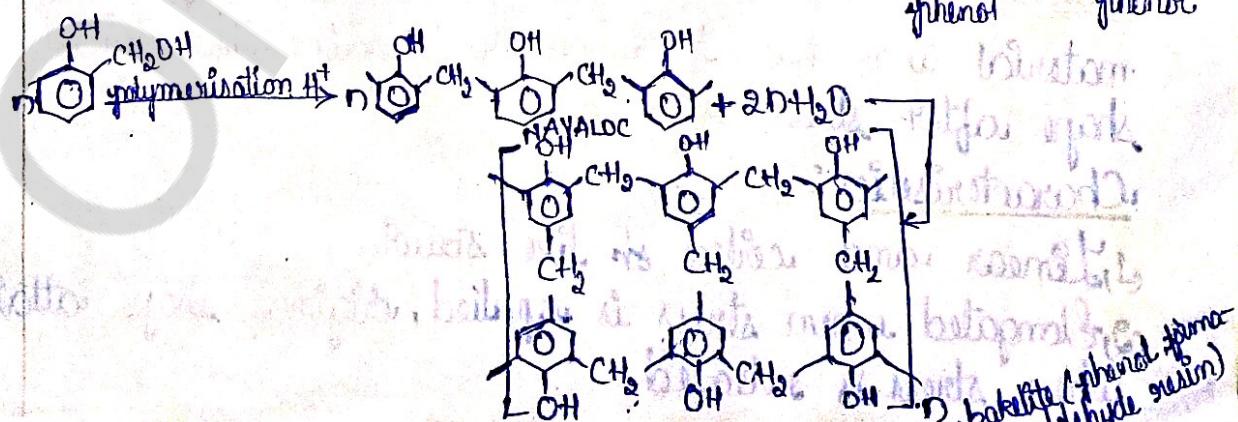
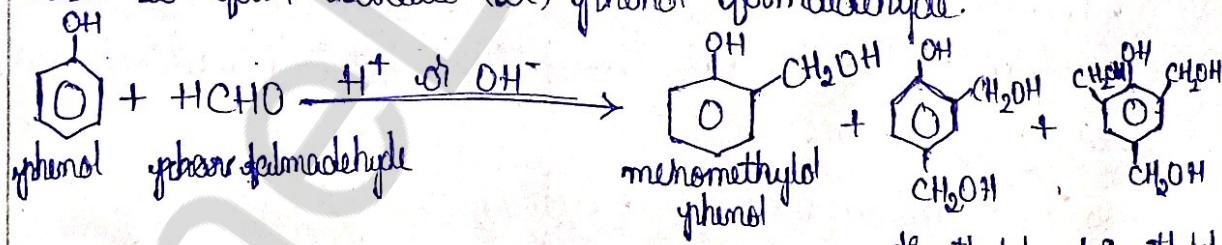
Brittle.

Uses: Unplasticized PVC: Helmets, refrigerators, cycle and motor cycle mud guards.

Plasticized PVC: (dibutyl phthalate is plasticizer).

Raincoats, curtains, table cloths, chemical containers, radio components, telephone parts, conveyor belts. (0.5 mm to 8mm thickness).

Bakelite: Condensation polymerisation between phenol and formaldehyde resin in the presence of acid or base to form bakelite (or) phenol formaldehyde.



Properties:

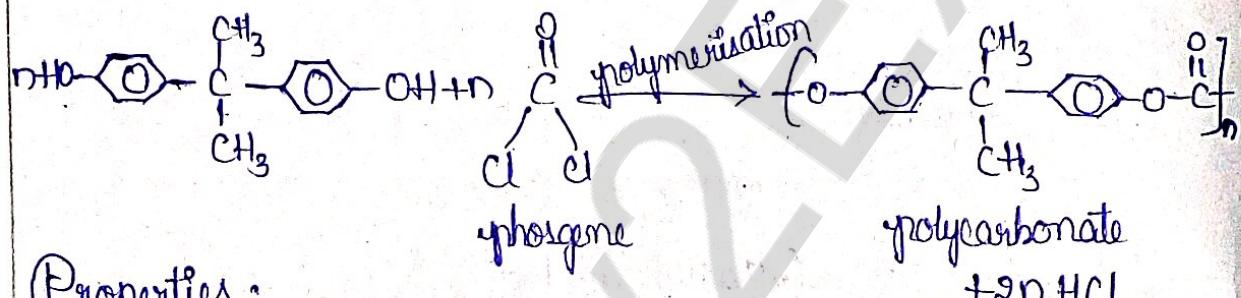
3 dimensional cross linking polymer and thermo plastic rigid (but) hard, scratch resistance and water resistance excellent electrical insulation.

Use:

Electrical insulation parts like switches, plugs, switch boards, heater handles, telephone parts (radio television) also used in paints (or) varnish.

Poly carbonates :

Bis-phenol-A(BPA) when polymerises with phosgene form polycarbonate.



Properties :

- 1) These are durable material.
 - 2) These are used in high lenses parts.
 - 3) Glass transition temperature is 147°C .
 - 4) High plastic deformation without cracking and breaking.

Uses:

- (1) Poly carbonates are used in electrical devices with safety features.
 - (2) Telecommunication hardware.

Rubber and Elastomers: Elastomer is a polymeric material that has tendency to regain its original shape after stress is released.

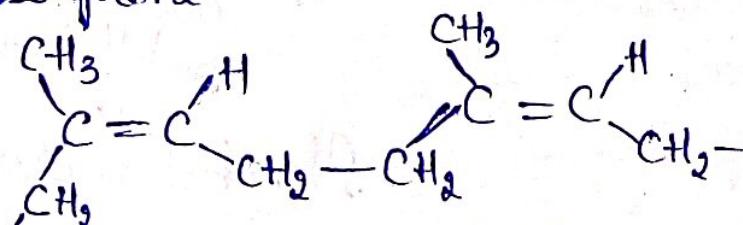
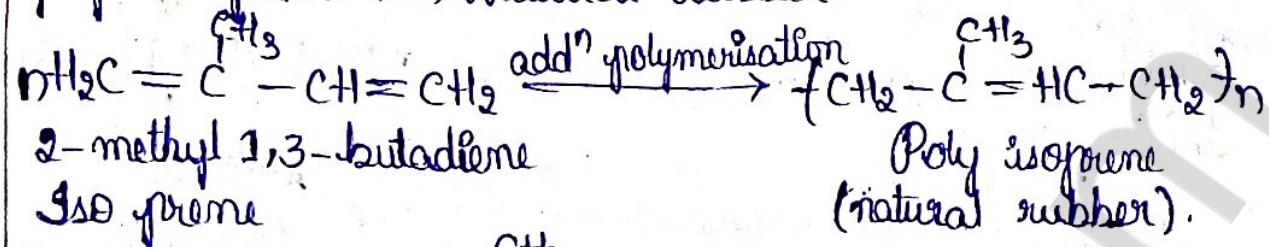
Characteristics:

- 1) Linear and coiled α -like structure.
 - 2) Elongated when stress is applied, original shape attained when stress is released.

3. Weak van der waal forces, 4. Low chemical resistivity

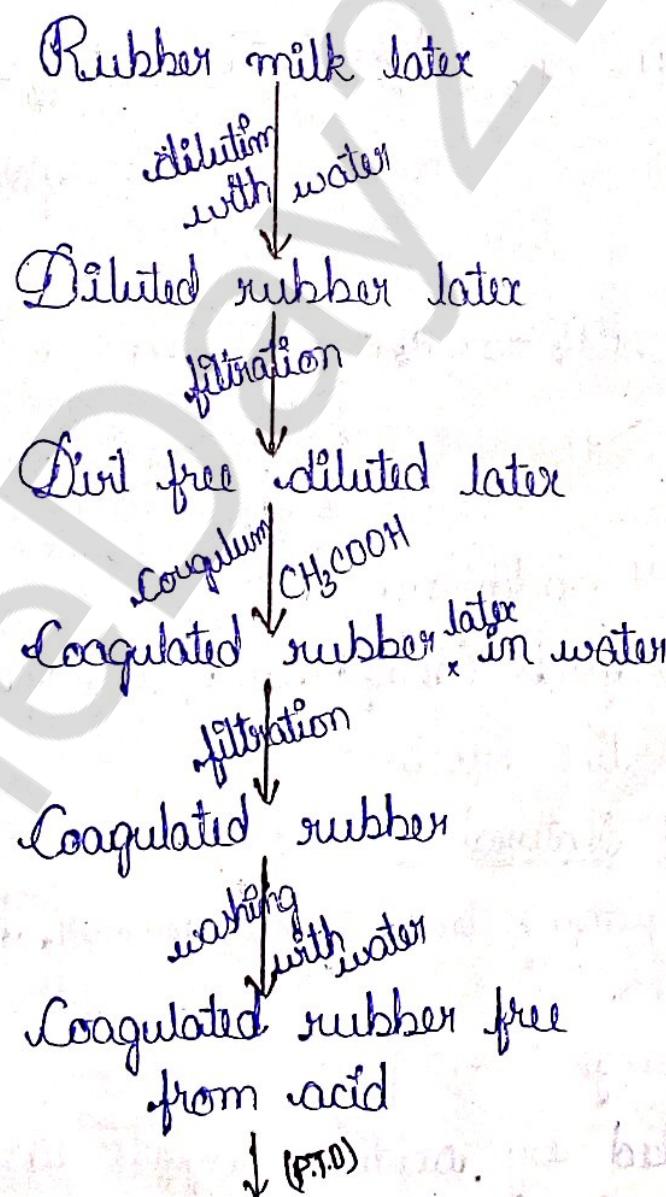
5. Sticky at higher temperature.

Natural Rubber: Iso prene when polymerises to form poly iso prene (or) Natural rubber.



cis 1,4-addition

13.09.19
Sunday
Flow chart for manufacturing of natural rubber from latex:



washing with NaHSO_3 , passing through a
pair of rollers

Rubber sheet \sim 1 mm
thickness

air
drying at
 50°C

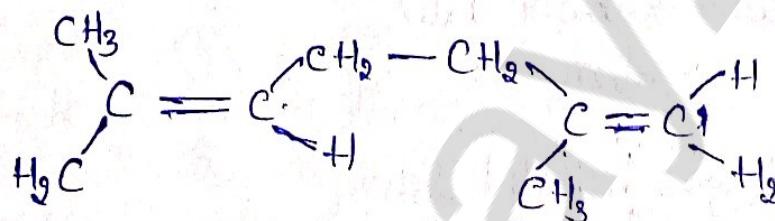
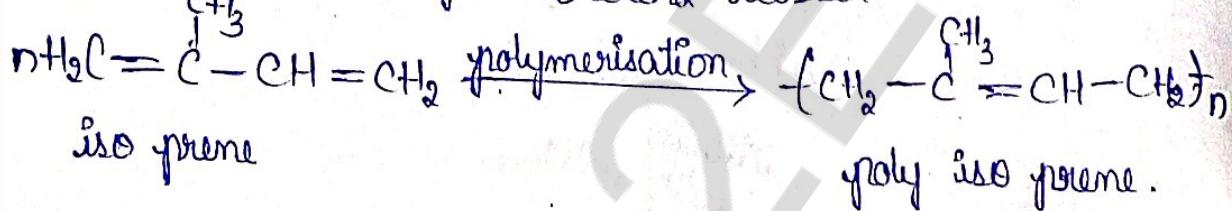
Crepe Rubber

Thick Rubber sheet

during at
50°C in
smoked chamber.

Smoked rubber

Gutta Percha Rubber: Iso propene polymerises to form poly iso propene or Gutta Percha rubber.



Trans 1,4-addition

User: *Dental parts (temporary filling parts)

* Bloom like substance

Drawbacks of Natural rubber:

* Soft and gummy in hot wet summer, hard and brittle in cold weather.

* Softening range 10 - 60°C.

* Easily attacked by oxidising agents like HNO_3 , H_2SO_4 .

* Swelling in wells.

* Shows tackiness (tackiness means two sheet combined to form simple shirt by over pressure).

* Permanent deformation.

*Not durable.

Compounding of rubber:

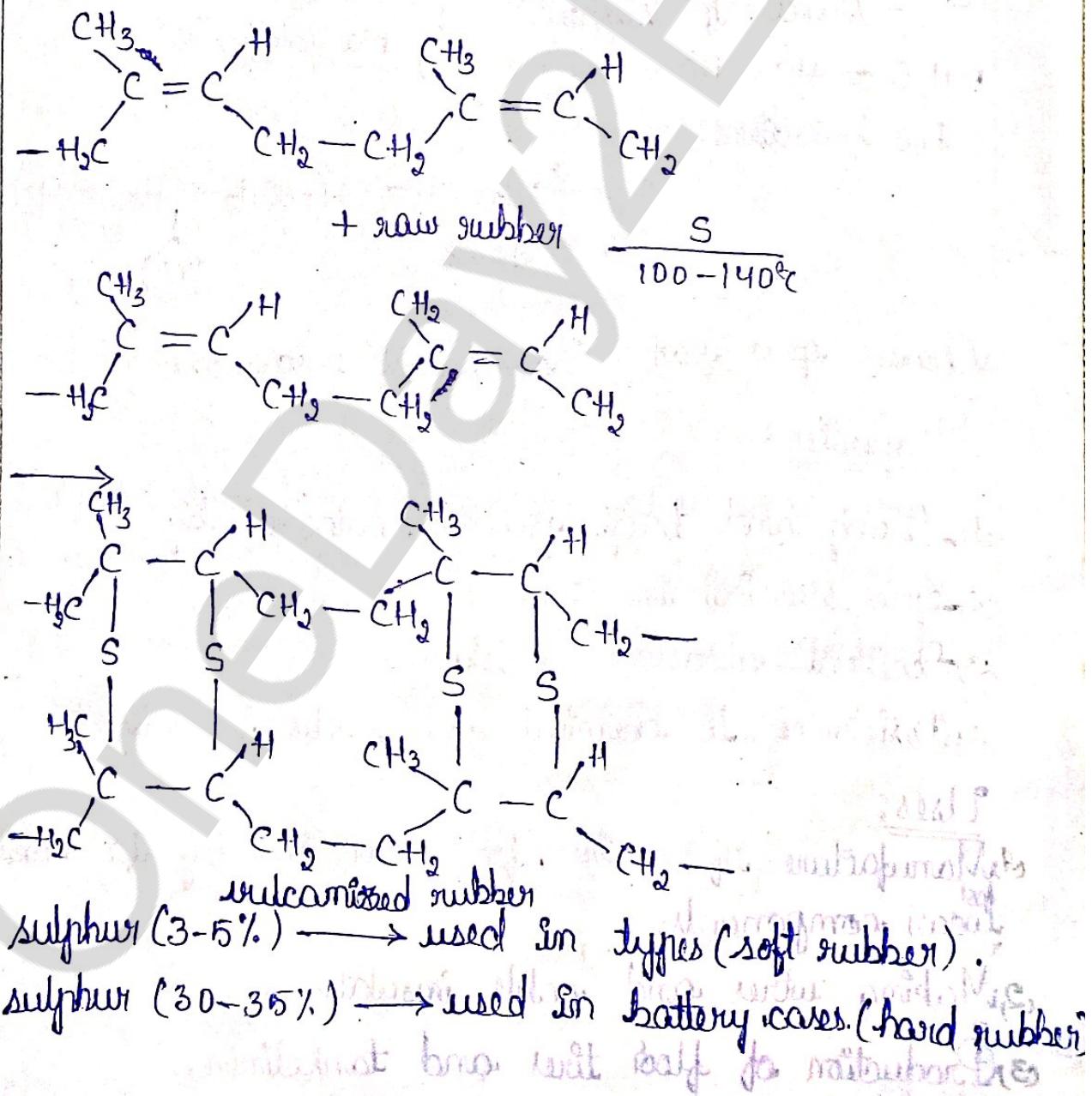
Mastication: The process of rubber into small pieces by mechanical stirring is known as mastication.

Rubber mechanical stirring small pieces.

Main important Ingredients: vulcanisation, accelerators, anti-oxidants, filters, reinforced filters, plasticizers, colouring agents.

Vulcanisation of rubber:

The process of heating of raw rubber with sulphur at $100-140^{\circ}\text{C}$ then formed vulcanised rubber.



Advantages of vulcanised rubber:

2

1. Good tensile strength.
2. Good electrical insulation.
3. Resistance to chemicals and corrosion.
4. Softening point 100-140°C.
5. Doesn't attain tackiness.

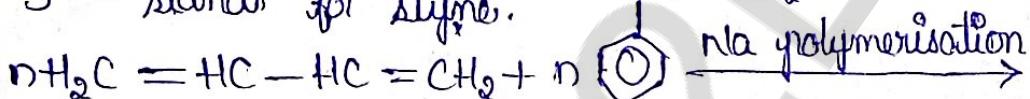
BUNA-S: styrene butadiene rubber (SBR), government butadiene rubber (GBR), Ameyrol

Co-polymerisation of 1,3 butadiene and styrene in the presence of sodium catalyst to form Buna-S.

BU - stands for 1,3 butadiene.

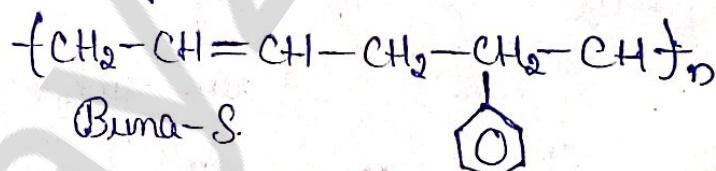
Na - stands for 'Na' catalyst.

S - stands for styrene. $\text{CH}_2 = \text{CH}_2$



1,3 butadiene.

Styrene



Charles good year - Founder of vulcanization.

Properties:

1. Strong and tough polymer, vulcanized by

2. Good electrical insulator.

3. Excellent abrasion resistance.

4. Resistance to chemicals but swells in oils.

Uses:

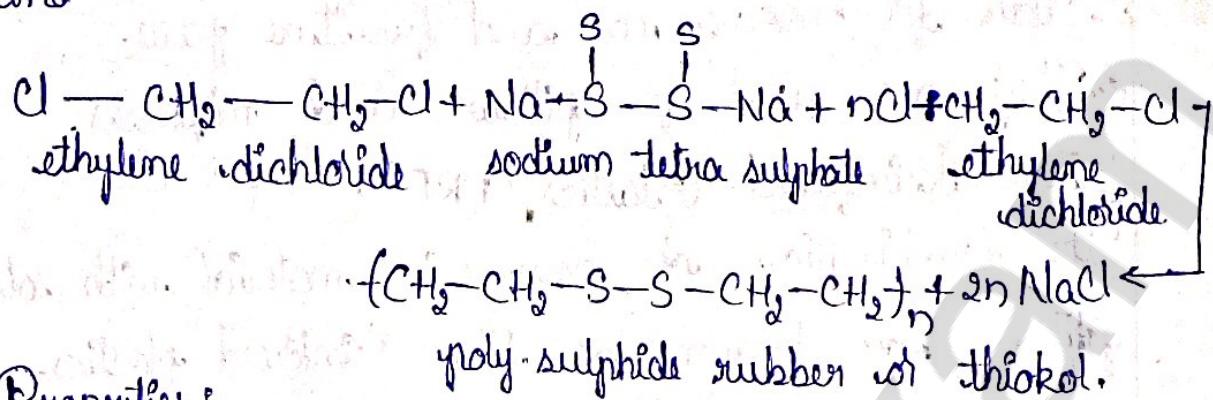
1. Manufacture of tires, foot wear industry for making foot wear components.

2. Making wires and cable insulation or.

3. Production of float tires and tank lining.

Poly sulphide rubber

(3) Polymerisation between ethylene dichloride and sodium tetra sulphide (poly sulphide) to form poly sulphide rubber and



Properties:

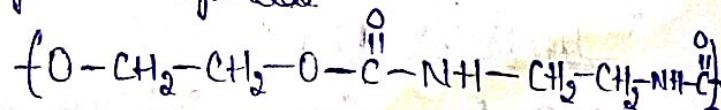
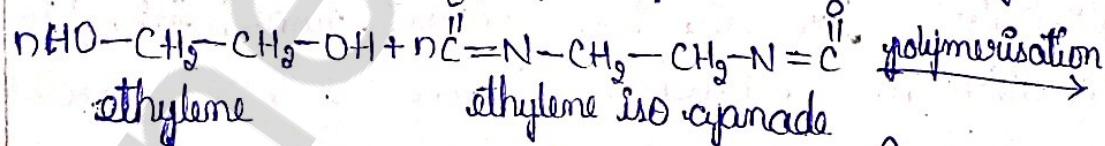
1. Resistance to swelling in oils.
2. Can't be vulcanization.
3. Poor heat resistance, abrasion resistance and low tensile resistance.
4. Loss its shape and continuous pressure.

Uses:

1. Used to make sealants, gas cuts, balloons, fabric protection.
2. Used to make gas lines, hoses.
3. Used in sodium fuel rocket

16-09-19
Monday Poly urethane rubber (iso cyanate rubber):

Polymerisation between ethylene glycol and ethylene iso cyanate to form poly ethyl urethane (iso cyanate rubber)



poly urethane (iso cyanate rubber).

Properties:

1. Highly resistance to oxidation, many organic solvents, heat, abrasion and weather.

2, Easily attacked by acids and alkalis.

Applications:

1, Surface coatings of vehicle dance floors.

2, Used for ^{the} enhancing of life time of tyres.

3, Used for making car and furniture parts.

4, They are used for pillows and mattresses.

Fibre Reinforced Plastics (FRP): (bullet proof, times stronger than steel)

The combination of polymeric material with solid filaments are known as fibre reinforced plastics.

Two components:

1, Polymer or Resin or Fibre: Thermoplastics and Thermo setting plastics.

2, Fillers or Matrix: Carbon black, nylon products, clay, gypsum, asbestos, guite, sic, berillium etc.

Properties:

1, Space craft, aeroplanes, acid

2, Motor cars and building materials.

3, Making baskets.

Advantages:

1, Low co-efficient of thermal expansion, High dimensional stability, Low cost of production, good tensile strength, low dielectric constant, non-flammable, corrosion and abrasion resistance.

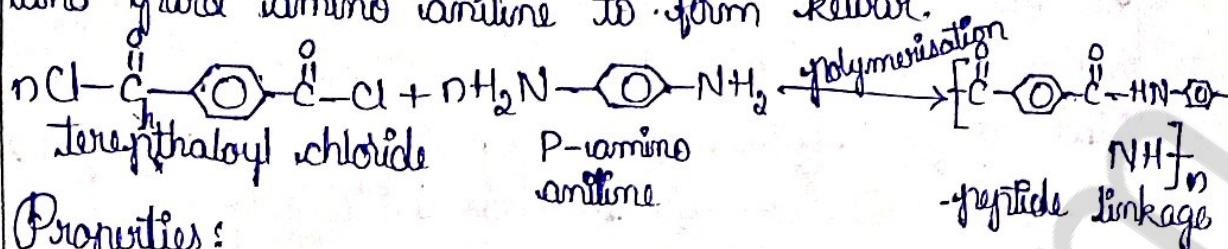
* Types of FRP:

1, Carbon fibre reinforced plastics.

2, Glass fibre reinforced plastics.

Bullet Proof Polymer (Aramid fibre reinforced polymers):

* Kevlar: Poly condensation between terephthaloyl chloride and para amino aniline to form Kevlar.



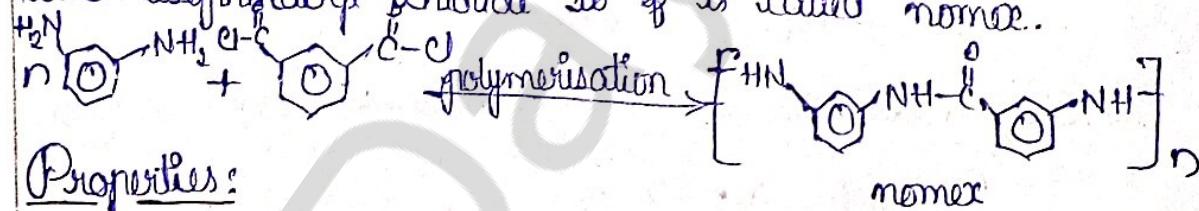
Properties:

- 1) Kevlar is exponentially strong (5 times stronger than steel and 10 times stronger than aluminum).
- 2) High heat stability and flexibility.
- 3) More rigid than nylons.

Applications:

Used to make bullet proof jackets, ropes, cables, motorcycle helmets, car parts and also used in aircraft industries.

* Nomex: Condensation between meta-phenylene diamine and isophthaloyl chloride to form is called Nomex.



Properties:

- 1, 5 times stronger than steel, weighs only yellow in appearance.
- 2) Low density, high strength, thermal resistance, chemical and abrasion resistance.

Uses:

• Bullet proof jackets, aircraft parts, clutch plates, gaskets, adhesives and sealants.

Methods of fabrication of FRP (or) moulding technique,

uses of FRP:

- 1) Injection moulding.
- 2) Hand lay-up.
- 3) Spray up.
- 4) Continuous lamination.

13-09-19 Biodegradable Polymer:

Biodegradable polymers are those polymers which can be degraded by the action of naturally occurring micro organisms like bacteria, algae, fungi.

- Two ways (1) Naturally occurring biodegradable polymers.
(2) Synthesised biodegradable polymers.

1, Naturally occurring biodegradable polymers:

Ex: Poly saccharides : cellulose starch.

Proteins : silk, wool.

Polyesters : polyhydroxy alkanoic acids.

Others : natural rubber, shellac.

2, Synthesised biodegradable polymers:

Ex: Poly alkylene esters, poly acetic acid and co-polymer poly vinyl chloride, poly amide esters, poly vinyl alcohol.

1, Degradation (Aerobically) : in presence of oxygen.

Product + for O₂ → CO₂.

2, Degradation (Anaerobically) : in absence of oxygen.

Product → methane.

Another degradation methods:

(1) HBP (Hydroxy Biodegradable polymers):

in presence of water → CO₂ + biomass +

(2) OBP (Oxy biodegradable polymers):

methane

in presence of oxygen

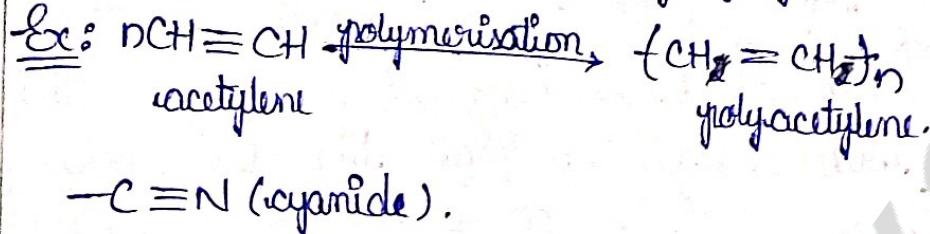
Applications:

1, These are used as suture components, control drug release, tissue engineering.

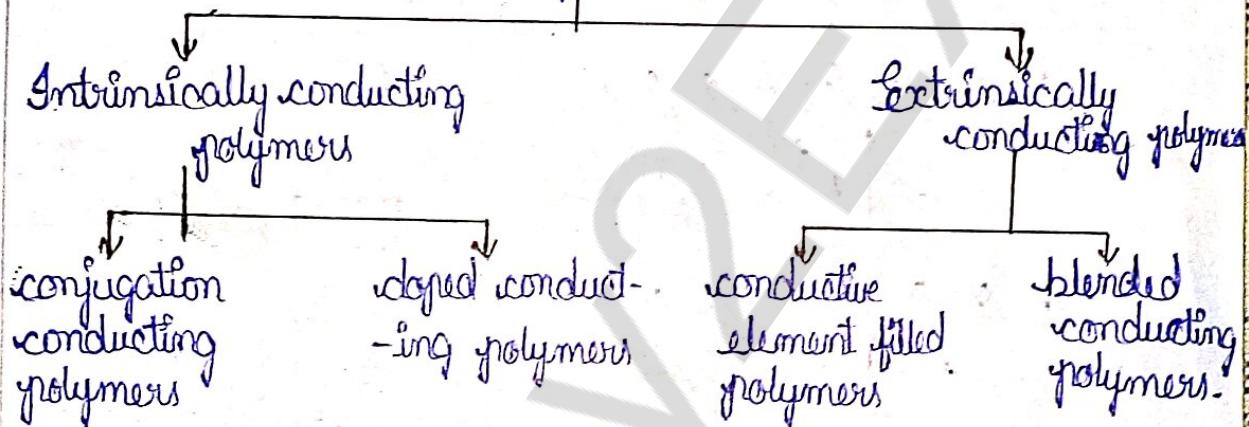
2, These are used as in dental devices and orthopaedic fixation products.

(3) These are used to make carrying bags or shopping bags, fishing nets, food carrying components like plates, cups, cutlery, tray and straw.

Conducting polymers: Most of the polymers are insulators but some polymers having conductance those polymers are called conducting polymers.



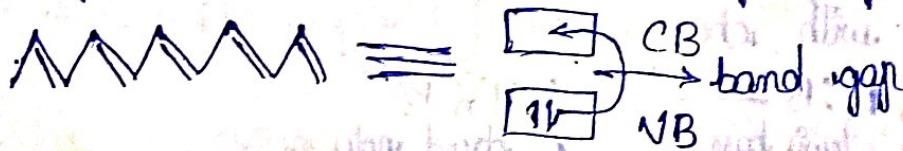
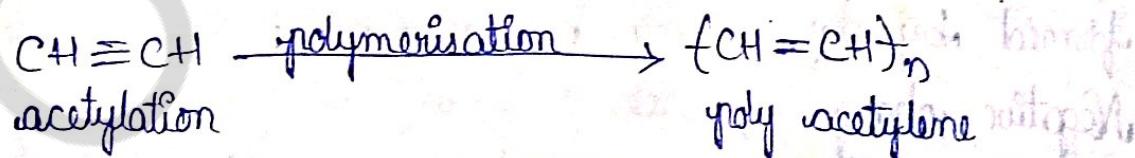
Conducting Polymers



i) Intrinsically conducting polymers: Electrical conductance can be formed by extensive $\pi - \pi$ conjugation.

ii) Conjugation conducting polymers: These polymers contain $\pi - \pi$ conjugation throughout ^{the polymer} of the back bone of, which results in delocalization and overlapping of π orbitals leads to formation of ^{valency} bonding bond and conduction band with some band gap.

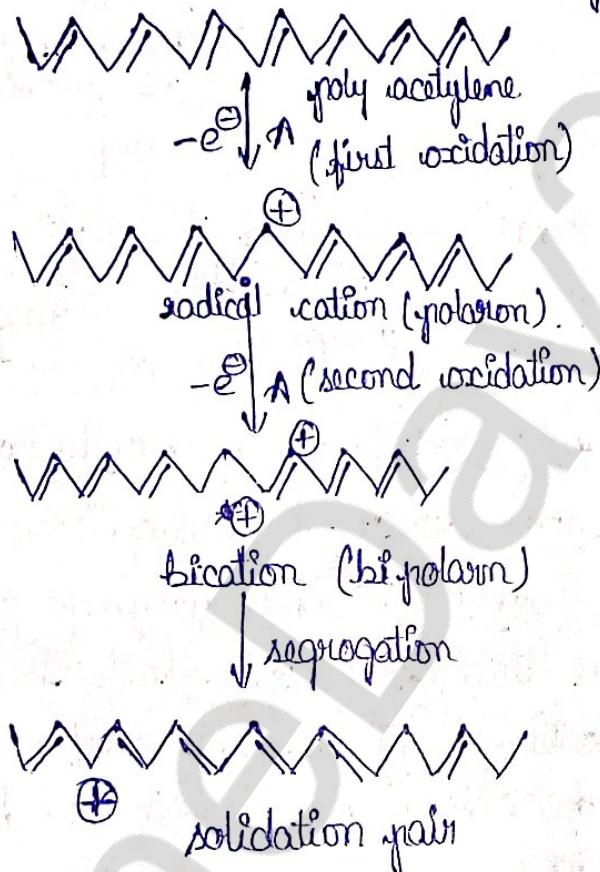
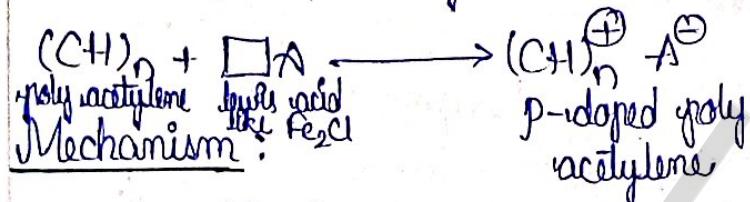
Doped Conducting Polymer:



18-09-19
Wednesday

Doped conducting polymer: The conductivity of conjugating conducting polymers can be enhanced by doping with positive or negative charge and back bone of the polymer with charge transfer agencies. There are two types

1, P-doped conducting polymer: These polymers are formed by doping with p-doped conducting polymer. Positive charge of back bone of the polymer throw oxidation with charge transfer agent like Lewis acid.



□ covalent bond
→ band gap

□ valency bond

□ covalent bond
□ → band gap

□ valency bond

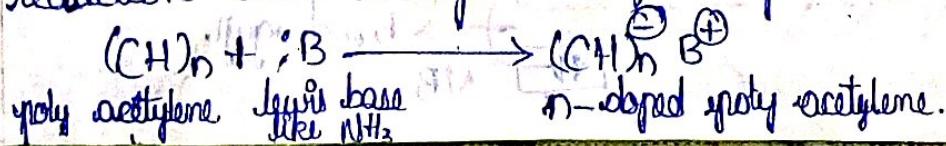
□ C.B
□ → band gap

V.B

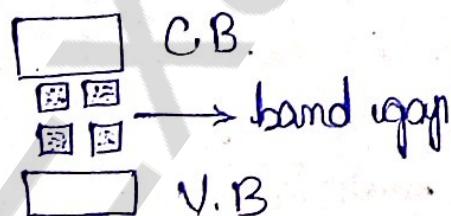
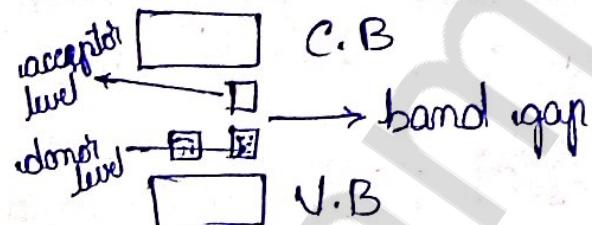
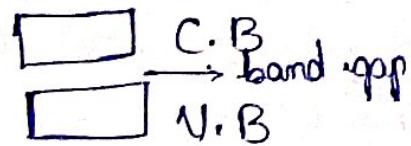
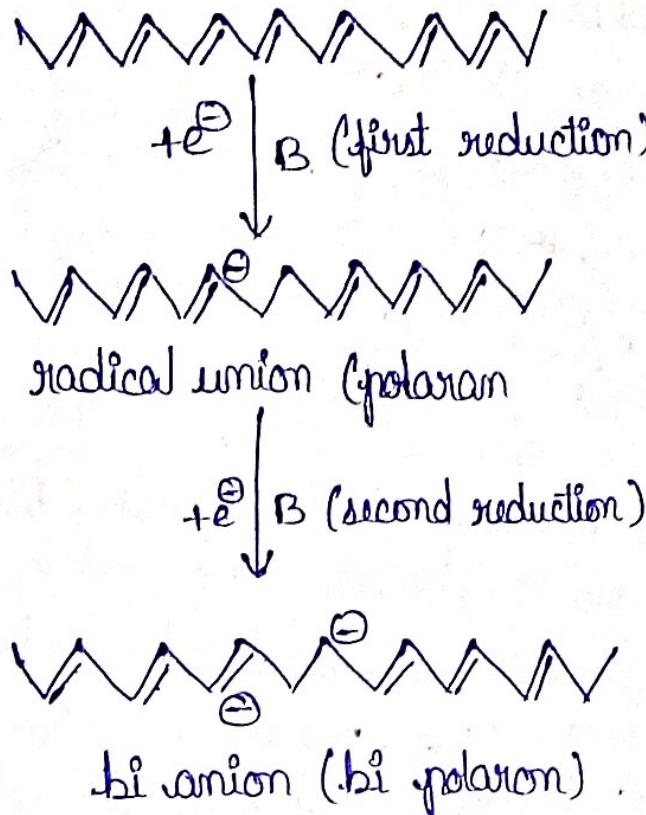
□ C.B
□ → band gap

V.B

2, n-doped conducting polymer: These polymers are formed by doping with n-doped conducting polymer. Negative charge of back bone of the polymer throw reduction with charge transfer agent like Lewis base.



Mechanism :



Extrinsically Conducting polymer:

Conductive element filled polymer:

Resin (or) polymer + fillers → low cost, strength mechanical

fillers : carbon black, ash, gypsum metal powder, double \rightarrow , double ↑

Disadvantages : Breakable after strong elongation.

Blended Conducting polymers: These polymers include improve physical, chemical and mechanical properties.

Applications of conducting polymers:

(1) Button type battery are rechargeable.

(2) Used in sensors.

(3) Photo, volatile devices.

(4) Micro electric devices.

(5) Bio medical applications.

(6) Molecular wires and switches.

(7) Making ion exchanger.