Synthesis and Applications of Industrial Polymers

Polymer
- Poly → many
- mer → units

* **Polymers**: Polymers are macromolecules formed by the combination of many small molecules called monomers.
* molecular wt. of polymers: $500 - 10^6$ u

* **polymerization**: The process of formation of polymers from monomers is called polymerization.

eg. polyethylene is made by repeatedly linking ethylene.

$$nCH_2=CH_2 \longrightarrow (-CH_2-CH_2)_n$$

ethylene (monomer) → polythene

* **classification of polymers**

classification on the basis of:

- Origin
  - natural
  - semisynthetic
  - synthetic
    - addition
    - condensation
- molecular forces
  - thermoplastics
  - thermosette
  - elastomers
  - fibers
- structure
  - linear
  - branched
  - crosslinked

Origin: 1. **Natural polymers**: obtained from natural sources like cotton, wood, natural rubber, proteins etc

2. **Semisynthetic polymers**: obtained by modifying the properties of natural polymers. for eg. natural rubber is weak, sulphur is cooked into it to make vulcanized rubber. Vulcanized rubber is many times stronger & harder than natural rubber.

Other examples: cellulose acetate, cellulose nitrate (celluloid)

3. **Synthetic polymers**: are completely man-made

addition polymers: unsaturated monomers undergo addition reaction to form a saturated polymer. for eg. polyethylene, poly vinyl chloride

condensation polymers: condensing of saturated bi-functional monomers

eg. polyamide, polyester, polyether.

Differences between addition and condensation polymerization

Addition polymerization / polymers	Condensation polymerization / polymers
1. Monomers add on to each other without forming any by products	1. Monomers condense to form polymers low wt. molecules like H_2O, HCl are formed as by products.
2. condition: monomer must have at least a single double bond.	2. condition: monomer must have 2 diff / identical functional groups.
3. chain-forming rxn.	3. step-wise rxn (product may take hrs or days to form).
4. addition polymerization is fast, gives rise to high molecular wt polymers	4. is slow, gives rise to low molecular wt. polymers.
5. thermoplastics are formed	5. thermosettes are formed
6. non-biodegradable, not recyclable	6. biodegradable, recyclable
7. molecular wt = an integral multiple of wt. of monomer	7. molecular wt ≠ an integral multiple of the wt of the monomer.

Classification of polymers on the basis of molecular forces.

⇒ Thermoplastics & Thermosettes

Thermoplastics	Thermosettes
1. Formed by addn. polymerization	1. formed by condensation polymerization
2. bound by ~~ee~~ Vanderwaal's forces (sometimes inter-chain hydrogen bonding)	2. bound by covalent bonds
3. linear / branched long chain polymers	3. network-like structure
4. soften on heating. This is because their binding Vanderwaal's forces can easily be overcome on applying heat & pressure	4. do not soften on heating as the covalent bonds maintain their strength.

5. Harden on cooling	5. harden on heating
6. can be remoulded multiple times	6. cannot be remoulded once set
7. soft, weak, less brittle	7. hard, strong, more brittle
8. low melting pt	8. high melting pt
9. low tensile strength	9. high tensile strength
10. Formed by extrusion, blow moulding, transverse moulding	10. formed by compression & injection moulding
11. eg. PE, PVC	11. bakelite, urea-formaldehyde

Fibres • structure → thread like
• bonding → H bonding
• properties → high tensile strength such that they can be drawn into threads (stronger than thermoplastics)
• eg → nylon, PET

Elastomers : structure → coiled chains
• bonding → weak Vanderwaals forces
• properties → can be elongated under stress, regains the original shape after removing stress
• eg → natural rubber, butyl rubber

Classification on the basis of structure

• **Linear polymers** : • monomers linked by covalent bonds
long chains linked by Vanderwaals forces / hydrogen bonding
• chains closely packed ⇒ high density polymers like HDPE

• **Branched homo polymers** : • some chains ⊥r to the main chain
• chains are farther apart ⇒ low density polymers like LDPE

• **Crosslinked polymers** : linear chains are linked by covalent bonds, network like structure
• polymer is hard and brittle, eg. bakelite

(draw diagrams.)

Functionality : no. of reactive / bonding sites in a monomer is called its functionality

- All monomers are molecules, but all molecules are not monomers.

For eg. water is a molecule, but it cannot undergo polymerizations. It is not a monomer. Its functionality is 0.

Consider the alcohols, methanol (monohydric alcohol) and ethylene glycol, which is a dihydric alcohol. Methanol can dimerize to form dimethyl ether, but it would undergo no further rxn after that. However, ethylene glycol would dimerize to form poly ethylene glycol, which is capable of further polymerization.

In other words, for a molecule to become a monomer, its functionality should be ≥ 2.

Significance: • Bifunctional monomers yield linear polymers. But under certain experimental conditions, they can form branched polymers too. eg. LDPE.

- If a mixture of bifunctional, trifunctional monomers are used, excessive branching occurs ⇒ crosslinked polymers are formed

Degree of polymerization : no. of monomer units present in a polymeric chain. For eg. in polyethylene, $-(CH_2-CH_2)-_n$ n is an integer representing the degree of polymerization.

Mathematically, $DP = \dfrac{\text{molecular wt. of the polymer}}{\text{molecular wt. of the monomer}}$

Addition Polymerization

1. cationic
2. anionic
3. free radical
4. coordination.

The steps involved are initiation, propagation & termination.

Cationic Polymerization

Initiator : Lewis acids / mineral acids like BF_3, $AlCl_3$, $ZnCl_2$

co-catalyst : water

terminator : toluene

(1) Polymerization of ethylene

monomer : ethylene

polymer : polyethylene

Initiation

(i) $BF_3 + H^+ \longrightarrow [BF_3OH^-] + H^+$

(ii) $CH_2 = CH_2 + H^+ \longrightarrow \overset{+}{C}H_2 - CH_2(H)$

Propagation

$CH_3 - \overset{+}{C}H_2 + CH_2 = CH_2 + [BF_3OH^-] \longrightarrow CH_3 - CH_2 - CH_2 - \overset{+}{C}H_2$

$CH_3 - CH_2 - CH_2 - \overset{+}{C}H_2 + CH_2 = CH_2 \longrightarrow CH_3 - CH_2 [CH_2 - CH_2]_n CH_2 - \overset{+}{C}H_2 + [BF_3OH^-]$

Termination

$CH_3 - CH_2 [CH_2 - CH_2]_n CH_2 - \overset{+}{C}H_2 + [BF_3OH^-] \xrightarrow{-H^+}$

$CH_3 - CH_2 [CH_2 - CH_2]_n CH = CH_2 + BF_3 + H_2O$

(HDPE & MDPE formed)

Note: • In termination, the carbon carrying the +ve charge will not lose hydrogen.

• The product is a live polymer, chain keeps growing, and after termination, the end is a unsaturated unit.

(2) Polymerization of propylene

Initiation: $BF_3 + H_2O \rightarrow H^+ + [BF_3OH^-]$

$CH_3-CH=CH_2 + H^+ \rightarrow CH_3-\overset{\oplus}{C}H-CH_2-H$

* when there are substituents, the +ve charge is on the C next to the substituent.

Propagation

$$CH_3-\overset{\oplus}{C}H-CH_3 + CH_3-CH=CH_2 + [BF_3OH]^- \longrightarrow CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{\oplus}{C}H-CH_3$$

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{\overset{\oplus}{CH}}} + CH_2=CH-CH_3 + [BF_3OH]^- \longrightarrow CH_3-\underset{CH_3}{\underset{|}{CH}}\left[CH_2-\underset{CH_3}{\underset{|}{CH}}\right]_n CH_2-\underset{CH_3}{\underset{|}{\overset{\oplus}{CH}}}$$

Termination

$$CH_3-\underset{CH_3}{\underset{|}{CH}}\left[CH_2-\underset{CH_3}{\underset{|}{CH}}\right]_n CH_2-\underset{CH_3}{\underset{|}{\overset{\oplus}{CH}}} + [BF_3OH^-] \xrightarrow{-H^+} CH_3-\underset{CH_3}{\underset{|}{CH}}\left[CH_2-\underset{CH_3}{\underset{|}{CH}}\right]_n CH=\underset{CH_3}{\underset{|}{CH}} + H_2O + BF_3$$

③ Polymerization of butylene

Initiation

$BF_3 + H_2O \longrightarrow [BF_3OH^-] + H^+$

$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 + H^+ \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_2-H$$

$$= (CH_3)_3C^+$$

Propagation

$$(CH_3)_3C^+ + CH_2=\underset{CH_3}{\underset{|}{C}}-CH_3 + [BF_3OH^-] \longrightarrow (CH_3)_3C-CH_2-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_3 + [BF_3OH]^-$$

$$(CH_3)_3C-CH_2-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_3 + CH_2=\underset{CH_3}{\underset{|}{C}}-CH_3 + [BF_3OH^-] \longrightarrow (CH_3)_3C\left[CH_2-\overset{CH_3}{\underset{CH_3}{\underset{|}{\overset{|}{C}}}}\right]_n CH_2-\overset{CH_3}{\underset{CH_3}{\underset{|}{\overset{|}{C}}}}\ +$$

Termination

$$(CH_3)_3C - \left[CH_2 - \underset{CH_3}{\overset{CH_3}{C}} \right] - CH_2 - \underset{CH_3}{\overset{CH_3}{C^+}} + [BF_3OH^-] \xrightarrow{-H^+}$$

$$(CH_3)_3C - \left[CH_2 - \underset{CH_3}{\overset{CH_3}{C}} \right] - CH = \underset{CH_3}{\overset{CH_3}{C}} + BF_3 + H_2O$$

Anionic Polymerization

(groups ~~show~~ that have substituents that show -I effect (aka pull electrons to themselves Cl, CN) undergo anionic polymerization.

Initiator: Lewis base like soda amide ($NaNH_2$) or KNH_2

terminator: alcoholic ammonia

(1) Preparation of PAN: polyacrylonitrile

Initiation

$$KNH_2 \longrightarrow K^+ + \bar{N}H_2$$

$$H_2N^- + CH_2 = CH - CN \longrightarrow H_2N - CH_2 - \underset{CN}{\overset{\ominus}{CH}}$$

Propagation

$$H_2N - CH_2 - \underset{CN}{\overset{\ominus}{CH}} + CH_2 = CH - CN \longrightarrow H_2N - CH_2 - \underset{CN}{CH} - CH_2 - \underset{CN}{\overset{\ominus}{CH}}$$

$$H_2N - CH_2 - \underset{CN}{CH} - CH_2 - \underset{CN}{\overset{\ominus}{CH}} + CH_2 = CH - CN \longrightarrow H_2N - CH_2 - \underset{CN}{CH} - CH_2 - \underset{CN}{CH} - CH_2 - \underset{CN}{\overset{\ominus}{CH}}$$

$$= H_2N - CH_2 - \underset{CN}{CH} \left[CH_2 - \underset{CN}{CH} \right]_n CH_2 - \overset{\ominus}{CH} - CN + K^+$$

Termination

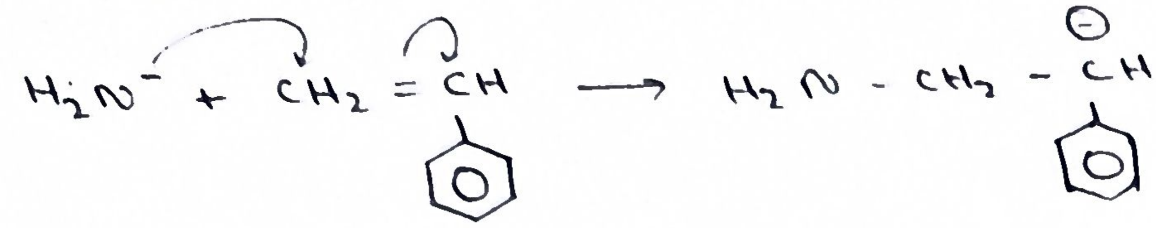
$$H_2N - CH_2 - \underset{CN}{CH} \left[CH_2 - \underset{CN}{CH} \right]_n CH_2 - \overset{\ominus}{CH} - CN + K^+ \xrightarrow{NH_3}$$

$$H_2N - CH_2 - \underset{CN}{CH} \left[CH_2 - \underset{CN}{CH} \right]_n CH_2 \underset{CN}{CH_2} + KNH_2$$

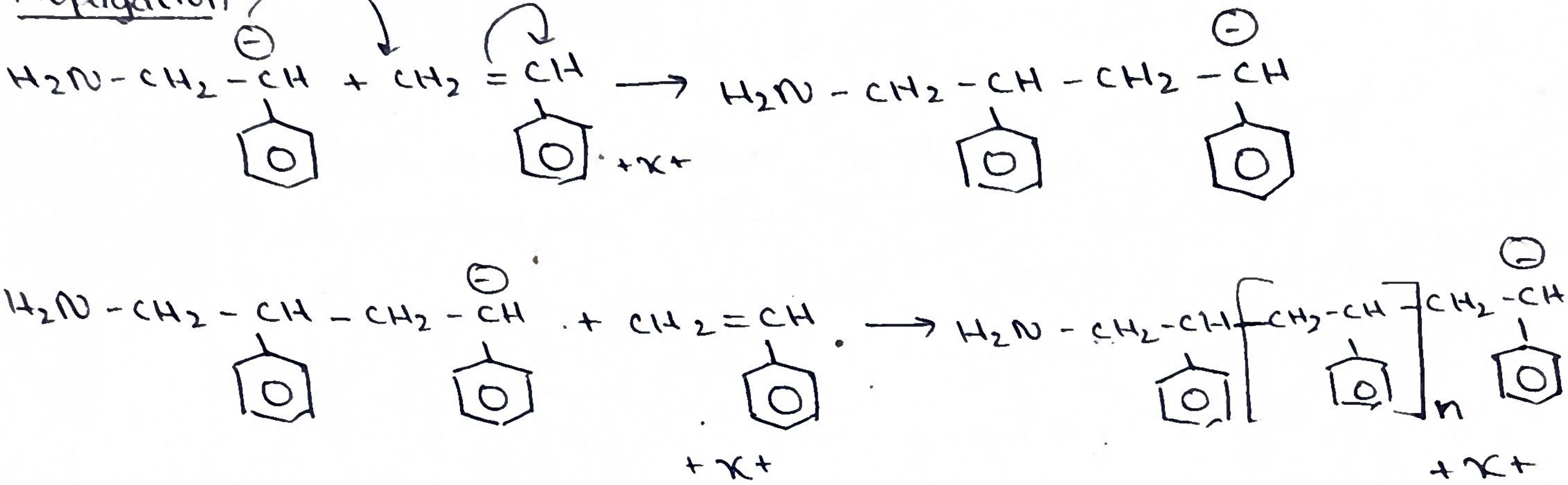
(2) Preparation of polystyrene

Initiation

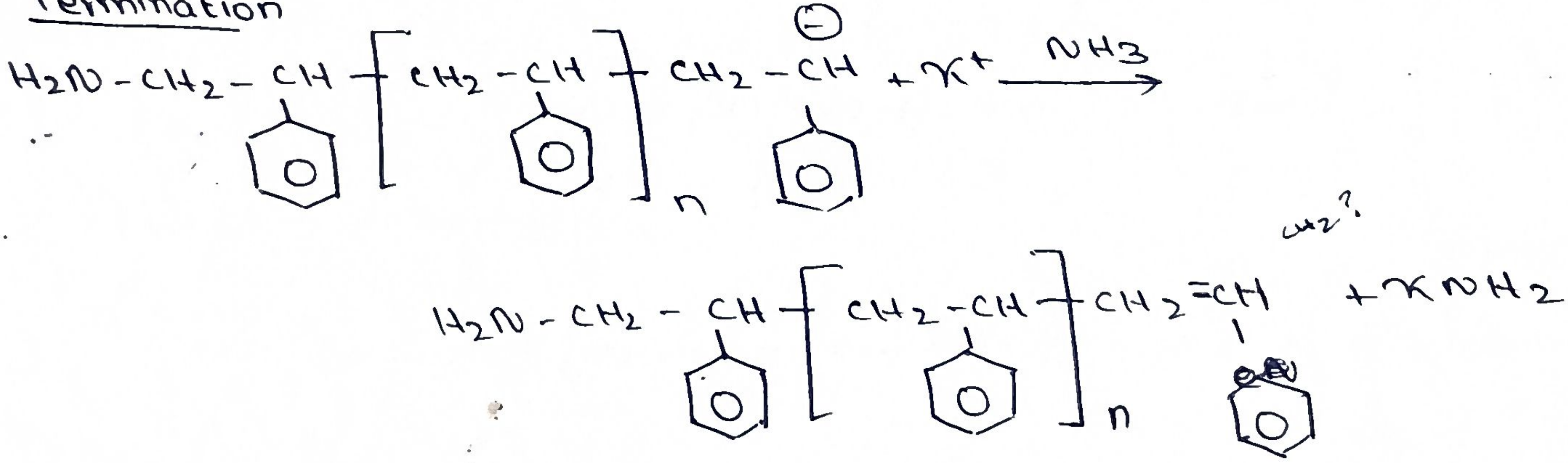
$KNH_2 \longrightarrow K^+ + \bar{N}H_2$



Propagation



Termination



Note: usually dead polymers are formed during anionic polymerization

Free Radical Polymerization

Initiator: peroxides like

(a) benzoyl peroxide : $C_6H_5-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5$

(b) acyl peroxide : ~~C6H5~~ $CH_3-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-CH_3$

(c) allyl peroxide : $C_6H_5-O-O-C_6H_5$

(d) (OR) use AIBN: azo bis iso butyro nitrile : $CN-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-CN$

Temperator : 200°C

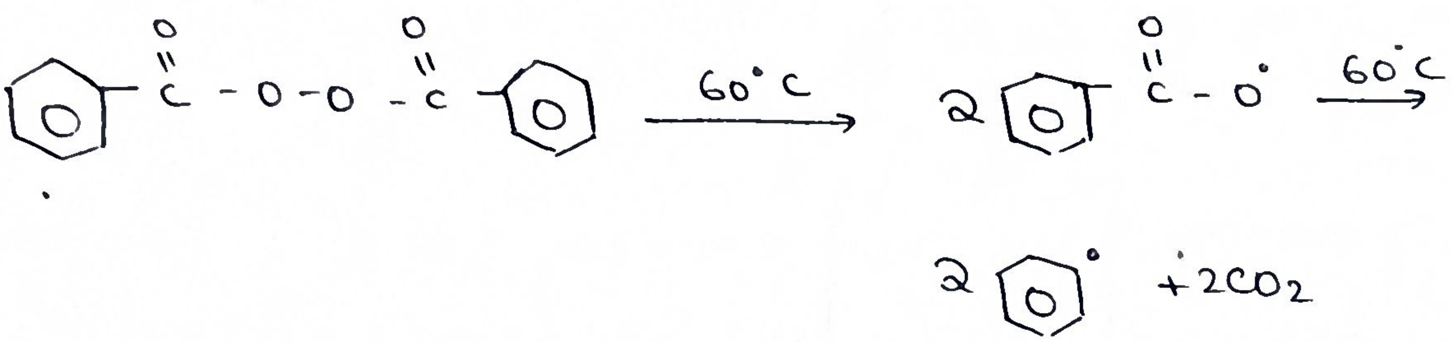
Time : a few minutes

Pressure > 500 atm

Terminator: alcohols / ketones

Preparation of LDPE

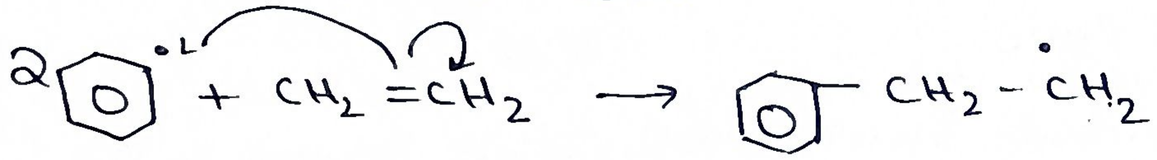
Initiation: (i) decomposition of initiator via homolytic cleavage



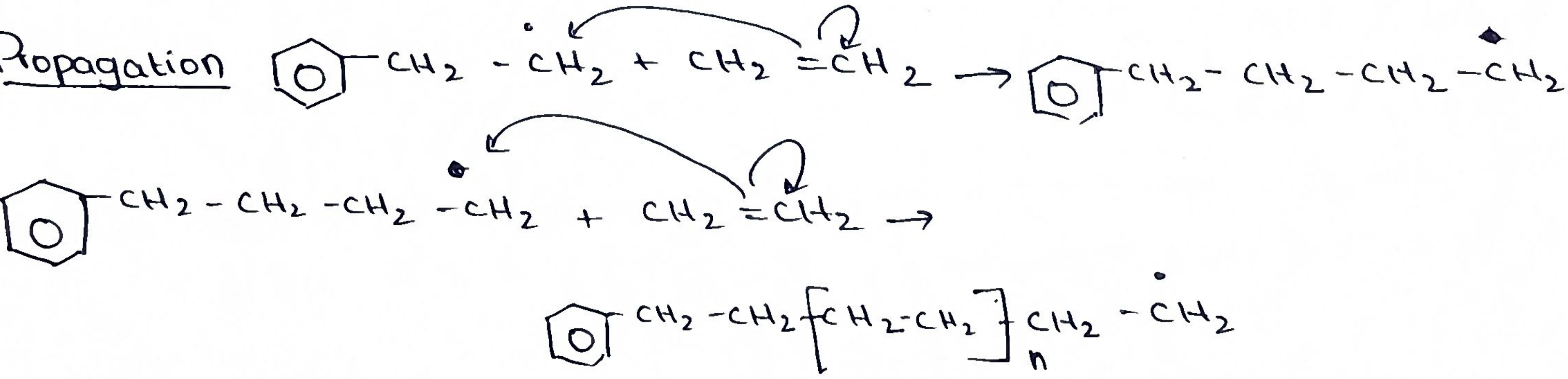
with AIBN

$$CN-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-CN \xrightarrow{\Delta} 2\,CN-\underset{CH_3}{C}-N^{\circ} \xrightarrow{\Delta} 2\,CN-\underset{CH_3}{\overset{CH_3}{C^{\circ}}} + N_2$$

(ii) formation of carbon radical

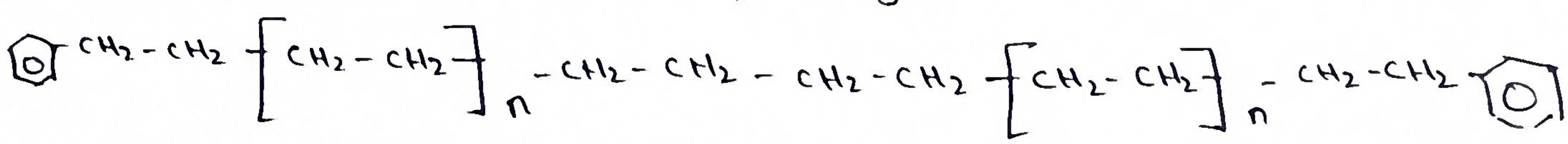


Propagation



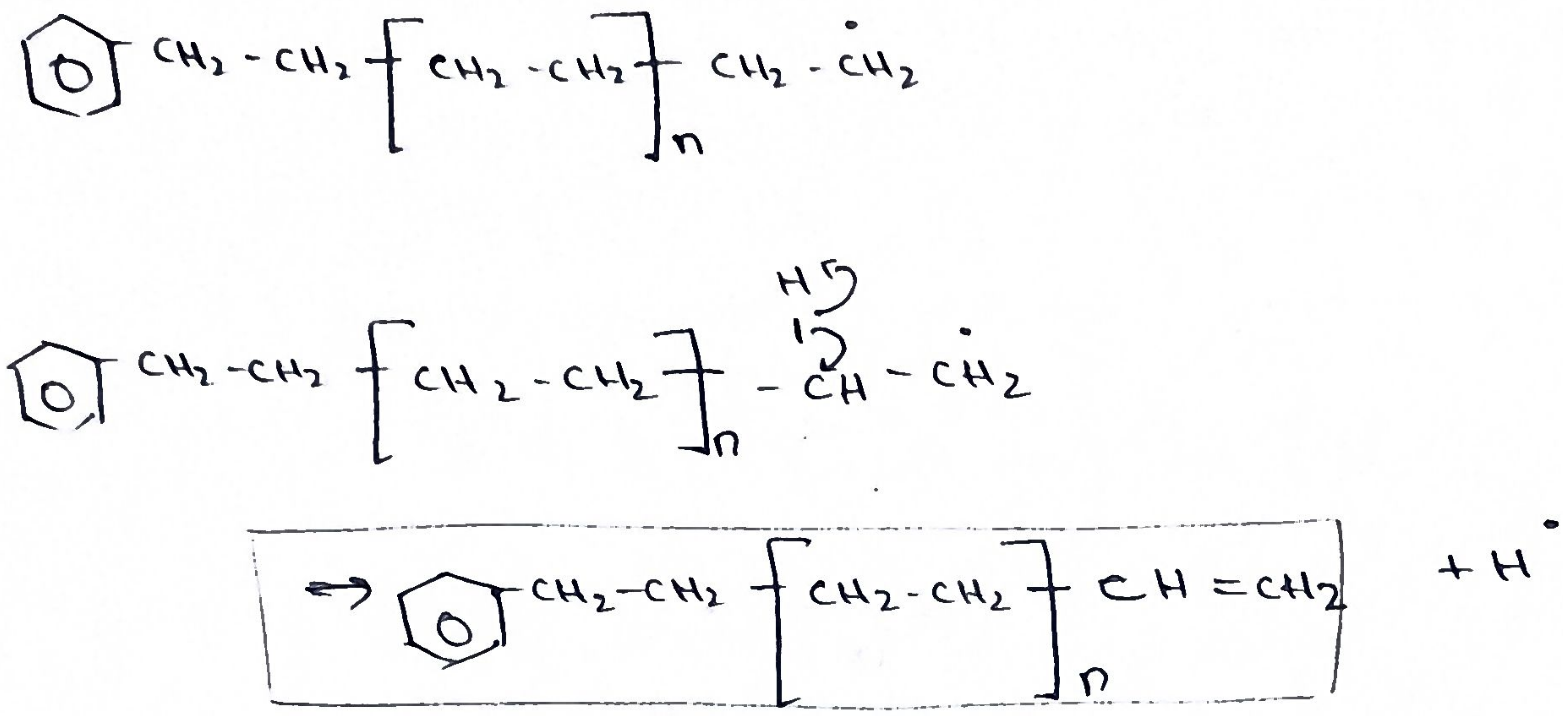
Termination

(i) By combination / coupling to form a dead polymer

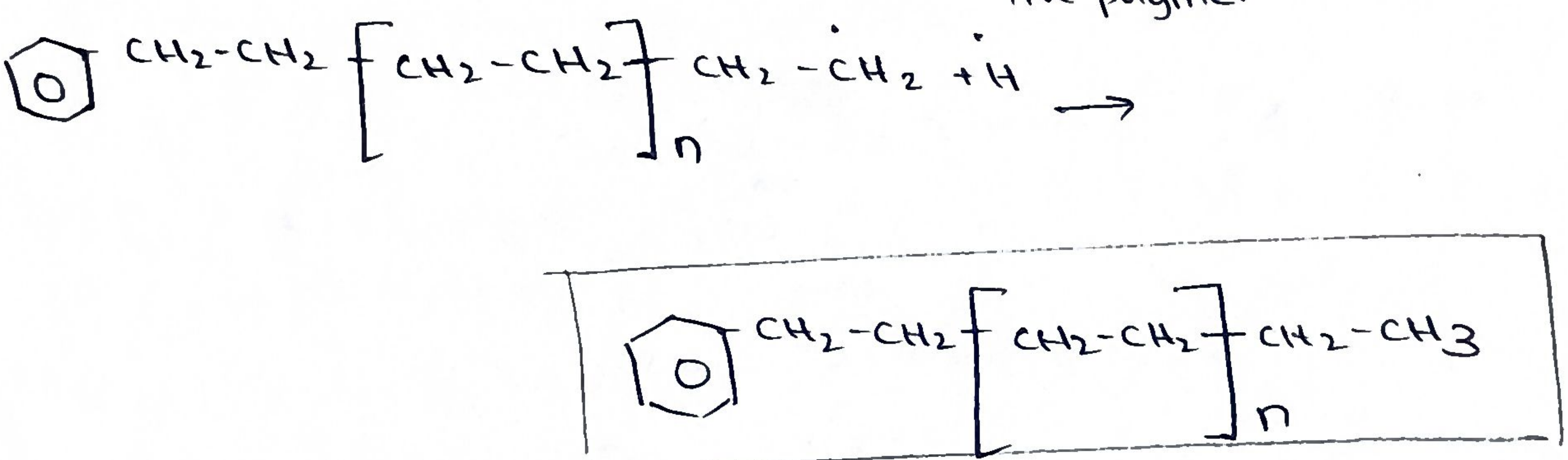


(dead polymer)

(ii) By disproportionation



live polymer



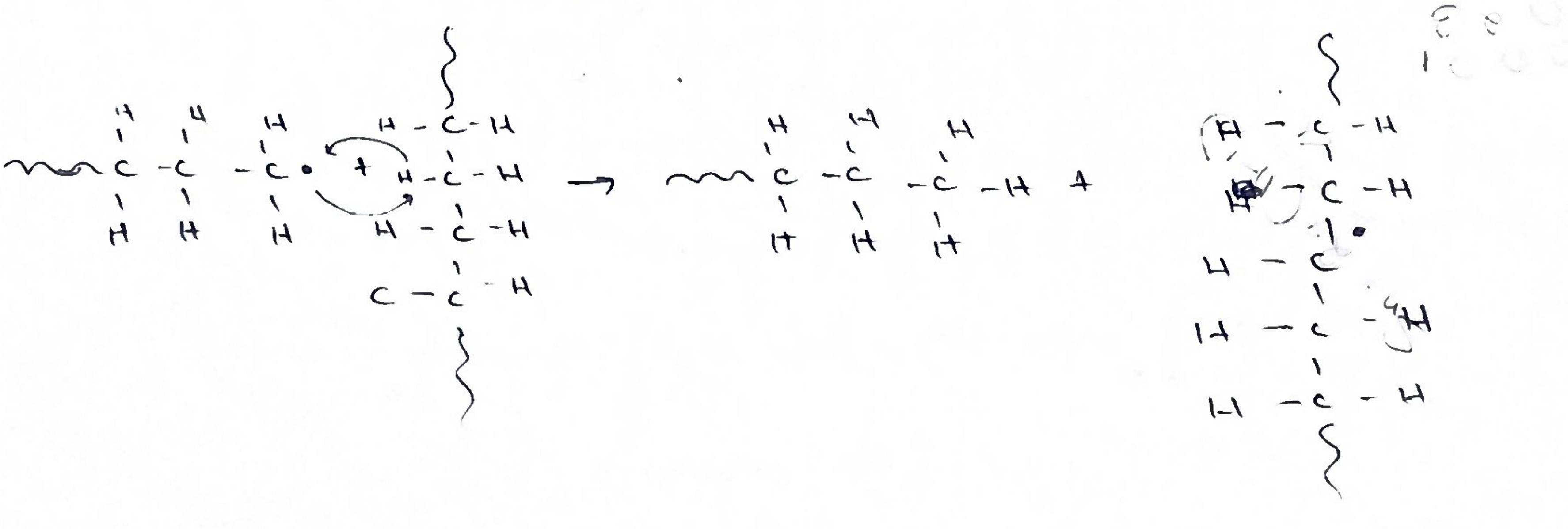
dead polymer.

Branching in PE / Formation of LDPE

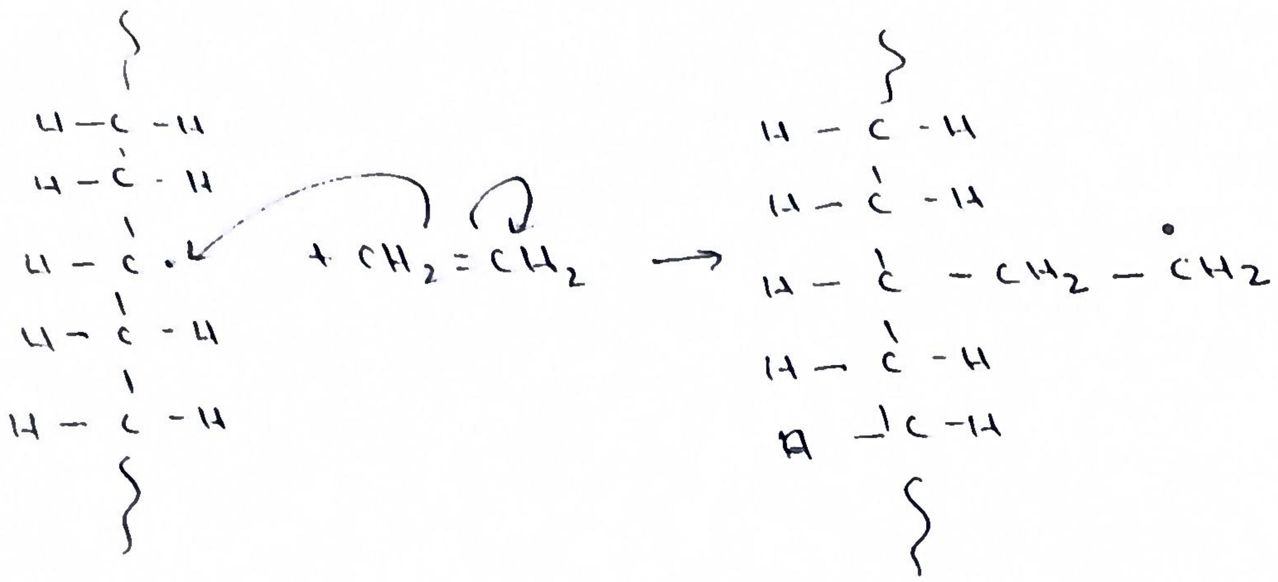
Depending on the time, temp, pressure branching may occur, leading to the formation of LDPE.

It happens as follows:

(a) Formation of a radical in the middle of a chain due to the transfer of H° from one chain to another.



(ii) Addition of a monomer to the newly formed radical



Coordination Polymers

Stereo specific polymers are prepared using coordination polymerization

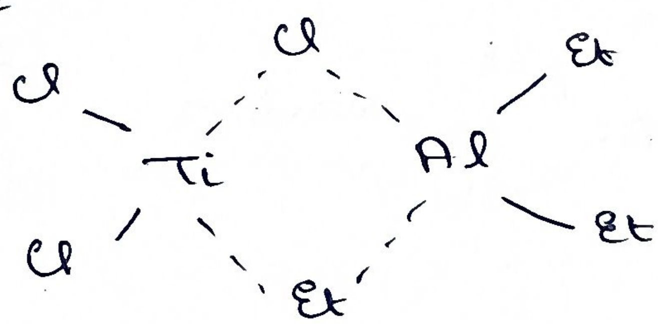
For eg. isotactic polyacetylene is formed at $-78°C$

syndiotactic polyacetylene is formed at $150°C$

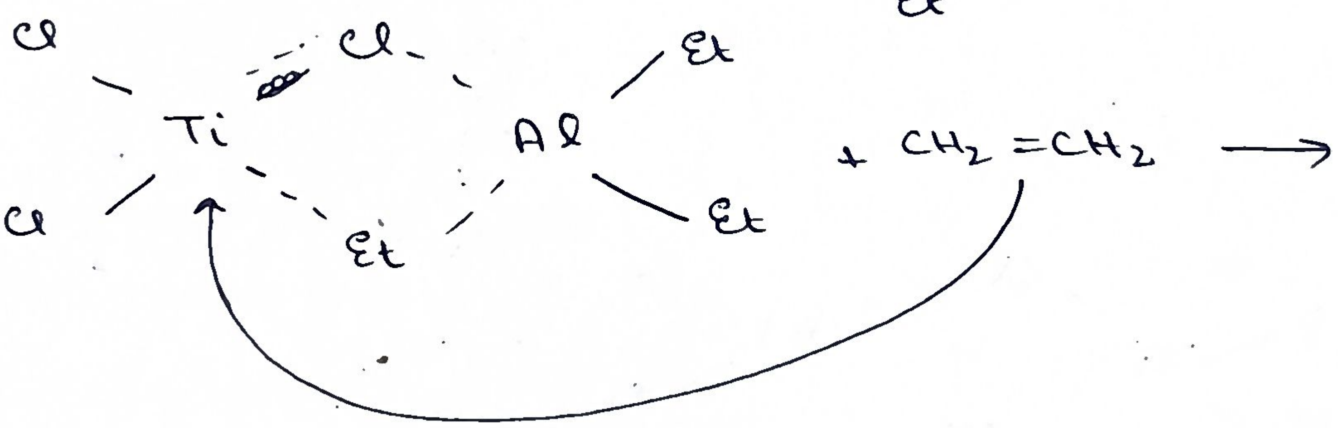
Preparation of polyethylene

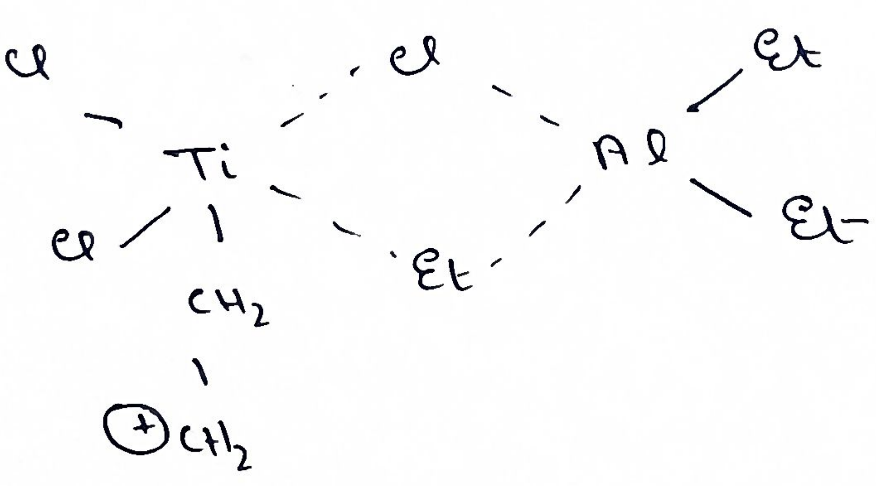
Ziegler Natta Catalyst

$TiCl_3 + Al(Et)_3 \rightarrow$

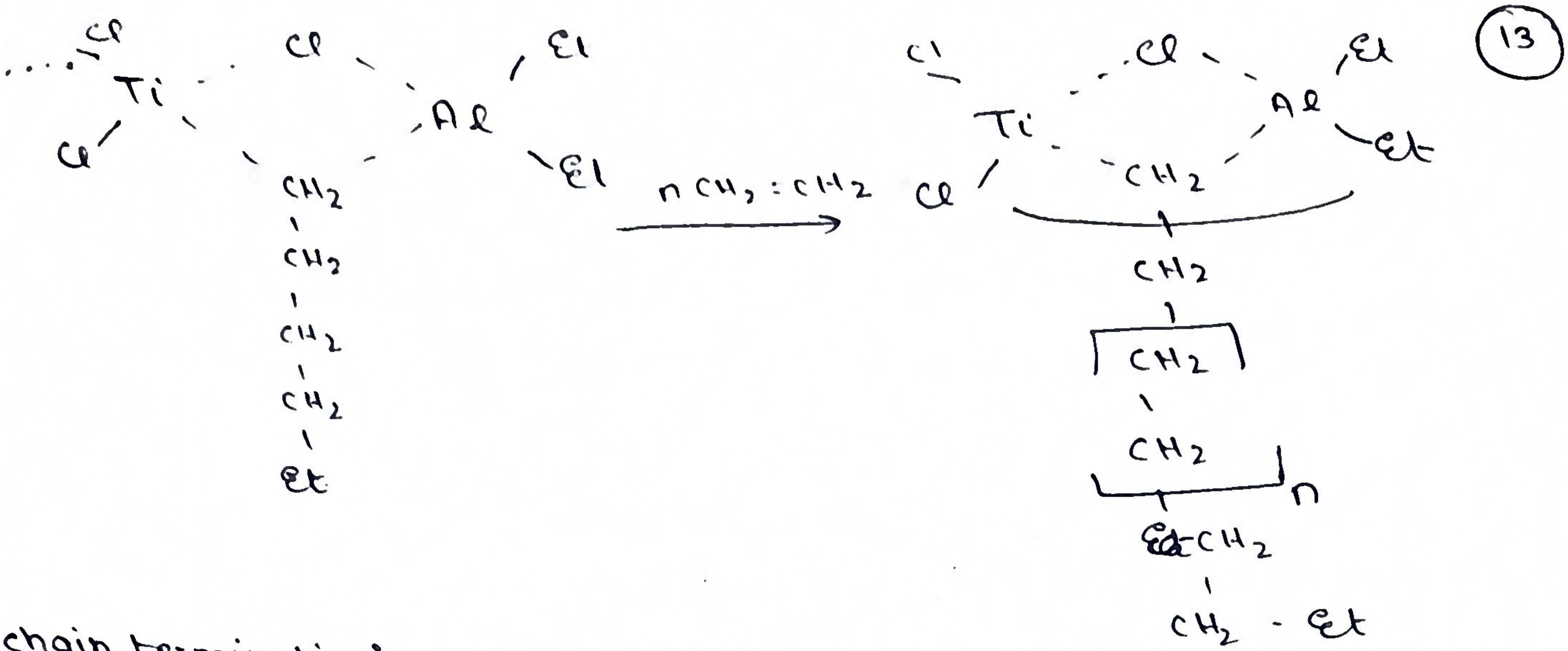


chain initiation

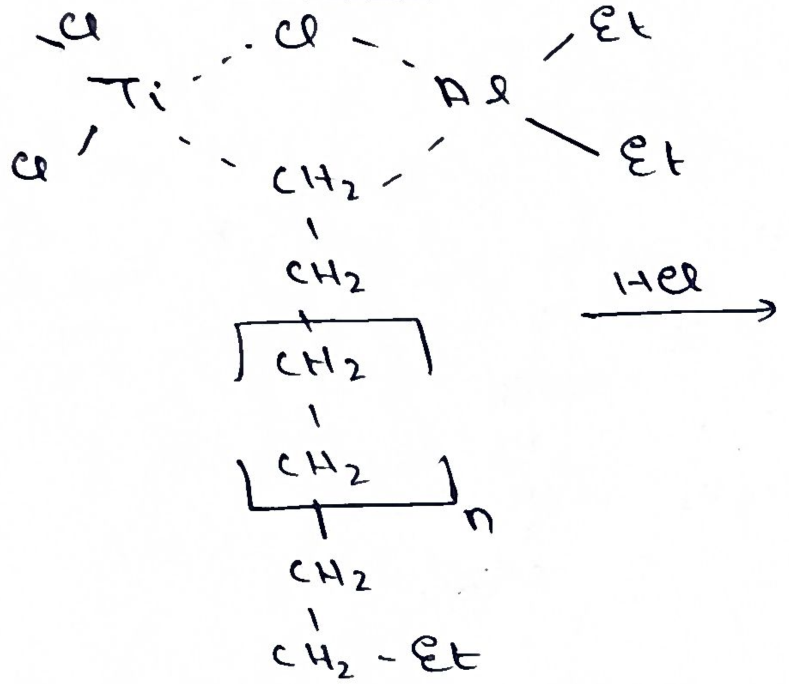


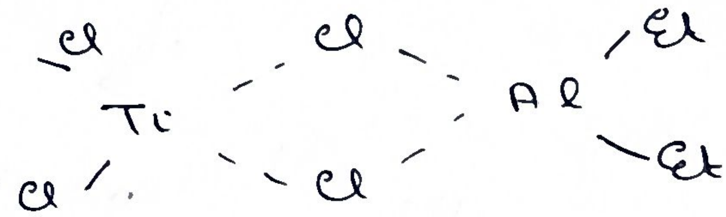


(ii) chain propagation involving the migration of the ethyl group



chain termination:





modified Ziegler Natta catalyst

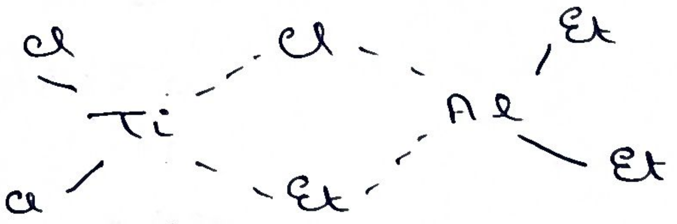
+

$CH_3-CH_2-[CH_2-CH_2]-CH_2-CH_2-Et$

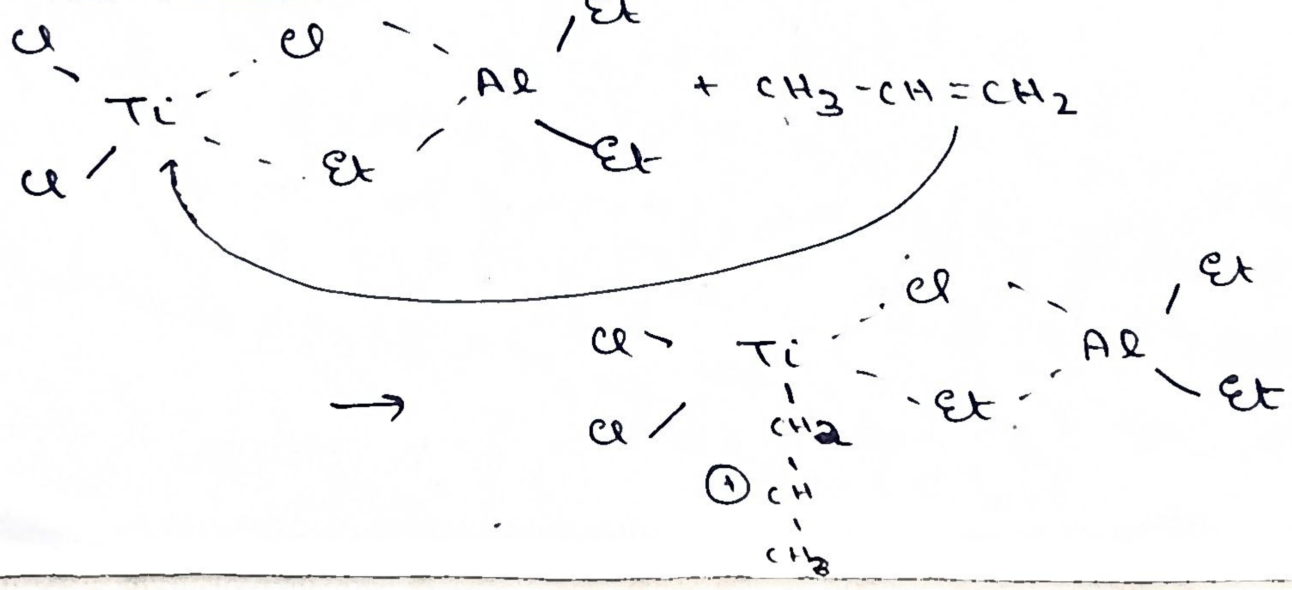
Polymerization of propylene

Ziegler Natta catalyst

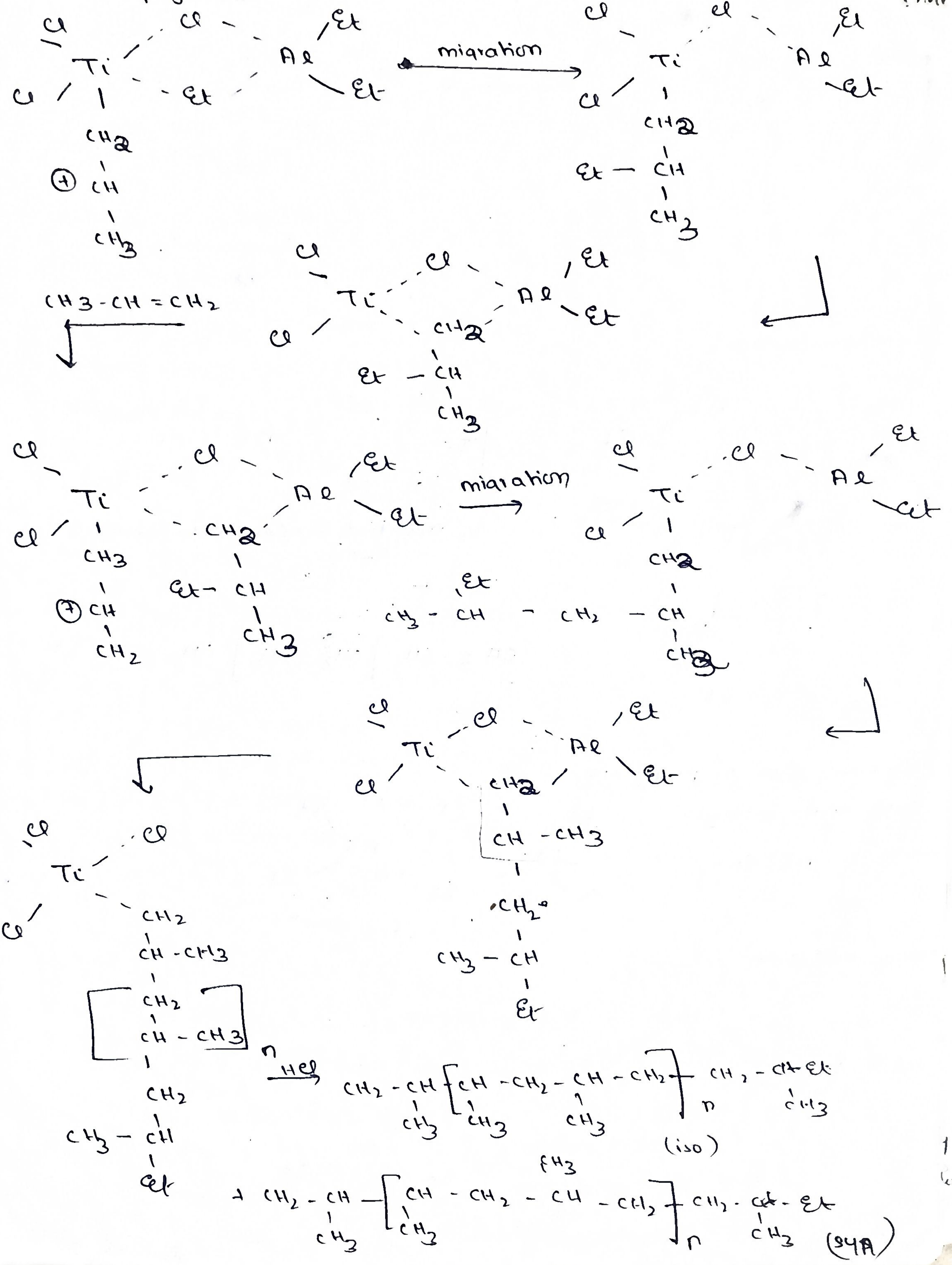
$TiCl_3 + Al(Et)_3 \rightarrow$



chain initiation



(ii) chain propagation



Polymers (contd).

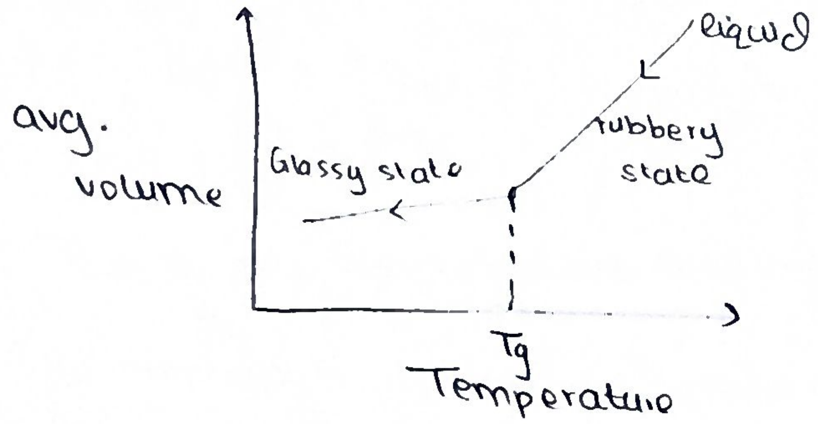
Copolymerization :- It is the addition or condensation of two different types of monomers.

- It is superior to homopolymerization as it yields polymers for commercial use with unique properties.
- Copolymers are also called polymer alloys.
- Copolymers are of 4 different types
  (a) alternate copolymers : - A - B - A - B - A - B -
  (b) random copolymers : A-A-B - B - B - B - A - B-B - A - A -
  (c) block copolymers : - A-A - A - A - B - B - B - B - A-A-A-A -
  (d) graft copolymers : - A - A - A - A - A -
  -B - B - B -

example: ABS = Acrylonitrile Butadiene Styrene

Properties of polymers

1. Glass Transition Temperature: It is a property that is related to the amorphous regions of a polymer and not the crystalline regions. It is defined as the temperature below which the amorphous polymer chain becomes ~~se~~ hard and brittle and above which it becomes soft and rubbery.



- On heating, temperature increases, the intermolecular forces decrease, interchain mobility increases. ⇒ The polymer becomes soft & rubbery
- On cooling, temp. decreases, the extended polymer chain comes closer, hence inter chain mobility decreases ⇒ The polymer becomes hard & brittle.

Factors influencing Glass Transition Temperature:

1. Crystallinity : greater the crystallinity, greater is the GTT.

2. Molecular weight : GTT increases w/ molecular weight upto a ~~se~~ certain ~~Rt~~ mass (saturation pt). Beyond that, the GTT remains a constant.

3. Presence of side chain : This decreases inter chain mobility => GTT ↑.

4. Addition of plasticizers reduces inter chain attraction. => GTT ↓

(ii) Molecular weight

→ molecular wt. plays an important role in determining the physical and mechanical prop.

→ polymers have chains of varying length => molecular wt. is not a ~~const~~ constant.

→ statistical methods are adopted to calculate molecular wt. These include
(i) number average molecular weight
(ii) weight average molecular weight

Number average molecular weight

- It is defined as the ratio of the sum of the molar masses of individual molecules to the total no. of molecules present in the mixture

- Consider a polymer mixture with n_1 molecules of ~~wt~~ molar mass M_1, n_2 molecules of molar mass M_2 and so forth. Then

$$M_n = \frac{n_1M_1 + n_2M_2 + \dots n_iM_i}{n_1 + n_2 + \dots n_i}$$

$$M_n = \frac{\Sigma n_iM_i}{\Sigma n_i}$$

- It is measured using colligative properties like depression in freezing pt, elevation in boiling pt, osmotic pressure.

Weight Average molecular weight

- Consider a ~~molecular~~ polymer mixture where w_1 is the weight of ~~M~~ molecules w/ a molar mass M_1, w_2 is the weight of molecules with a molar mass M_2 and so forth

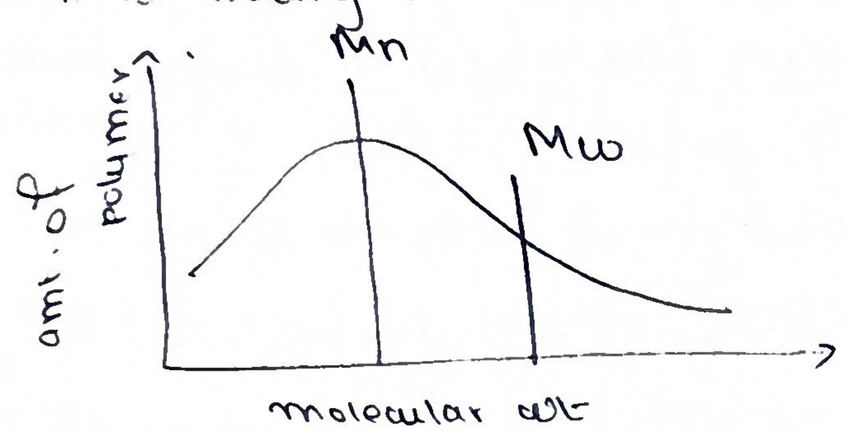
$$M_w = \frac{w_1M_1 + w_2M_2 + \ldots w_iM_i}{w_1 + w_2 + \ldots w_i}$$

But $n = \frac{w}{M} \Rightarrow w = nM$

$$M_w = \frac{(n_1M_1)M_1 + (n_2M_2)M_2 + \ldots (n_iM_i)M_i}{n_1M_1 + n_2M_2 + \ldots n_iM_i}$$

$$M_w = \frac{\sum n_iM_i^2}{\sum n_iM_i}$$

M_n is usually lesser than M_w.



- M_w is measured using ultra centrifugation & light scattering techniques

iii) Polydispersity Index (PDI): It is a measure of the broadness of the molecular weight distribution of a polymer. It is defined as the ratio of the ~~molecular~~ wt. average molecular weight and number average molecular wt. of a polymer.

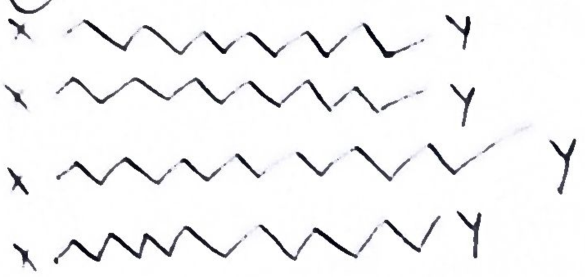
$$PDI = \frac{M_w}{M_N}$$

- The larger the polydispersity index, greater is the range of molecular wt.
- A monodisperse polymer (proteins) : PDI = 1
- controlled synthetic polymers (narrow range molecular wt polymers) PDI = 1.02 to 1.10
- condensation polymers : PDI ≈ 2
- addition polymers : 1.5 to 20.

greater chain length control:

condensation polymer: PDI = 1 to 2

1



inconsistent chain length:

2 addition polymers

* Determination of average molecular weight and degree of polymerization by viscosity method

Aim: To determine

(i) the relative viscosity of various concentrations of a water soluble polymer.

(ii) the viscosity average molecular weight

(iii) the degree of polymerization

Principle: • Viscosity is an internal property of a fluid that provides opposition to its flow.

• The force of friction between 2 parallel layers of fluid having their area in sq.cm and separated by a distance is given by:

$$F \propto A\frac{dV}{dx} \quad \text{or} \quad F = \eta A\frac{dV}{dx}$$

η = coefficient of viscosity.

The coefficient of viscosity is defined as the force of friction that is required to maintain a velocity gradient of 1cm/s between parallel layers of fluid.

• The addition of a polymer to a solvent of low viscosity increases the viscosity of the solution. The extent of increase in viscosity depends upon the molecular wt & nature of polymer added.

Let
η_0 = viscosity of solvent
η = viscosity of solution

then relative viscosity, $\eta_r = \eta / \eta_0$

the ratio: $$\frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$
$$= \eta_{sp}$$
= specific viscosity.

reduced viscosity = η_{sp} / C

The reduced viscosity is the relative increase in viscosity per unit concentration of the polymer, which is a function of molecular weight.

• This ratio varies with concentration, which means that the plot of η_{sp}/c to c is extrapolated to infinite dilution.

i.e $$\lim_{c \to 0} \eta_{sp}/c = [\eta] = \text{intrinsic viscosity}$$

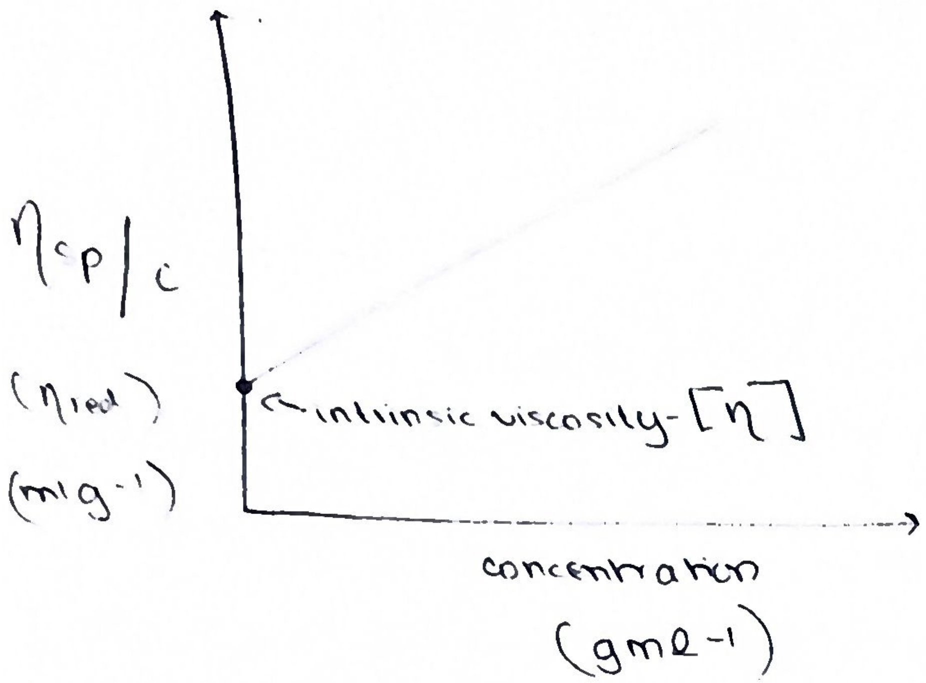
units of $[\eta]$ = deciliter per gram

• The relation between the intrinsic viscosity and the average molecular wt. of the polymer is given by the empirical Mark Houwink eqn

$$[\eta] = K M^{\alpha}$$

where $[\eta]$ is obtained by plotting η_{red} (η_{sp}/c) vs. Concentration,
K is a constant for a given polymer-solvent system
α depends on the shape of the molecule.

Model Graph



Procedure: Preparation of the various concentrations of polymer solution

- A 1% solution of the polymer is provided. (The Mark Houwink formula deviates for higher concentrations).
- At least 4 solns. of different dilutions are prepared (from 0.1% to 0.9%).
- Dilution is done using the volumetric expression $V_1N_1 = V_2N_2$.
- The upper mark of the viscometer is kept parallel to the eyes and the distilled water is allowed to flow to the lower limit. A stopwatch is used to measure the time accurately. This is repeated twice to find the average efflux time (t_0).
- The same procedure is repeated to find the efflux time of the polymeric solutions of different dilutions. (t_1, t_2).
- The readings are tabulated.

$$t_s = (t_1 + t_2)/2$$

$$\eta_r = t_s/t_0$$

$$\eta_{sp} = \eta_r - 1$$

$$\eta_{red} = \eta_{sp}/c$$

- A plot of η_{red} vs. c is drawn. It gives a straight line. It is extrapolated to find intrinsic viscosity $[\eta]$.

Calculation: $\log M = \left\{ \dfrac{\log[\eta] - \log K}{\alpha} \right\}$

$$M = \text{antilog} \left\{ \frac{\log[\eta] - \log K}{\alpha} \right\}$$

average molecular wt. of polymer (M_p) = ______ g/mol

molecular wt (M_m) = ______ g/mol

degree of polymerization = M_p / M_m = ______

Thus, the intrinsic viscosity $[\eta]$, viscosity average molecular weight & degree of polymerization of the polymer are calculated.

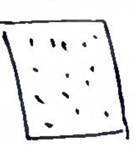
Composites

- A composite is a material that is produced from 2 or more constituent materials that have notably different physical & chemical properties.
- The material which is present in excess is the primary phase or the matrix phase. It is usually continuous and ductile.
- The secondary phase has material in the form of plastics, sheets or fibers. It adds strength to the matrix phase, and it is called the reinforced or dispersed phase.
- The matrix and the reinforced phase can be made of ceramics, metals or polymers.

Difference between blends & composites : The 2 main constituents of composites remain recognizable but that of blends may not be recognizable.

Classification of composites

I Based on the nature of the reinforced material

(i) particle reinforced composites 

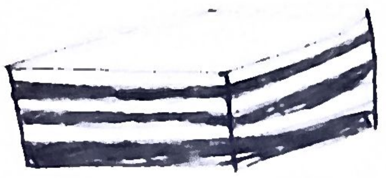
(ii) fibre reinforced composites with

a. ~~un~~ continuous fibres uniformly arranged 

b. ~~cor~~ discontinuous fibres uniformly arranged 

c. discontinuous fibres ~~non-u~~ randomly oriented

(iii) structural composites



II based on the nature of the matrix material

1. Matrix metal composites (MMCs) : a mixture of ceramic and metals such are cemented carbide and other cement. This is to increase the stiffness, and provide high strength and fracture toughness.

2. ~~Ad~~ Ceramic metal composites (CMCs) : made of silicon carbide, silicon nitride or aluminium oxide They retain strength upto 3000° F.

3. polymer matrix composites (PMCs) : ~~Th~~ Polymer resins are generally embedded with fillers or with reinforcing agents.

Advantages of ~~p~~ composites

1. Abrasion resistant
2. Corrosion resistant
3. High strength
4. Low density
5. Light weight
6. Tailorable properties
7. Wear resistant

Fibre Reinforced Plastic - a composite material with a polymer (resin) matrix and a fibre reinforcing dispersed phase.

Matrix : It is the continuous phase
made from a thermoset like polyester, epoxy resin

Functions :
- medium for binding reinforcement
- protect reinforcement from environmental degradation
- to transfer load from one insert to another
- to provide texture, colour, finish, durability

Fibre : It is the discontinuous phase.

Nature of the composite depends on the reinforcin nature & orientation of the fibres.

- Fibre can be natural or synthetic
  - natural → jute, cellulose
  - synthetic → glass, alumina, carbon fiber

Functions : provide strength & stiffness
durability
mouldability
maintain light weight

Advantages of FRP

(i) corrosion resistant
(ii) light wt.
(iii) low density
(iv) long lasting
(v) high performance.

Applications of FRP

Automotive Industry : (i) to make luxury cars (replaces metal bodies)
- increase fuel consumption and speed
- can easily be moulded into the required shape.

Aerospace Industry : • as lightweight & strong as aluminium
- can withstand high temperatures and harsh temperatures
- expand little w/ heat, maintain stiffness

Marine Infrastucture : • a suitable alternative to wood
- can be used on ships, waterfronts
- resists corrosion & reduce structural weight

Construction Industry : • provide structural reinforcement to beams, pillars
- can also be used to make guardrails, signboards

Consumer Equipment : • camera tripods
- camping equipment
- musical instruments

· <u>Protective equipment</u> : Fibres with aramid have high thermal & impact resistance, mechanical strength.
used to make bullet proof vests, blast protection vehicles, fire resistant suits.

<u>Power industry</u> : most FRPs are electrically insulating, tolerate harsh chemicals, are relatively non-flammable.
FRPs with glass are non-magnetic, spark resistant & can be used to make a variety of power components.

Preparation, Properties and Uses of Industrially Important Polymers

1. Poly Vinyl Chloride (PVC)

Preparation: PVC is obtained by heating a water emulsion of vinyl chloride in the presence of a small amount of benzoyl / hydrogen peroxide in an autoclave under pressure.

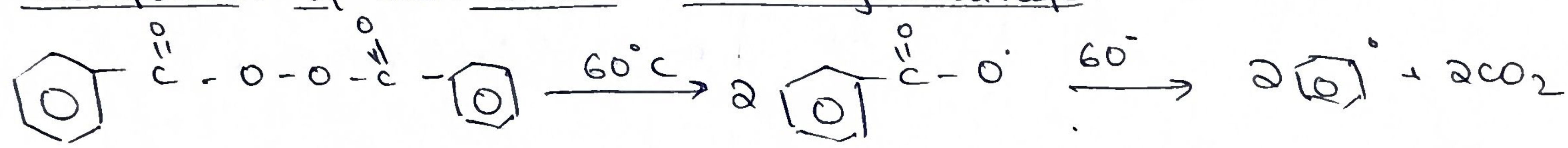
Free Radical Polymerization

Initiation:

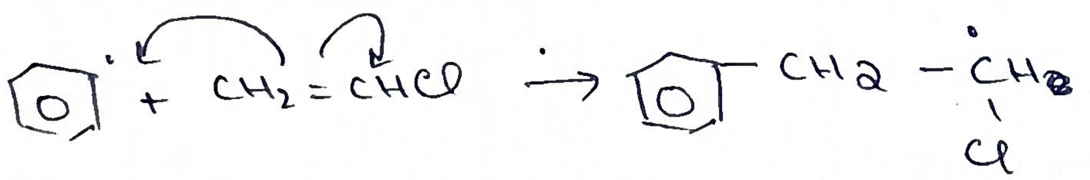
Formation of vinyl chloride monomer:

$$CH \equiv CH + HCl \longrightarrow CH_2 = CH - Cl$$

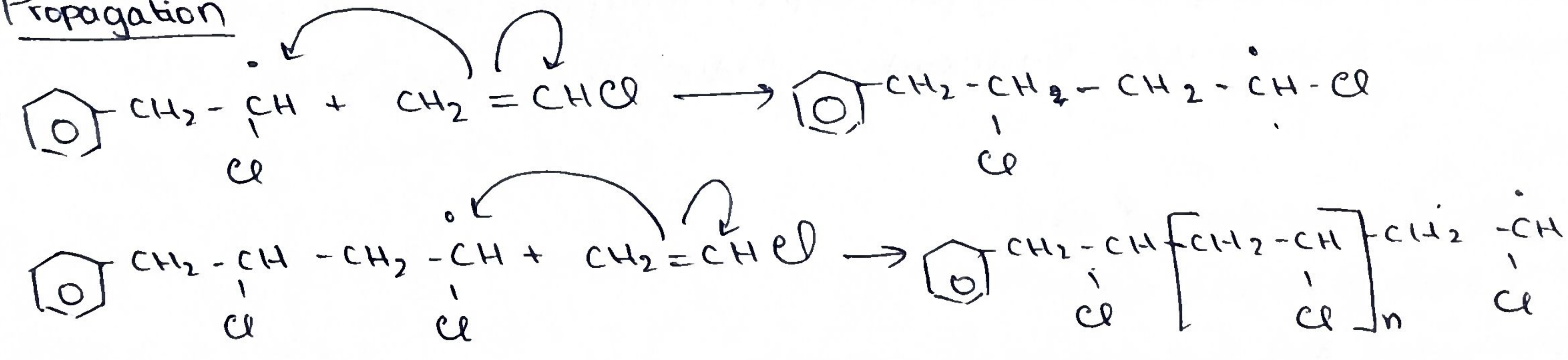
Decomposition of ~~initiat~~ initiator via homolytic cleavage:



Formation of carbon radical

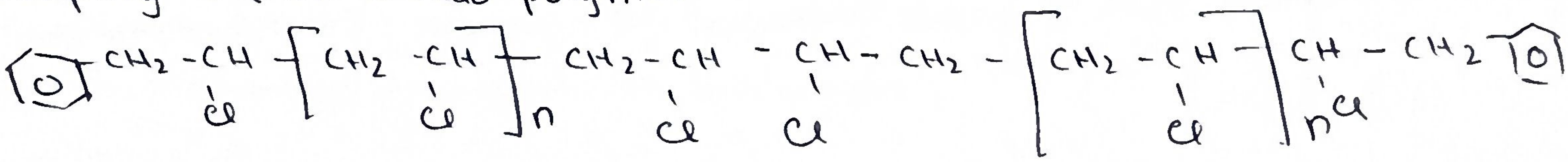


Propagation



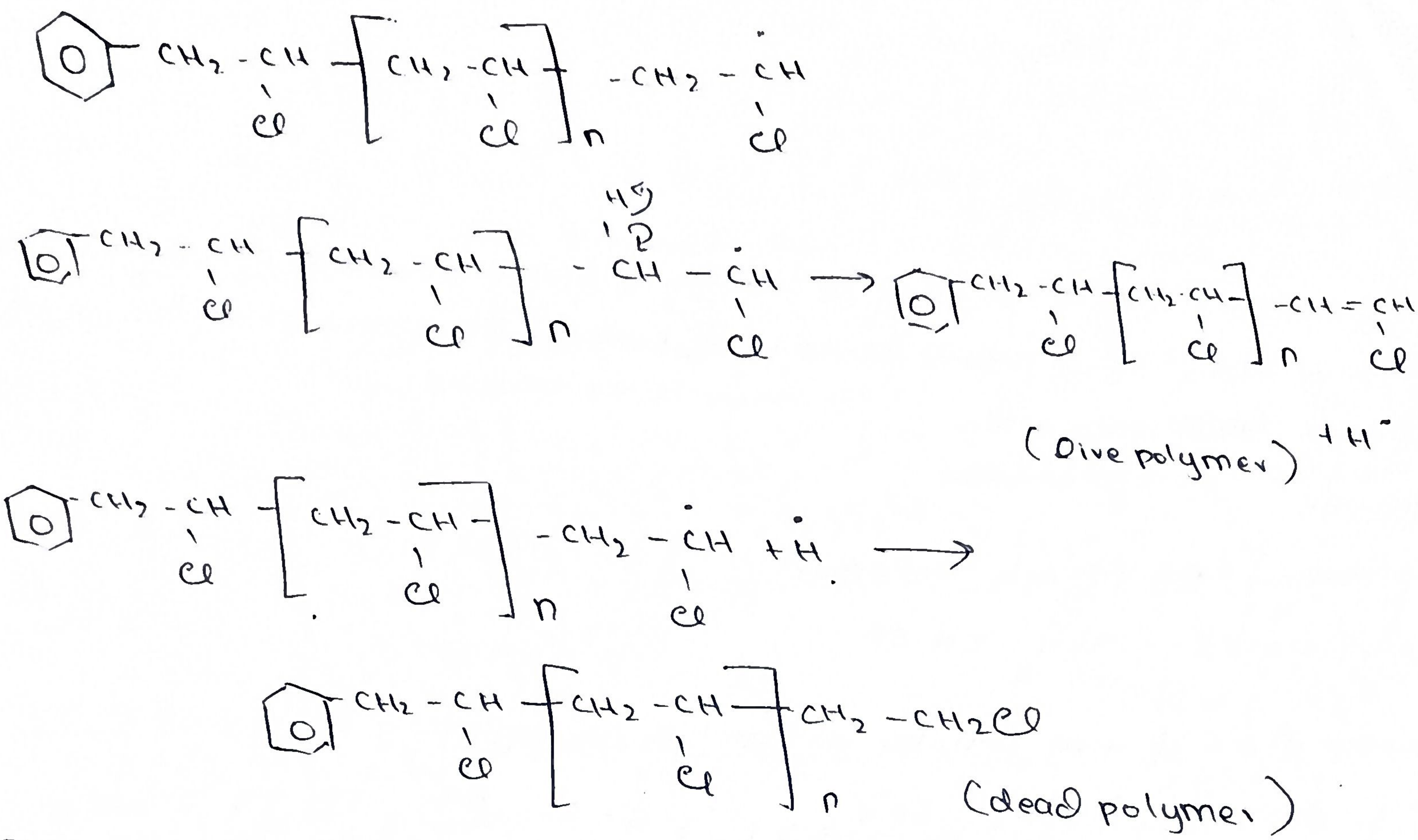
Termination

(i) coupling to form a dead polymer



(dead polymer)

(ii) disproportionation to form a live and a dead polymer



__Properties__ CRNS

- non flammable, has a high softening pt (145° - 150°)
- stiff, rigid & brittle
- colourless, odourless, chemically inert
- resistant to atmospheric oxygen, light & inorganic acids & alkali, but soluble in halogenated hydrocarbons (like ethyl chloride, THF)

__Uses__

- electrical insulator on wires
- PVC pipes transport water
- plasticized PVC = water proof, used to make raincoats, shoes, skiing equipment.
- PVC containers used to collect biological test samples (blood, urine etc.)

(a) Polyethylene (PE)

Preparation: By heating ethylene in the presence of a suitable catalyst

LDPE : AIBN, 250°C & high pressure

refer free radical polymerization mechanism

HDPE : using Ziegler - Natta catalyst 6-7 atm

refer coordination polymerization

$$nC_2H_4 \longrightarrow \left[CH_2 - CH_2 \right]_n$$

Properties

	LDPE	HDPE
structure	branched	linear
softening temp.	98-115°C	130-137°C
crystallinity	low	high
water & gas permeability	low	high
density	0.915 - 0.925 g/cm³	0.941 g/cm³
users	packing covers squeeze bottles ~~covers~~ mugs	hard bottles cables industrial containers

(3) Polystyrene (PS)

Preparation : made from the addition polymerization of styrene with benzoyl peroxide.

$$\text{Styrene} = \begin{array}{l} CH_2 = CH \\ \qquad\;\; | \\ \qquad C_6H_5 \end{array}$$

refer to free radical polymerization mechanism.

Properties

(i) Amorphous, ~~has~~ low specific gravity

(ii) hard, brittle, transparent, high refractive index

(iii) softening temp. 90±10°C

(iv) non-polar, but soluble in oil

(v) on combining with elastomers, impact strength increases, is called High Intensity Polystyrene (HIPS).

<u>Uses</u>

(i) talcum powder boxes, combs, brushes

(ii) expanded PS = styrofoam, false ceilings and thermocols

(iii) HIPs used to make TV cabinets, disposable plates, cups, refrigerator liners

4) <u>Polyurethane</u>

- They are polymers containing the urethane ($NH-\overset{O}{\overset{\|}{C}}-O$) group

<u>Preparation</u> : They are prepared by ~~treating isocyanates~~ the addition polymerization of diisocyanates with diols / triols.

- During the addition process, the H-atom of the -OH groups attaches to the N atom to form the $NH-\underset{O}{\underset{\|}{C}}-O$ group.

~~R-N-C-O~~

$$O=C=N-R-N=C=O + HO-R'-OH \longrightarrow \left[-\overset{O}{\overset{\|}{C}}-NH-R-NH-\overset{O}{\overset{\|}{C}}-O-R'-O-\right]_n$$

- The structure of polyurethane is similar to polyamides ($NH-\overset{O}{\overset{\|}{C}}-$) but the additional oxygen atom in the polyurethane chain increases its flexibility.

<u>Properties</u>

- oil & water resistant
- abrasion resistant
- corrosion resistant
- manufactured economically
- electrical insulator

Uses

- oil resistant ⇒ used in tyre retreading
- abrasion resistant ⇒ gym, dance floors
- PU foam in cushions, mattresses
- water resistant ⇒ used to make swimsuits

Nylon 6-6

It is made by the condensation of adipic acid and hexamethylene diamine

$$\underset{\text{adipic acid}}{HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{hexamethylene diamine}}{H_2N-(CH_2)_6-NH_2}$$

$$\downarrow -H_2O$$

$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH_2$$

hexamethylene diamine

adipic acid

$$\rightarrow H_2N-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$$

$$\downarrow \text{n times}$$

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

Properties

- Translucent
- High melting pt
- High abrasion resistance
- High Thermal stability

HH GG SS

high impact strength

good thermal stability

self lubricating

high melting pt.

good abrasive resistance

sol. in polar solvents

Uses

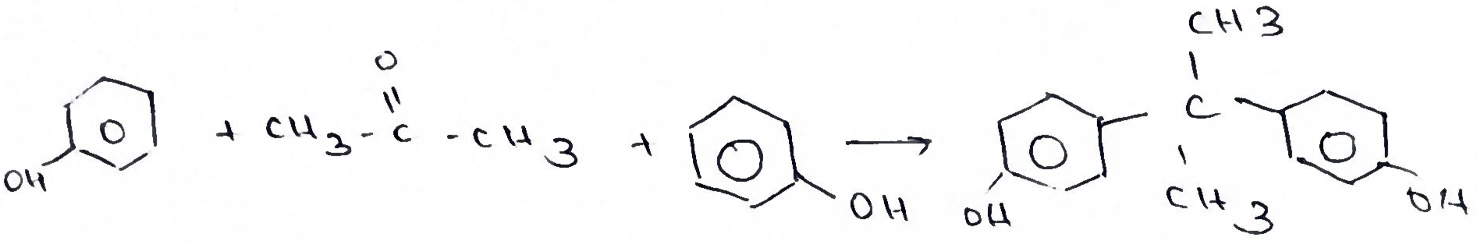
- cocks
- carpets
- dresses
- rugs
- upholstery

Epoxy Resin

made by the condensation polymerization of Bisphenol A & epichlorohydrin

Step 1: preparation of bisphenol-A.

Two moles of phenol & one mole of acetone



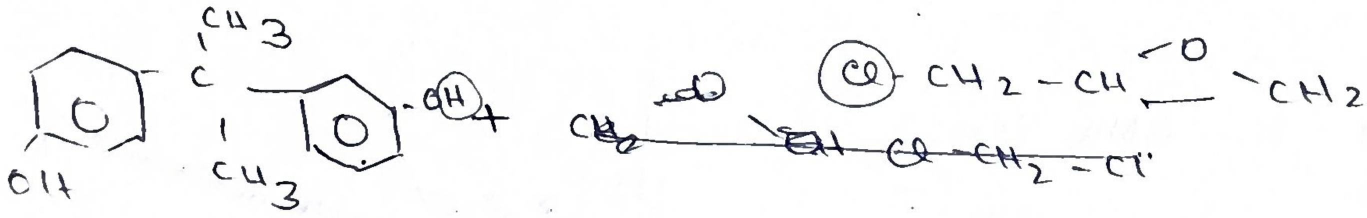
Step 2: preparation of epichlorohydrin from propylene

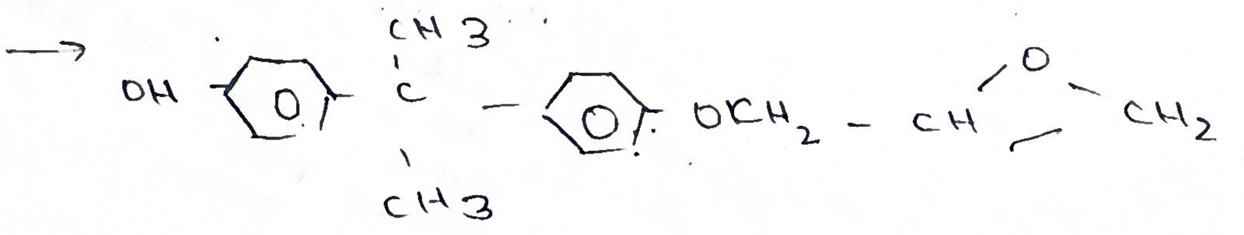
$$CH_3-CH=CH_2 + Cl_2 \longrightarrow CH_2=CH-CH_2Cl \;\Big\downarrow HOCl$$

$$CH_2Cl-CH\overset{O}{\frown}CH_2 \xleftarrow{CaO} CH_2Cl-CHOH-CH_2Cl$$

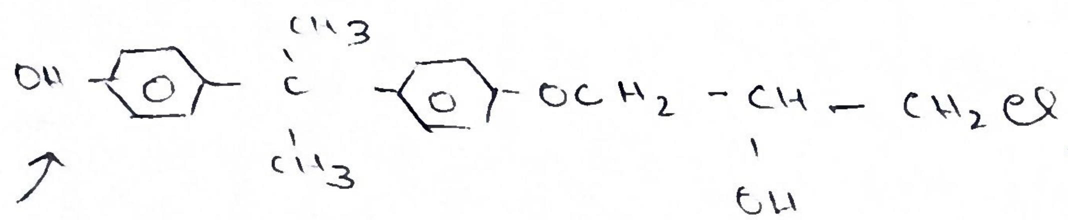
~~water is removed~~.

Step 3: condensation of bisphenol A and epichlorohydrin



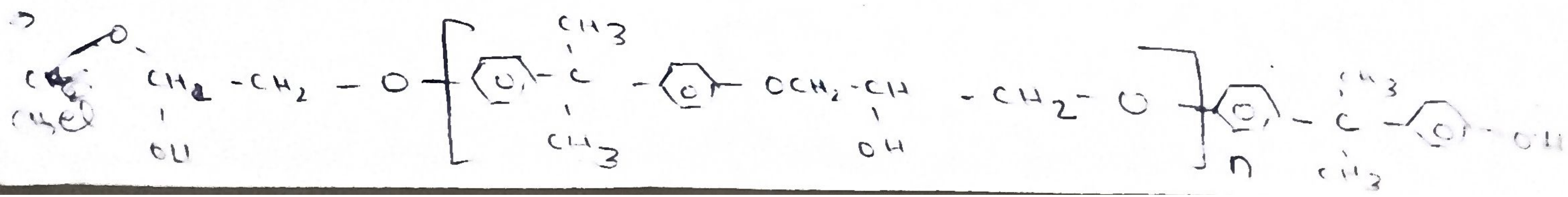


HCl hydrolyses the epoxy group



epichlorohydrin

bisphenol A.



: Properties

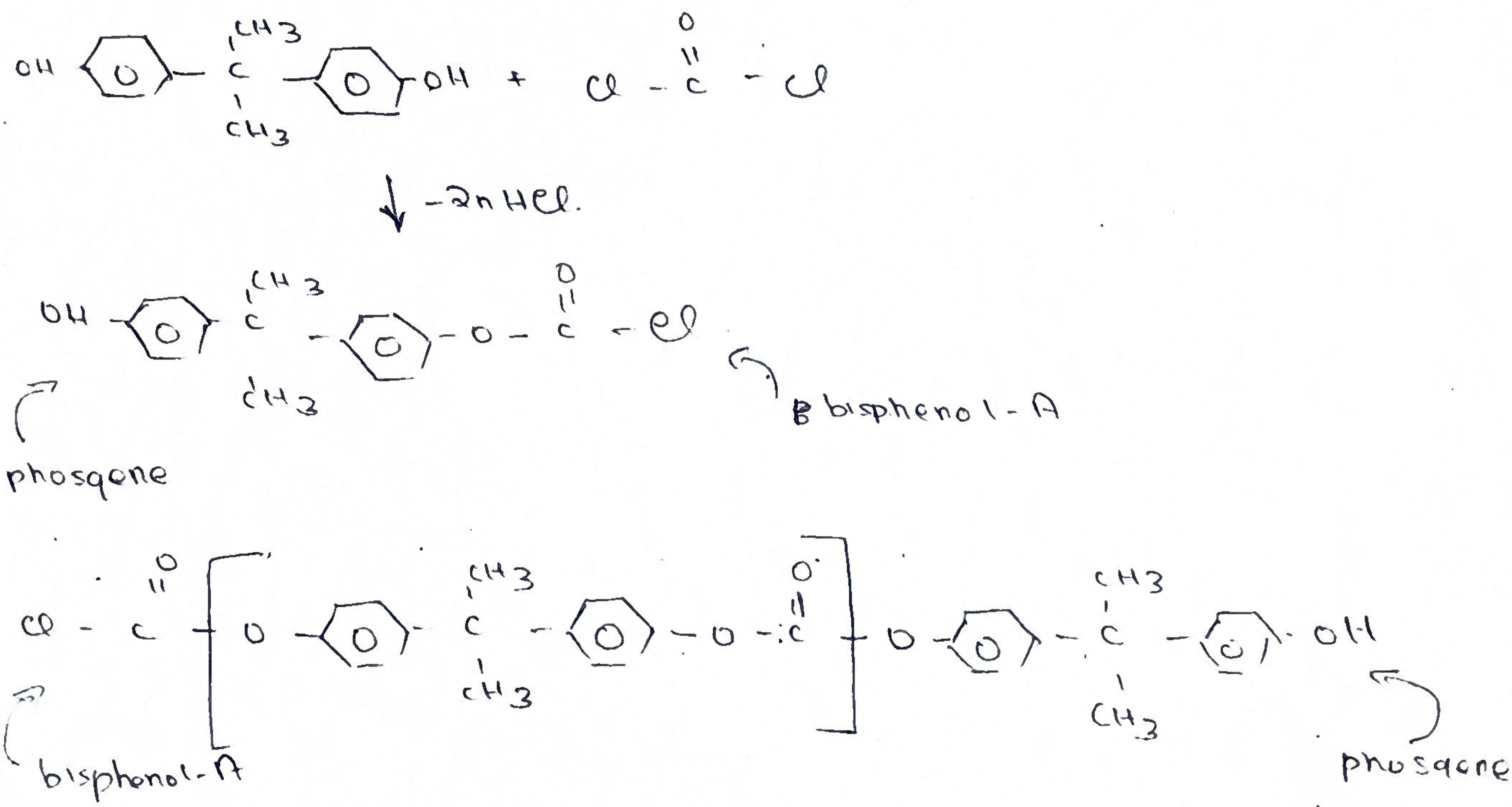
- has an ether linkage, meaning it is resistant to water, acid & alkali
- polar nature => good adhesive property
- non porous film => resistance to corrosion
- presence of cross-links => thermal and electrical resistivity

uses

- to bind metals & composites in automobiles & aircraft
- domestic purpose epoxy resin = araldite, used for sealing tiny holes in water pipes
- m-seal to seal cracks
- industrial floors, foam

Polycarbonate

made from the condensation polymerization of bisphenol-A and phosgene



For every repeating unit form, 2 molecules of HCl are precipitated out.
If sodium salt of bisphenol-A is used, the byproduct would be NaCl rather than HCl.
This is advantageous as NaCl would precipitate out in an organic solvent & easily removed.

Properties

- high melting pt
- high tensile strength
- high light transmittance

uses

- CD discs
- safety glasses
- ~~high~~ impact resistant window glass.