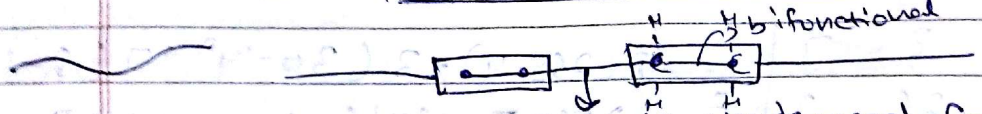
Polymer

Functionality: The no. of bonding site in monomer. It should have at least two

Homo Polymers and Copolymers are of 3 types.

① **Linear** → Bifunctional monomer (have atleast 2 bonding sites)

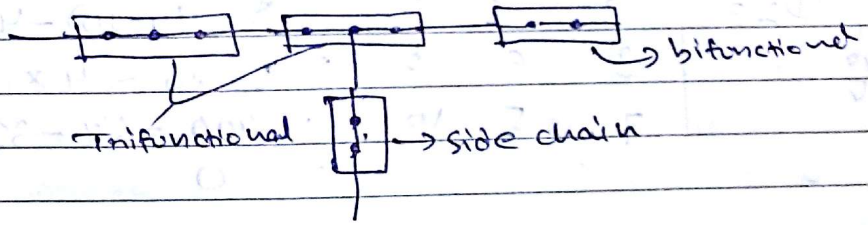


Eg. PVC, PVA

→ High mol. wt. have high density.

② **Branched**: Main part is called Backbone and side parts are branches

→ Bifunctional + Trifunctional

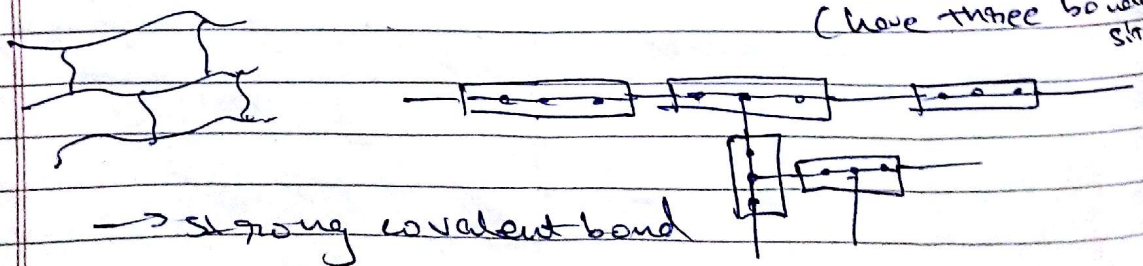


Eg. Polyisoprene

→ low wt., low density because they cannot be packed.

③ **Cross-linked**

→ Monomers are trifunctional (have three bonding sites)



→ Strong covalent bond

Eg. Polyester, Bakelite, Melamine

least two bonding sites.

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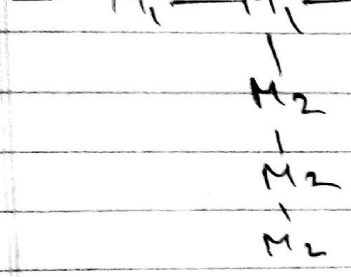
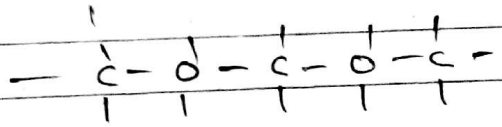
ypes:

* Graft copolymer - It has different monomer in backbone and side chain.



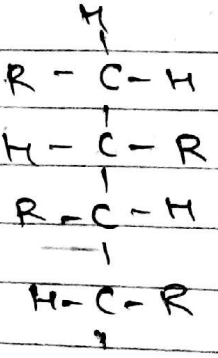
* Homochain polymer: — C — C — C — C — C — (Main chain contains same atom)

* Heterochain polymer: (Main chain contain different atoms)

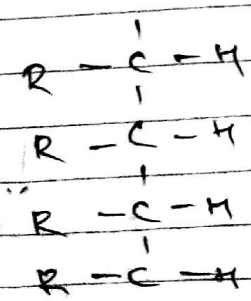


→ TACTICITY: Tacticity in polymer is about the arrangement of functional group around the same chain in a polymer, which might be orderly or disorderly manner.

Orderly arrangement: i, Syndio-tactic (alternate)



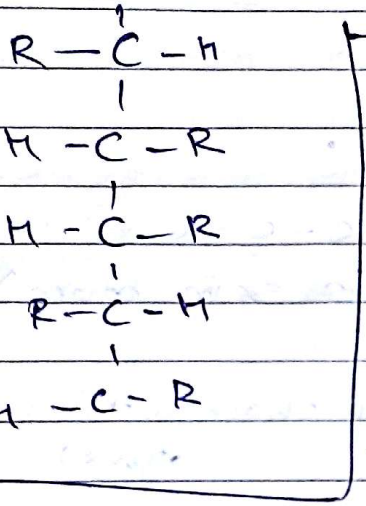
ii, Isotactic



Unorderly arrangement of fun'l group

i) Atactic (These types of polymers are soft)

eg. Polypropylene



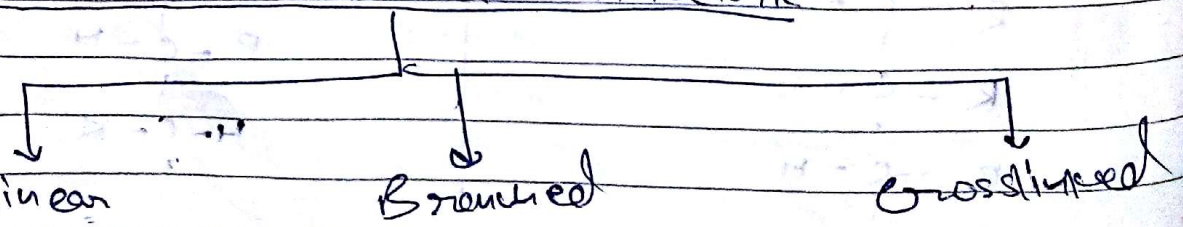
* In simple polymer we obtain a mix of orderly or unorderly arrangement func' group in a polymer.

* STEREOSPECIFIC POLYMER: It is the polymer with desired structure and properties which can be synthesised by using a mixture of proper catalyst, solvents and temp. in a process involving Ziegler Natta Polymerisation.

where combination of halides of transition metals along with organo-metallic compound is used as a catalyst.

Classification of Polymers

1) On the basis of structure



$nM \longrightarrow (M)_n$

monomer → polymer

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(i) On the basis of source

- **Natural**
  - eg. Rubber, Resin, latex
  - ① Natural Rubber → cis-polymer of iso-prene
  - ② Gutta Percha → a polymer of trans iso-prene
  - ③ Protein (polyamides and polypeptides) polymer of
  - ④ Starch (α-D glucose)
  - ⑤ Cellulose (β-D glucose)
- **Semi-synthetic**
  - eg. Rayon [cellulose + acetic acid] (natural polymer + chemical)
  - celluloid [cellulose + Nitric acid]
- **Synthetic Polymers** (man-made)
  - eg. PVC, PVA, polyesters, bakelite

(ii) on the basis of process/synthesis Reaction formation

- Addition polymer (chain-growth polymer)
- Condensation Polymer step growth polymer

→ Joint polymerisation of two or more monomer species.

eg. Thermoplastic

(1) Addition Polymer
(chain growth polymers)

same as [copolymerisation process]

$nM_1 + nM_2 \rightarrow (-M_1-M_2-)_n$

→ Polymers formed by addition rxn

→ The polymer obtained have the molecular wt. which is exact multiple of monomers taking part in the rxn. as no smaller molecules like (CO_2, H_2O) liberate during the process.

→ One polymer is added up to the reacting monomer species (M_2) at a time.

→ No. of units decreases steadily throughout the rxn

→ The mol. wt. of polymer does not change during the course of rxn and high mol. wt. of polymer is formed in the beginning.

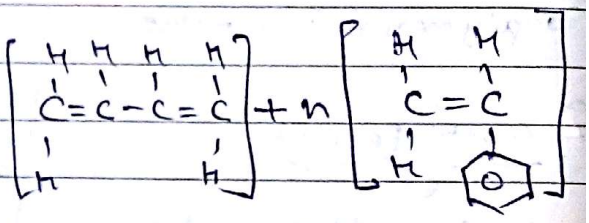
→ The yield of the polymer though gets increased during the rxn but not mol. wt.

eg. Additional polymerisation → Polyethylene, PVC

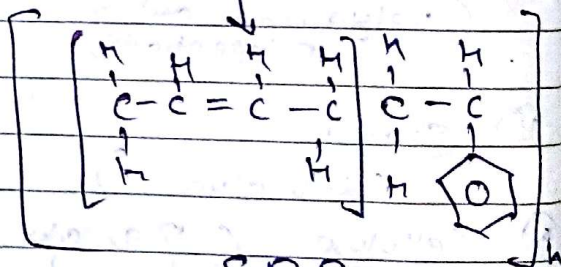
Condensation Polymer
(step growth polymers)

eg. [Styrene-(buta-di-e Rubber (SBR)

widely used polymer for manufacturing automobile tyres is an example of co-polymer process.



copolymerisation



SBR

→ Monomers are unsaturated molecules ★

eg. Thermosetting.

② **Condensation polymerisation process**

→ As in the rxn small molecules like H_2O, CO_2 liberate. hence, the mol. wt. of the polymer can never be exact multiples of the monomers taking part in rxn.

→ During the rxn two monomers can react at a given point of time.

→ Mol. wt of polymer increases steadily during the course of rxn.

→ Monomers disappears only in the rxn.

↔ Monomers must have two active functional groups

eg. Thermosetting plastic

(iv) On the basis of Molecular forces

1. Thermoplastic polymers - (Weakest)
2. Thermosetting polymers - (Strongest covalent bond)
3. Elastomers - (weakest mol. forces)
4. Fibres - (Strongest mol. forces as H-bonds are present)

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① Thermoplastic polymer- → manufactured by addition polymerisation

→ Monomers are added to form a chain which propagate in one direction

→ different chains have weaker intermolecular forces i.e. Weak Vanderwaal forces which can be broken by ease of heating.

∴ such polymer can be reshaped by re-heating again and again.

→ dissolve in organic solvent

→ reclaimed for waste

② Thermosetting polymer → synthesised by condensation polymerisation

→ has stronger covalent bond. develop 3-D cross-linked structure. As the breaking of stronger covalent bond is not possible even by strong heating.

→ These polymers gets blacken or charred on stronger heating but reshaping is not possible.

→ Shape attained during moulding is final

→ doesn't dissolve in organic solvent.

→ cannot be reclaimed. for waste

Mechanism of Polymerisation

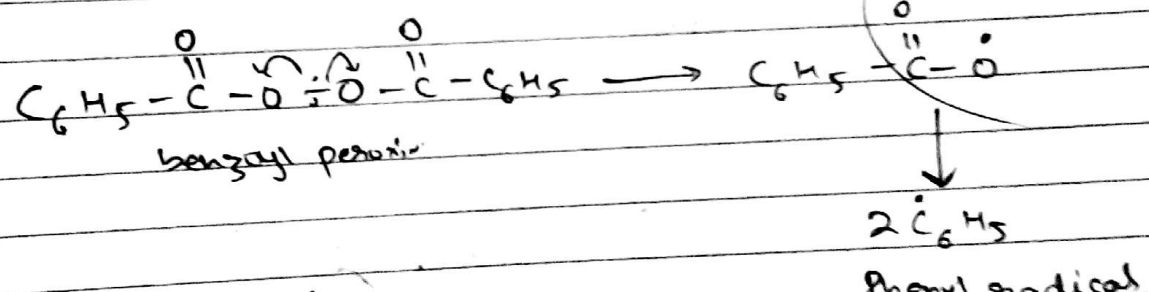
① Free radical mechanism ② cationic mech. ③ Anionic mech.

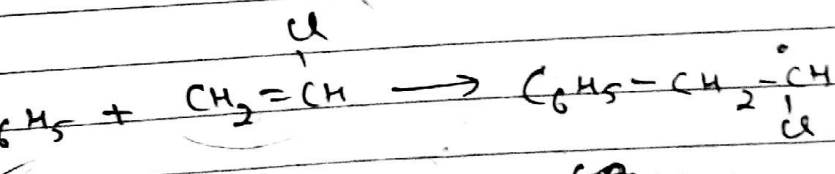
① FREE RADICAL POLYMERISATION: → [alkenes or dienes and their derivatives are polymerised]

i) Initiation step:

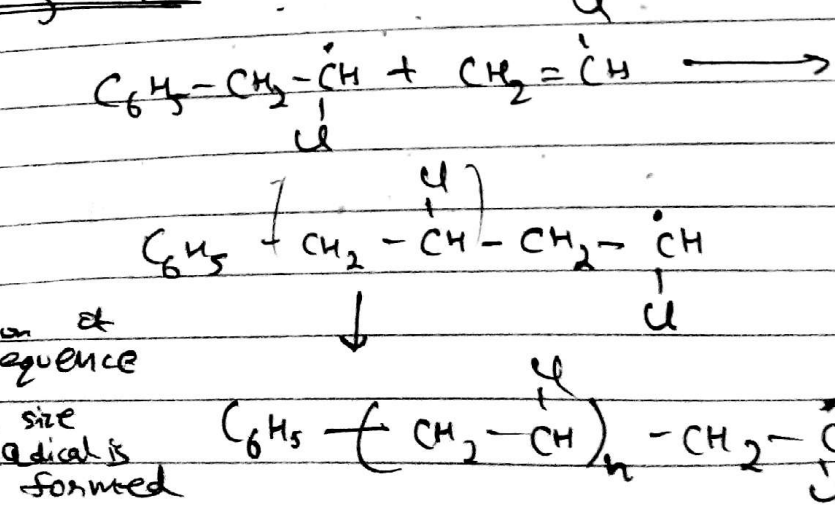
Vinyl chloride to polyvinyl chloride (PVC)

Initiator used (catalyst) → benzoyl peroxide



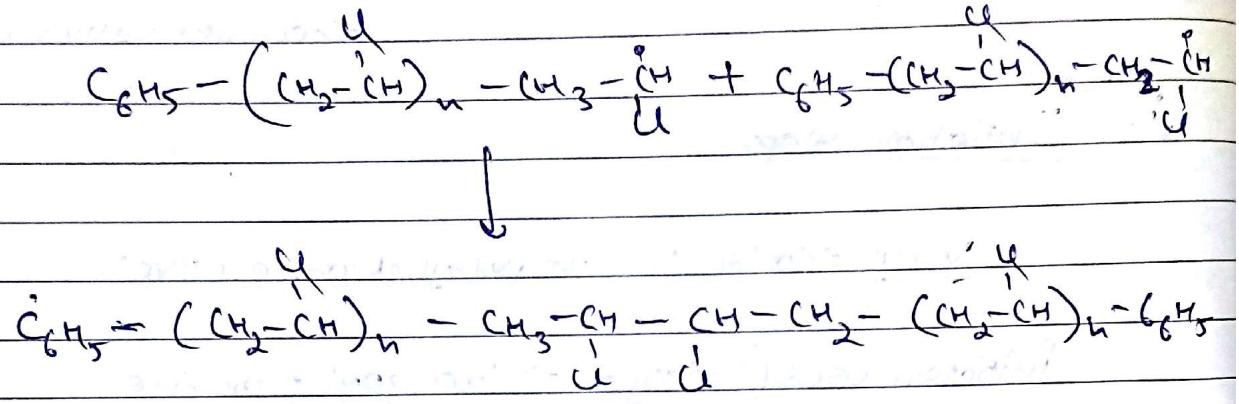


Propagating step:

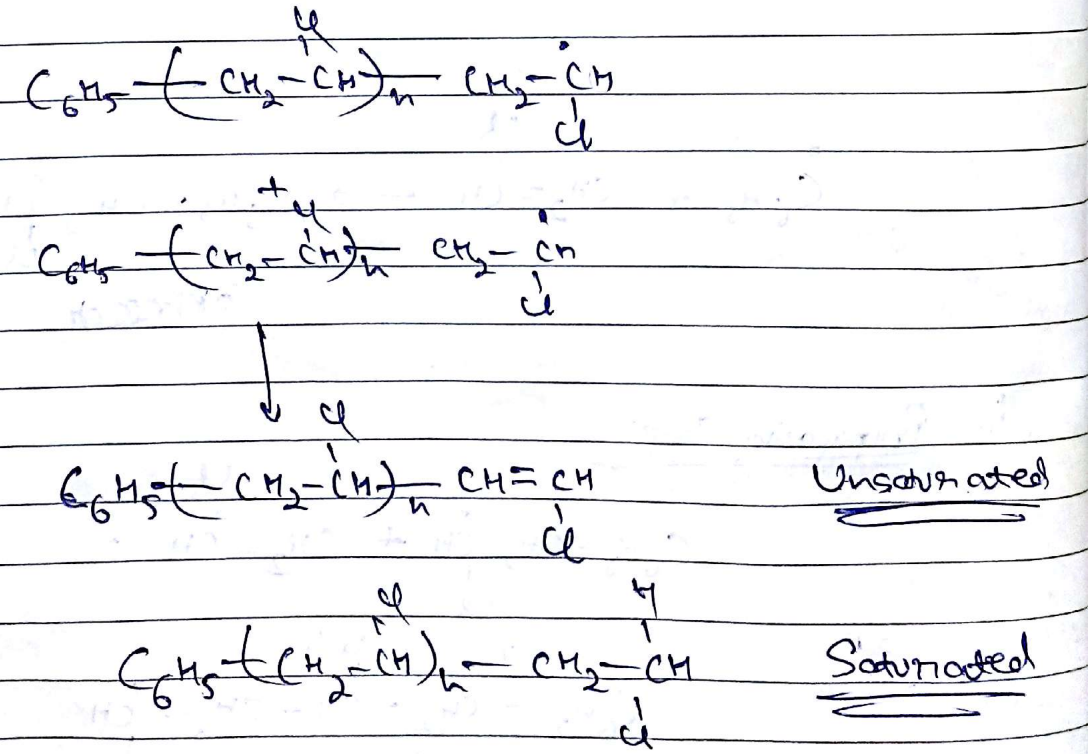


3. Terminating step: product radical formed reacts with another radical.

a) By coupling or combination



b) By disproportionation - H atom of one radical center is transferred to another



Cationic mechanism

i) Chain initiation step

$$Y^{+} + CH_2=\underset{\displaystyle X}{\underset{|}{CH}} \longrightarrow Y-CH_2-\overset{\oplus}{\underset{\displaystyle X}{\underset{|}{CH}}}$$

An acid (cation)

A new cation (Carbocation)

ii) Chain Propagation step

$$Y-CH_2-\overset{\oplus}{\underset{\displaystyle X}{\underset{|}{CH}}} + CH_2=\underset{\displaystyle X}{\underset{|}{CH}} \longrightarrow Y-CH_2-\underset{\displaystyle X}{\underset{|}{CH}}-CH_2-\overset{\oplus}{\underset{\displaystyle X}{\underset{|}{CH}}}$$

$$\downarrow \text{ repeating } n CH_2=CHX$$

$$Y-\left[CH_2-\underset{\displaystyle X}{\underset{|}{CH}}\right]_n-CH_2-\overset{\oplus}{\underset{\displaystyle X}{\underset{|}{CH}}}$$

iii) Chain Termination step

$$Y-\left[CH_2-\underset{\displaystyle X}{\underset{|}{CH}}\right]_n-CH_2-\overset{\oplus}{\underset{\displaystyle X}{\underset{|}{CH}}} \xrightarrow{Z^{-}} Y-\left[CH_2-\underset{\displaystyle X}{\underset{|}{CH}}\right]_n-\underset{\displaystyle X}{\underset{|}{CH}}-Z$$

an anion

Anionic Mechanism

i. Chain initiation step

$$Z^{\ominus} + CH_2=CH(X) \longrightarrow Z-CH_2-\overset{\ominus}{C}H(X)$$

A base (anion) → a new anion (carbanion)

ii. Chain Propagation Step

$$Z-CH_2-\overset{\ominus}{C}H(X) + CH_2=CH(X) \longrightarrow Z-CH_2-CH(X)-CH_2-\overset{\ominus}{C}H(X)$$

$$\downarrow\ n\,CH_2=CHX$$

$$Z-\left[CH_2-CH(X)\right]_n-CH_2-\overset{\ominus}{C}H(X)$$

iii. Chain Termination step

$$Z-\left[CH_2-CH(X)\right]_n-CH_2-\overset{\ominus}{C}H(X) \xrightarrow[\text{A Cation}]{H^+} Z-\left[CH_2-CH(X)\right]_n-CH_2-CH_2(X)$$

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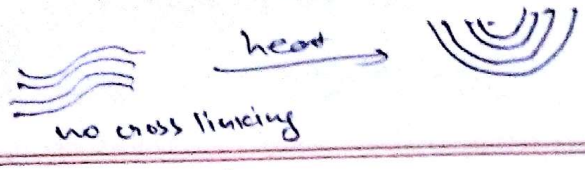
* **Plastics** → Organic material with high mol. weights.

→ moulded into any desired shape, when subjected to heat and pressure in presence of catalyst.

Properties: ① low density ② low cost ③ ~~[illegible]~~ ~~easily moulded~~ ⑤ low weight with high strength ⑥ less brittle ⑤ good toughness ⑥ corrosion resistance, water proofing. ⑦ Insulation of heat and electricity ⑧ easily moulded.

Advantages: ① Plastic is flexible than glass. ② consumes very less energy for recycle compared to glass. ③ used for packaging of various products. ④ plastics are durable.

Disadvantages: ① Non-Renewable ② Non-biodegradable. ③ water and land pollution ④ High toxic fumes when burnt ⑤ plastic bags or products present in water or land are harmful for marine and land animals.

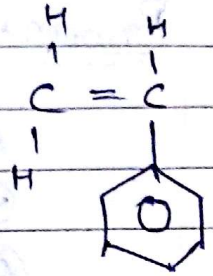


* Thermoplastics: Applications

① Cellulose acetate ② PS ③ PVC ④ Nylons ⑤ PTFE

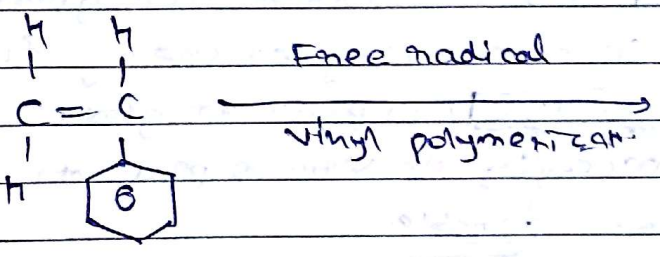
① PS (polystyrene)

Styrene →



↓ obtained by

Polymerisation of styrene dissolved in ethyl benzene in presence of benzoyl peroxide catalyst.



Styrene

Polystyrene

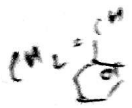
Properties: ① Transparent, light in weight, light stable, excellent moisture resistant.

~~②~~ High resistant to acids and other chemicals.

Uses:

Buttons, buckels, toys, radio.

Disadvantages: → low softening temperature (90-100°C) and brittle



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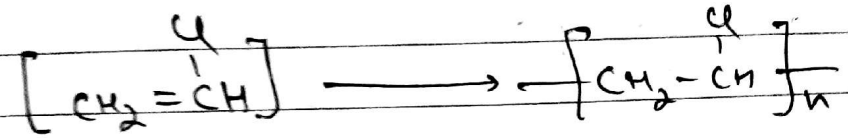
④ Polyvinyl chloride (PVC) → obtained by heating a water emulsion of Vinyl chloride in presence of small amount of benzyl peroxide or hydrogen peroxide in an autoclave under pressure.



Properties

→ Colourless, odourless, inflammable chemically inert, resistant to light.

→ resistant to inorganic acids but soluble in hot chlorinated hydrocarbons such as Ethyl chloride.

→ Greater stiffness and rigidity.

→ Pure resin possess a high softening pt. (148°C)

Uses ① Safety helmets, light fittings.

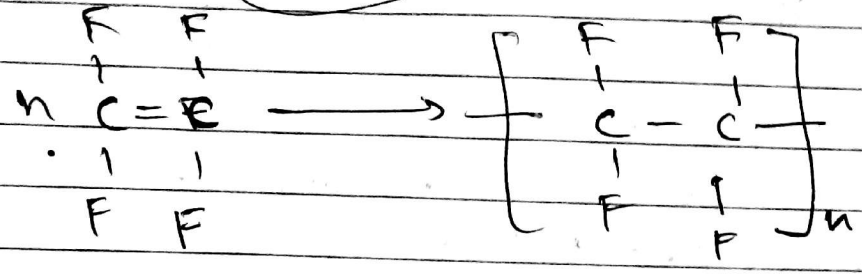
② Tyres ③ Cycle and motorcycle mudguards.

④ Used for making sheets which are employed for tank lining.

→ Plasticized PVC is used for making continuous sheets like table cloths and curtains.

(3) Polytetrafluoroethylene (PTFE) or TEFLON

→ polymerisation of ~~water~~ emulsion of tetrafluoroethylene under pressure in presence of benzoyl peroxide as a catalyst.



Properties: Due to highly electronegative fluorine atoms and regular configuration of teflon results in very strong attractive forces between the different chains.

→ Strong attractive forces give the material extreme toughness, high softening point, high density, waxy touch

Uses: ~~As~~ insulating material (for motors, transformers cables)

→ non-sticking non-stick surface coated utensils

④ **NYLON** (Synthetic fibres)

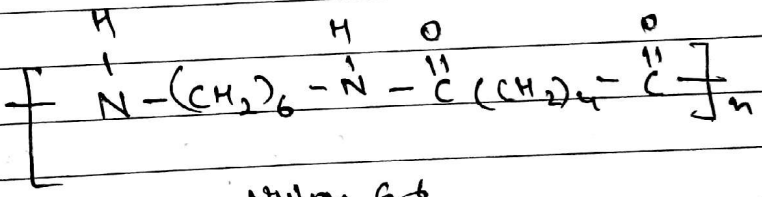
↓

possess amide linkage

Method of preparation: Condensation polymerisation of diamines with di-carboxylic acids and also of amino acids and their lactams. (↑ Water / H_2O)

i. **Nylon 6,6:**

$$n\ HOOC(CH_2)_4COOH + n\ H_2N(CH_2)_6NH_2 \xrightarrow[\text{High press.}]{553K}$$

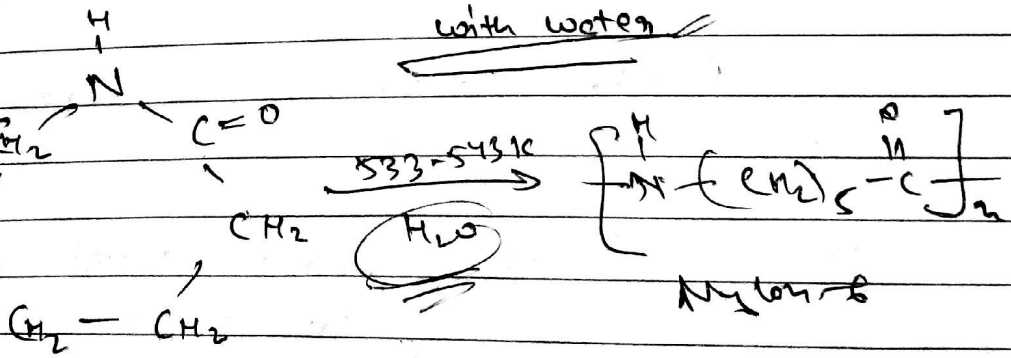


Nylon 6,6

ii. **Nylon**

Uses: Nylon 6,6 is used in making bristles of brushes and in textile industry.

iii. **Nylon-6** → On heating Caprolactum (8-amino caprylic acid) with water



Nylon-6

Uses:- Nylon 6 is used for ropes, fabrics, bearing.

Properties of Nylon:

→ transclucent, coltish, horny, high melting
→ Possess high temp. stability
→ good abrasion resistance
→ insoluble in common organic solvent
→ soluble in phenol and formic acid

(5) CELLULOSE ACETATE: → reacting natural cellulose with acetic anhydride or glacial acetic acid in presence of catalyst (H_2SO_4)

$$\left[C_6H_7O_2(OH)_3\right]_n + 3n\,CH_3COOH \xrightarrow{H_2SO_4}$$

Cellulose

(Cellulose triacetate)

$$\left[C_6H_7O_2(OCOCH_3)_3\right]_n + 3nH_2O$$

Properties

→ Toughness
→ high tensile strength
→ high dielectric properties
→ Resistance towards some mineral acids
→ spun into fibres

Uses: Combs, windows, musical instruments, goggles.

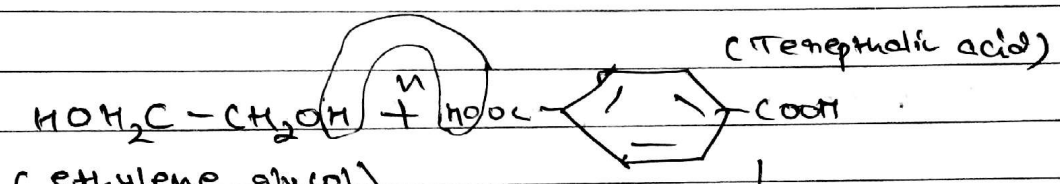
Thermosetting : Applications:

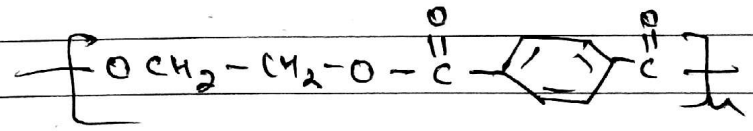
① Bakelite ② Polyesters ③ Epoxy Resins

① Polyesters: eg- Dacron or terylene

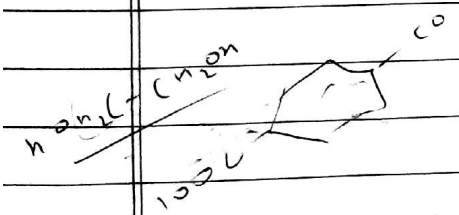
Mostly mixture of ethylene glycol and

terephthalic acid in presence of zinc acetate antimony trioxide catalyst.





↑ Terylene or Dacron



Characteristics

→ Polyesters fabrics and fibres are extremely strong.

→ Very durable : resistant to most chemicals, stretching and shrinking, wrinkle resistant, abrasion resistant.

→ Hydrophobic in nature and quick drying.

→ Polyester retains its shape.

→ easily washed and dried.

Uses of Polyester:

(1) To make polyester suits

(2) Due to its strength, it is used to make ropes in industries.

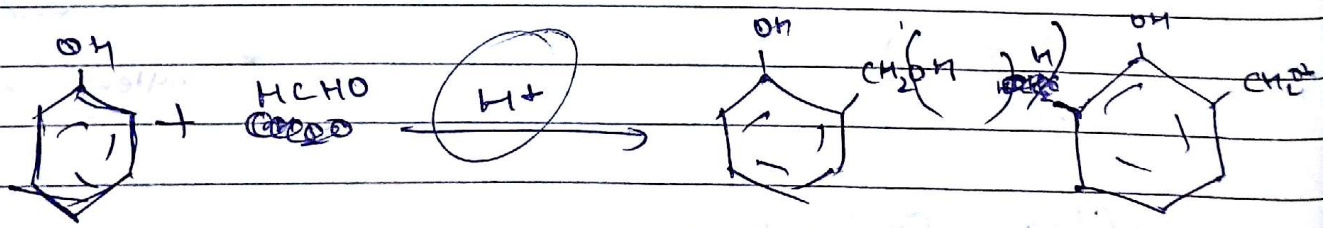
(3) PET bottles are most popular uses of polyester

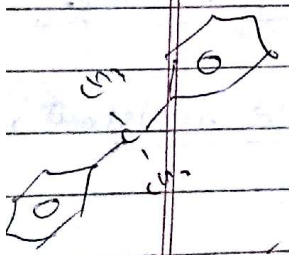
(4) Dacron fibre is crease resistant.

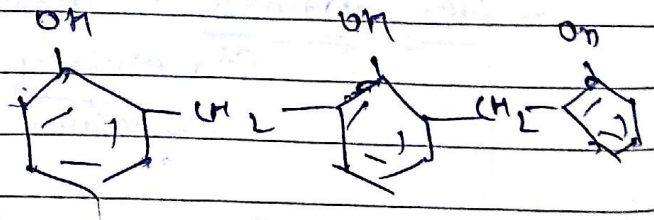
(5) Used for making safety helmets.

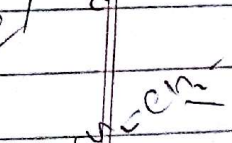
(2) BAKELITE, OR, PHENOL-FORMALDEHYDE POLYMER

→ formed from condensation reaction of phenol with formaldehyde in presence of catalyst such as zinc-chloride, HCl.









Novolac

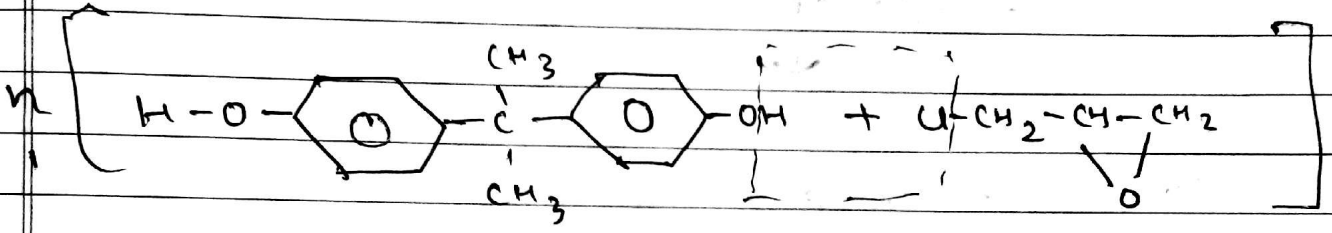
Δ

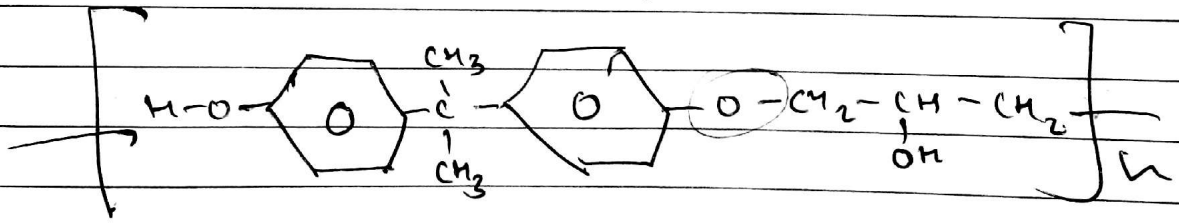
Cross linked

Bakelite

Uses: It is used for its electrical non-conductivity and heat resistant properties in electrical insulators, radio, firearms.

(3) EPOXY RESINS: Condensation of bis-phenol and epichlorhydrin





3-D cross linked structure

Properties: Due to presence of ether linkage: resistance to water, various solvents, acids, excellent adhesive in nature.

Uses: General purpose adhesives, as binders in cement and mortars.

Methods to find molecular mass of polymer

Classification of polymer masses

① **No. average** molecular mass: (good index of tensile strength)

$$M_n = \frac{w}{\Sigma N} = \frac{\text{Total mass of all molecules in polymers}}{\text{total no. of molecules}}$$

$$= \frac{\Sigma N_i M_i}{\Sigma N_i}$$

② **Weight average** molecular mass

→ measures molecular size

$$\bar{M}_w = \frac{\Sigma w_i M_i}{\Sigma w_i}$$

∴ w_i → weight fraction of molecules whose mass is M_i

③ **Viscosity - average**

$$M_v = \left[\frac{\Sigma w_i M_i^a}{\Sigma w_i}\right]$$

Elastomer → man-made rubber like polymers which can be stretched to at least thrice its length but it reverts to its original shape and dimensions as soon as stretching force is removed.

having low Young's Modulus
high failure strain.

Types: ① Thermosets
② Thermoplastic

→ Elastomers are usually thermosets (requires vulcanisation)

• Natural Rubber:

→ manufactured from rubber latex which is colloidal dispersion of rubber in water.

→ linear polymer of iso-prene (2 methyl -1,3 - butadiene)

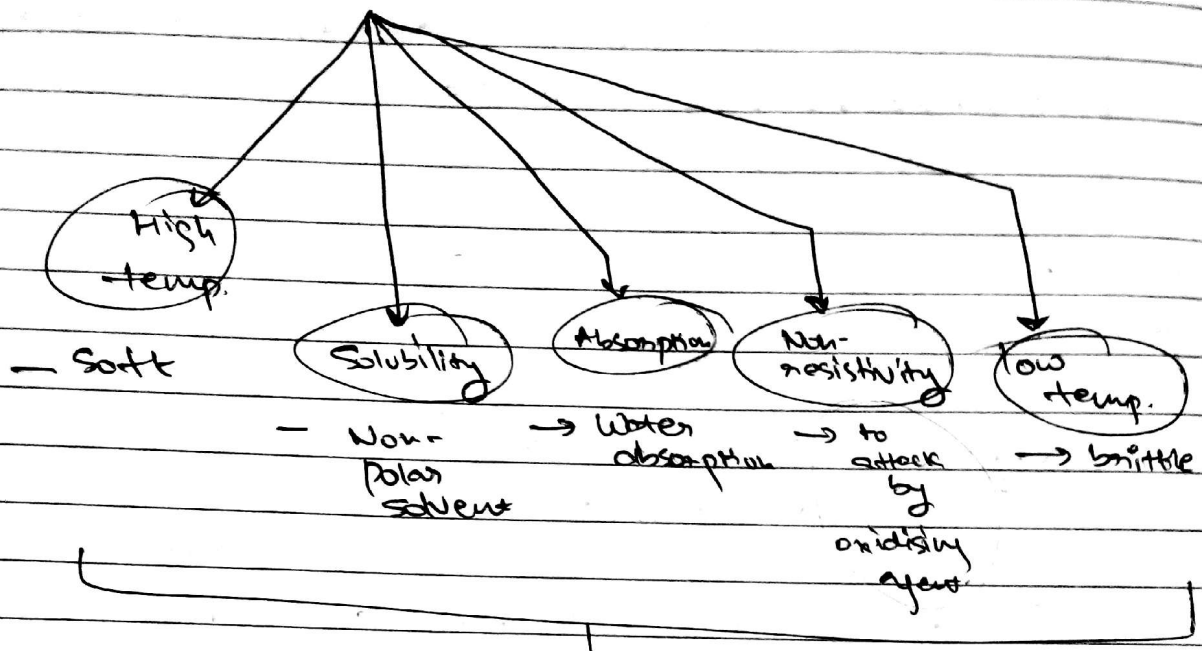
$$n\,CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH=CH_2 \longrightarrow \left[CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH-CH_2\right]_n$$

isoprene

Natural Rubber (polyisoprene)

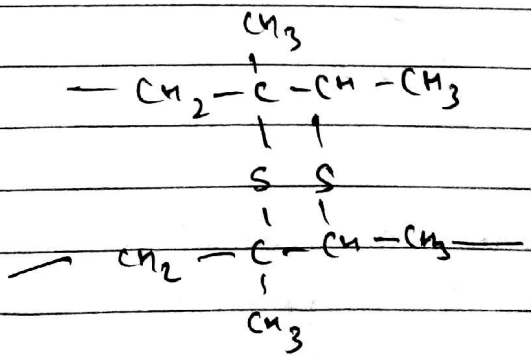
★★ Cis-polyisoprene consists of various chains held together by weak Vander Waals interaction and coiled structure. Thus it can be stretched like spring and exhibits elastic properties.

Natural Rubber



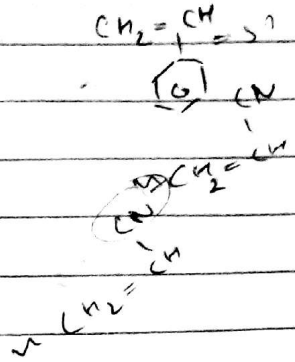
To improve this we need Vulcanisation.

The process of heating a mixture of raw rubber with Sulphur and an appropriate additive at a temp. range between 373K to 415 K. On Vulcanisation Sulphur forms cross links at the reactive site of double bond and thus the rubber gets stiffened.



Synthetic Rubber:

1. Styrene rubber (BUNA-S)
2. Nitrile rubber (BUNA-N)
3. Neoprene
4. Thiokol Rubber



1. Nitrile Rubber (Buna-N) (GR-A)

Copolymer of **Butadiene** and **acrylonitrile**

$$CH_2=CH-CH=CH_2 + nCH_2=\underset{\displaystyle CN}{\underset{|}{CH}} \xrightarrow{\text{copolymerisation}} \left(CH_2-CH=CH-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2\right)_n$$

(1,3-butadiene)

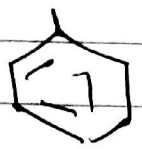
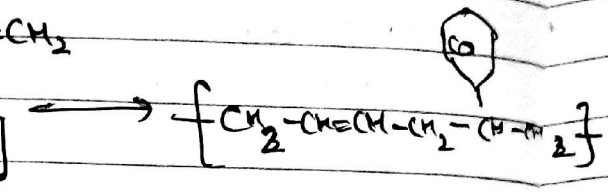
Properties: → **Less resistance** to alkali than natural rubber because of the presence of cyano group.

→ As the proportion of acrylonitrile is increased, the resistance to heat, oil, sunlight, acid and salt increases.

Uses: For making conveyer belts, high altitude aircraft components, printing rollers.

(2) Styrene Rubber: (Buna-S)- (GR-S)

copolymerisation of butadiene and styrene

$n\,CH_2=CH-CH=CH_2$ + n  → 

Chloroprene

Styrene

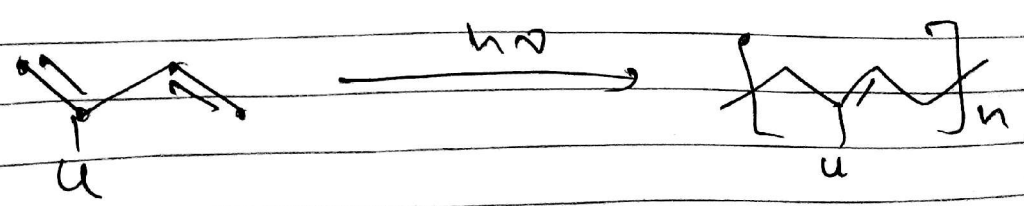
Properties: It resembles natural rubber in processing characteristics as well as quality of the finished product.

→ High abrasion resistance
→ High load bearing capacity
→ But gets readily oxidized.
→ It can be vulcanised by sulphur or sulphur monochloride (S_2Cl_2)

Uses:

Manufacturing tyres, floor tiles, shoe sole

(3) Neoprene (polychloroprene) (2-chloro 1,3 butadiene)



Properties: • Good mechanical strength
→ good aging resistance
→ good resistance toward chemicals.
→ moderate oil and fuel resistance
→ high ozone and weather resistance.

Biomedical use: (1) Neoprene suits may save women's life with obstetrical hemorrhage (heavy bleeding during pregnancy). It provides compression to the abdominal cavity. The compression realized by the suits moves blood from the inferior extremities and abdominal organs to vital organs.

Wetsuit: It traps water b/w suit and person's skin body heat warms the water against the skin which helps to reduce heat loss from the body. A person can stay longer in cold water.

(2) Thiokol Rubber

Condensation of 1-2-dichloroethane with sodium polysulphide

$$Cl-CH_2-CH_2-Cl + Na^+S-\overset{\overset{S}{\|}}{S}-\overset{\overset{S}{\|}}{S}-Na^+$$

Sodium poly sulphide

$$\left(-CH_2-CH_2-\overset{\overset{S}{\|}}{S}-\overset{\overset{S}{\|}}{S}-\right)_n + nNaCl$$

Thiokol rubber

resistant to action of petrol lubricants

Properties →

→ resistant to action of oxygen and ozone

→ impermeable to gases to large extent.

Uses:→ Thiokol mixed with oxidising agent can be used as a fuel in rocket engine.

→ Used in hoses and tank lining for handling and storage of oils and solvents.

* Rubber Compounding - It is mixing of rubber with other substances

* Following materials may be incorporated:

(1) Softeners or plasticizers.
- provide good tenacity and adhesion
eg. Vegetable oils, waxes etc.

(2) Vulcanizing agent
- Sulphur is added b/w 0.15 to 32 %.

(3) Accelerators:
- shortens the process of vulcanization time.
eg. 2-mercaptoil.

(4) Anti-oxidant: Natural rubber is prone to get oxidised easily and hence decomposed. therefore anti-oxidants materials are used.
eg. Complex amines

(5) Reinforcing fillers:

→ provide strength and rigidity to rubber products.

Eg. Carbon black.

(6) Colouring matter

→ added to give desired coloured.

Eg. Titanium dioxide → White colour

Coloured pigments → Chromium oxide - green

Ferric oxide - red

lead chromate - yellow

Harvesting in rubber is known as tapping.

LPG → Mixture of propane and butane. gaseous at normal atmospheric pressure, but may be condensed to liquid state at normal temp. by the application of moderate pressures. LPG vapour is denser than air.

→ They are stored and transported as liquids.

→ In still air. vapour will disperse slowly

Natural Gas → Methane is the main constituent (95% at total vol.)

→ high calorific value fuel requiring no storage facilities.

→ It mixes with air readily and does not produce smoke or soot.

→ It is lighter than air.

→ dispense in air easily in case of leak