Molecular weight determination

1. Cryoscopy (Depression in freezing point of ΔT_f)

$$\frac{\Delta T_f}{C} = \frac{R T_f^2}{\rho . \Delta H_f}\left(\frac{1}{\bar{M}_n} + BC\right)$$

This depends on no. of solute particles but not on the nature & size of solute particles

ΔT_f

C – Concentration

R – Gas constant

T_f – Freezing point of solvent

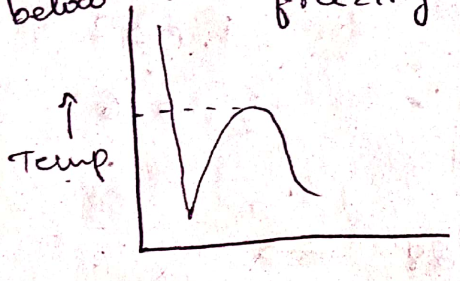
ρ – Density

ΔH_f – Enthalpy of fusion

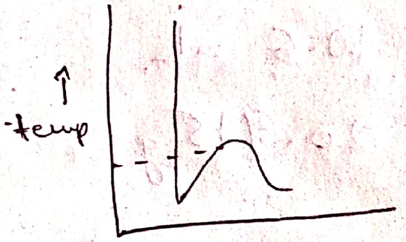
B – constant

$\bar{M}_n$ – No. avg. Mol. wt.

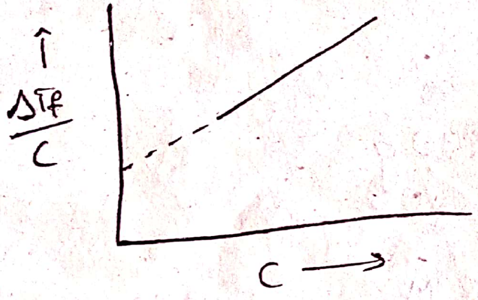
Freezing point of the pure solvent and for pure solution at different concentration is measured. It is done by supercooling the solvent & solution below its freezing point.



(Solvent)



(Solution)



Using this graph, above equation can be solved and we get the value of $\bar{M}_n$.

Limitations:

* Temperature difference obtained is so small that we cannot find the actual value. So

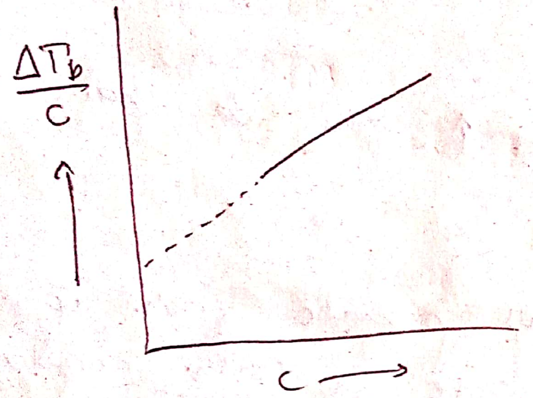
* Maximum value of mol. wt. can be measured is 30,000. This is because

$$\bar{M}_n \propto \frac{1}{\Delta T_f}$$

2. Ebuliometry:

$$\frac{\Delta T_b}{c} = \frac{RT_b^2}{\rho \Delta H_v}\left[\frac{1}{\bar{M}_n} + Bc\right]$$

$$\left(\frac{\Delta T_b}{c}\right)_{c \to 0} = \frac{RT_b^2}{\rho \Delta H_v} \cdot \frac{1}{\bar{M}_n}$$



Limit of $\bar{M}_n$ is 30,000

* To find ΔT_b, temperature, ~~[illegible]~~ measured using temperature sensor. of ~~[illegible]~~ boiling solvent & boiling mixture

* In second method, both solvent and solution are heated together & temperature is sensed using thermister.

Limitations:

B.P different is low
Low sensitivity

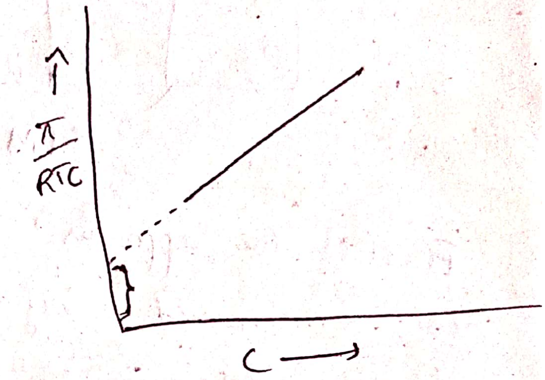
~~2> Membrane~~

3. Osmometry

i) Membrane osmometry
ii) HSMO
iii) Vapour phase osmometry

Membane osmometry

$$\frac{\pi}{RTC} = \frac{1}{\bar{M}_n} + BC$$

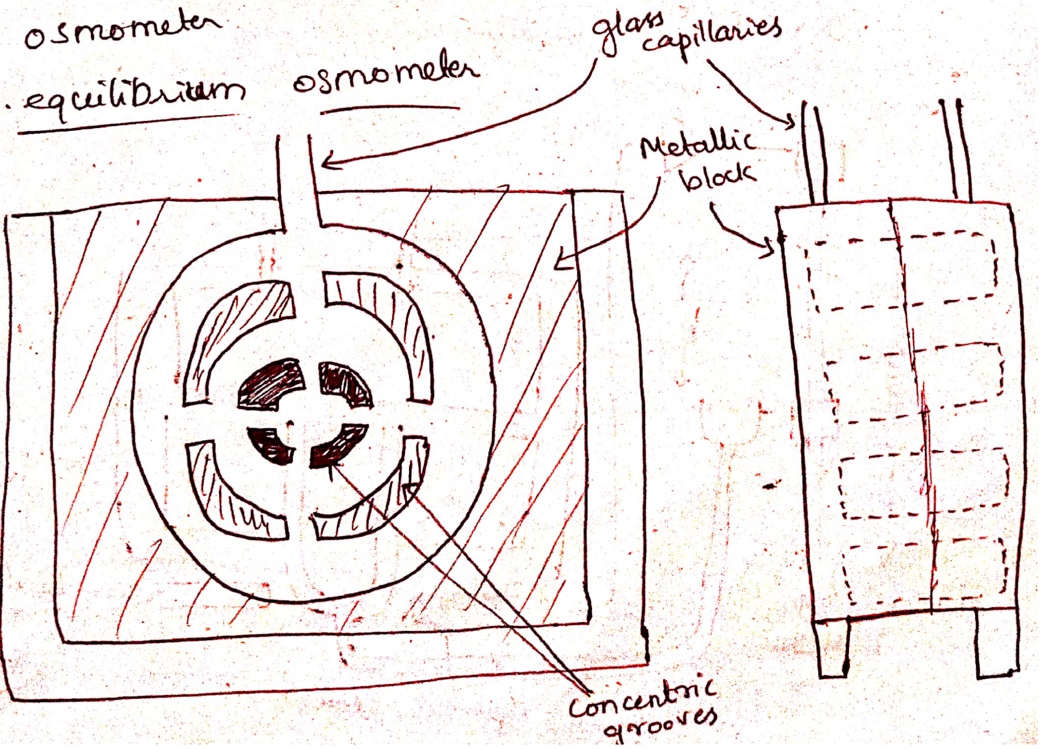


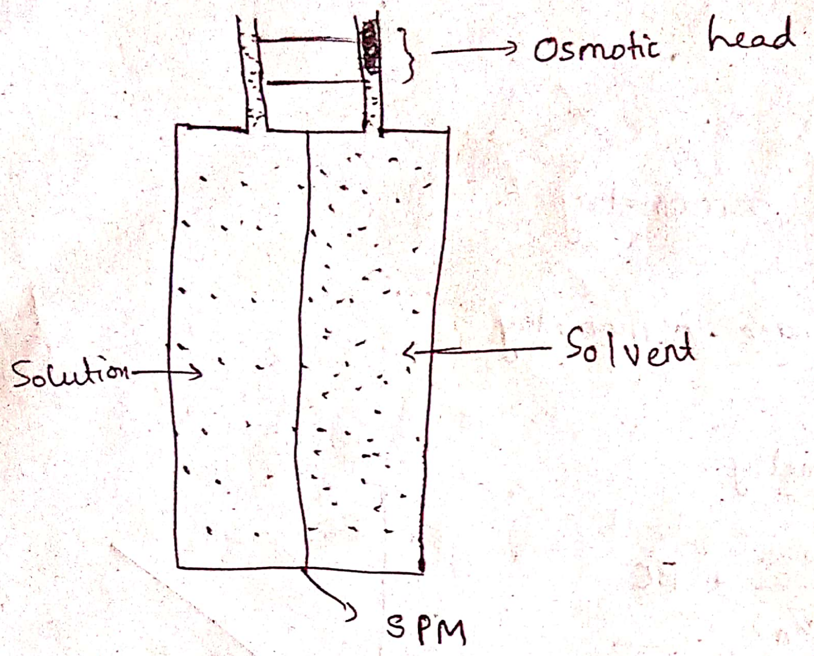
$$\left(\frac{\pi}{RTC}\right)_{C\to 0} = \frac{1}{\bar{M}_n}$$

π — osmotic pressure

Osmometers

Fuoss - Mead osmometer
Block osmometer
Pinner - Stabin glass osmometer
Stabin - Shell ~~ad~~ automatic osmometer
Reiff osmometer
static equilibrium osmometer



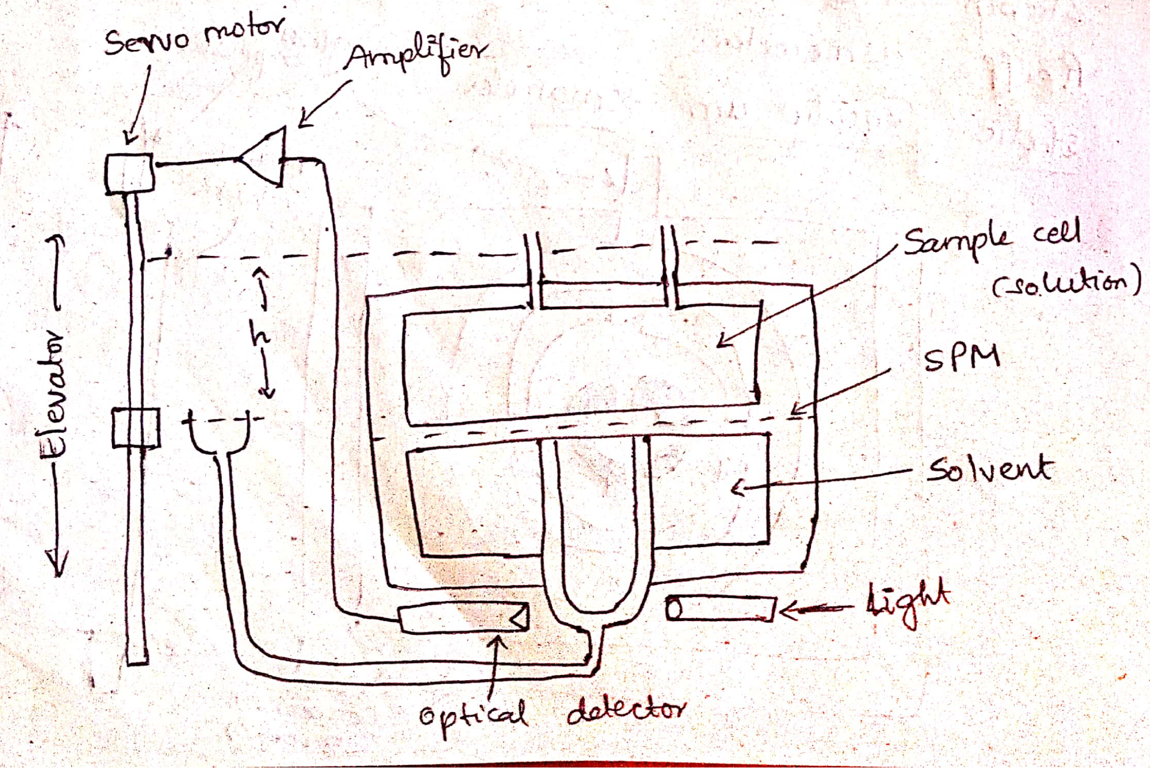


First the appartus filled by solvent. The osmotic pressure is measured by osmotic head. Then to ~~one~~ one half, Solution is filled & again measured. The difference gives the mol. wt

Limitations:

* Time consuming.

HSMO (High speed membrane osmometer)



* Mol. wt 30000 to 500000

Limitatio: Unavailability of true SPM

Vapour phase osmometry

Vapour phase Osmometry

In this method, a drop of solution & solvent are kept in a chamber. Vapours are filled in the chamber. The vapours will condense on solvent drop and solution drop. So size of solvent drop increases. & solution becomes dilute. So there is change in heat. This is because of ~~as~~ ~~lat~~ latent heat of condensation.

Latent heat of Condensation

Amount of energy released when vapour condenses to vapour state to liquid state

End group analysis

- We get number average molecular weight
- Only polymers having functional group at the end can be analyzed.

Carboxy terminated polybutadiene (CTPB)
Hydroxy terminated polybutadiene (HTPB)

- Functional group equalent is measured per 100 g
- In ~~a~~ the polymer that made from above to two molecules, functionality is 2 (one from each)

So, $\bar{M}_n = \frac{\text{functionality}}{\text{Functional group equivalent}}$

- Carboxyl value : No. of carboxyl group
  Toluene : ethanol (1:3) - titrate against 0.1 N KOH

Drawback

- Applicable only for straight chain polymers

Viscometry

[Physical lab]

Ultracentrifugation

1. Sedimentation velocity
2. Sedimentation equilibrium.

Sedimentation velocity : The speed of movement of molecule in sedimentation during centrifugation. Done at high RPM. for short time period.

$$\bar{M} = \frac{S_0 R T}{D(1-\rho\bar{v})}$$

S_0 - sedimentation

D - Diffusion

ρ - Density

$\bar{v}$ -

Sedimentation equilibrium:

Done at low RPM for longer period.

$$\bar{M} = \frac{2RT \ln(C_a/C_b)}{\omega^2(1-\rho v)(x_1^2 - x_2^2)}$$

C_a & C_b : conc. value in the cell at distances x_1 & x_2 from the axis of rotation

Drawback:

- It takes many days since it is at low RPM

Light scattering method

- Weight average molecular weight is obtained.
- Scattering is proportional to mass of polymer

Light source $\xrightarrow{\text{Light}}$ Condensing lens → Monochromator

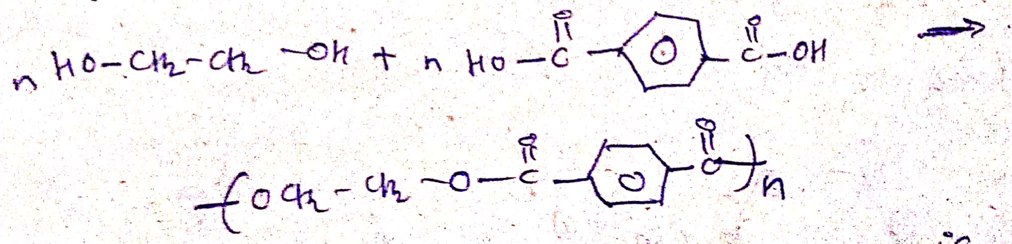
Disadvantages:

- Expensive
- Molecular weight : 10000 to 1 crore g/mol can be calculated.

Journal of polymer science, 8, 257 (1952)
Pure & Applied chemistry, 12, 645 (1966)
Macromolecules 1973

Common names of polymers

Hevea braziliansis — Rubber - Place Brazil
Nylon 6,6. & Nylon 6,10 — no. of Carbon atom
Bakelite :- Scientist ! Leo Bakeland
Polystyrene :- Based on source (styrene)



PET common name is
Terylene / Dacron

Types of Polymerization

① Chain polymerization:

- No byproduct
- Chain polymerization is also known as vinyl polymerization where successive addition of monomeric unit occur to form the product. There is no byproduct in this type of polymerization. Monomers with double bond undergo chain polymerization.

i) Free radical polymerization.
ii) Cationic "
iii) Anionic "
iv) Coordination "

Step polymerization:

i) Poly condensation
ii) Polyaddition
iii) Ring opening

Vinyl compounds → $CH_2=CHX$

Allyl compounds → $CH_2=CH-CHX$

Free radical polymerization

- Thermally unstable initiators are used

Eg :- Azo - bis - cyano valeric acid

Azo - bis - diphenyl methane

Azo - bis - methyl isobutyrate

Azo - bis - isobutyronitrile (AIBN)

BPO

H_2O_2

APS

KPS

Initiation:

$$\dot{R} + CH_2=CH-X \rightarrow \dot{R} + \dot{C}H_2-\dot{C}H-X \rightarrow$$

$$R-CH_2-\dot{C}H-X$$

The free radical intiator uses one of the π bond electrons to form a stable bond with another carbon and the other electron returs to another carbon and makes it a free radical.

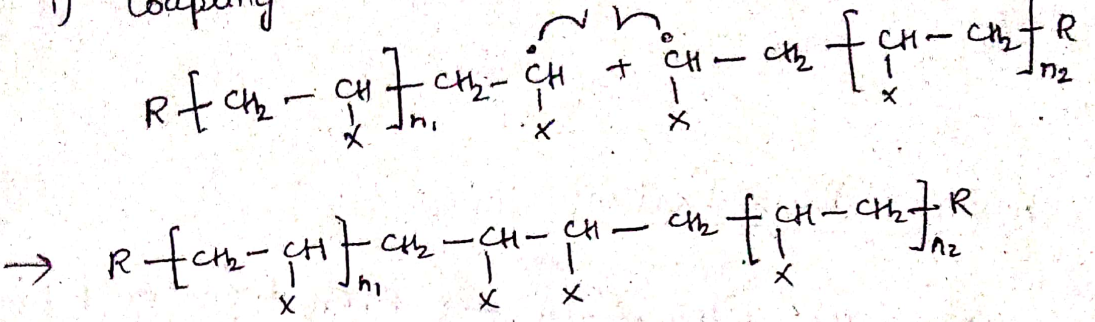
Propagation

$$R-CH_2-\dot{C}H-X + CH=CH-X \rightarrow R-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{\dot{C}H}$$

The next addition can be head to tail or tail to tail or head to head or tail to head

Termination:

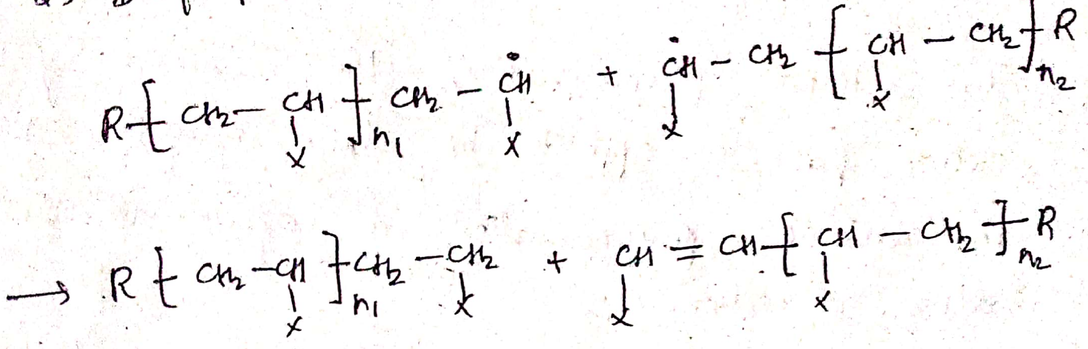
i) Coupling



$$R\{CH_2-\underset{X}{CH}\}_{n_1}CH_2-\underset{X}{\dot{C}H} + \underset{X}{\dot{C}H}-CH_2\{\underset{X}{CH}-CH_2\}_{n_2}R$$

$$\rightarrow R\{CH_2-\underset{X}{CH}\}_{n_1}CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2\{\underset{X}{CH}-CH_2\}_{n_2}R$$

2) Disproportion



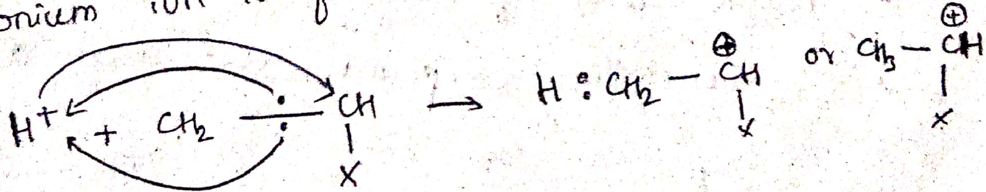
$$R\{CH_2-\underset{X}{CH}\}_{n_1}CH_2-\underset{X}{\dot{C}H} + \underset{X}{\dot{C}H}-CH_2\{\underset{X}{CH}-CH_2\}_{n_2}R$$

$$\rightarrow R\{CH_2-\underset{X}{CH}\}_{n_1}CH_2-\underset{X}{CH_2} + \underset{X}{CH}=CH\{\underset{X}{CH}-CH_2\}_{n_2}R$$

$(CH_2=\underset{X}{CH})$ group is called as end group

Cationic polymerization:

In Cationic polymerization a proton is introduced. It pulls π electron pair towards it and the positive charge of the proton is transferred to the farther end of monomer, and a carbonium ion is formed.



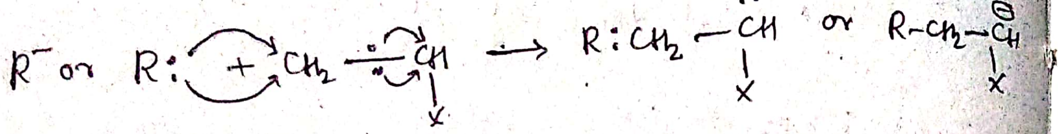
$$H^+ + CH_2 \,\vdots\, \underset{X}{CH} \rightarrow H:CH_2-\underset{X}{\overset{\oplus}{CH}} \text{ or } CH_3-\underset{X}{\overset{\oplus}{CH}}$$

Carbonium ion attracts π electron of second monomer

* Lewis acid like BF_3 are used as catalyst and water / methanol is used as co-catalyst.

* Termination occurs due to the collision q C^+ ion and an anion which may be a counter ion

Anionic Polymerization:



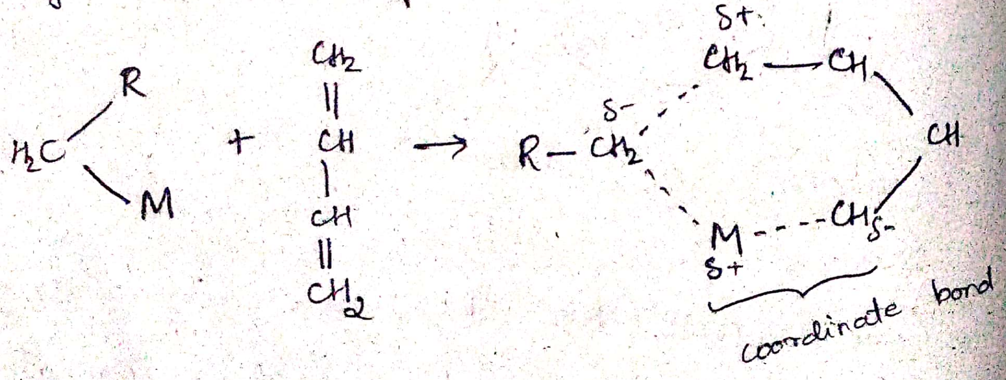
$R^- \text{ or } R\!: + CH_2 = \underset{X}{\underset{|}{CH}} \rightarrow R\!:CH_2 - \underset{X}{\underset{|}{\ddot{C}H}} \text{ or } R-CH_2-\underset{X}{\underset{|}{\overset{\ominus}{C}H}}$

In cationic polymerization, the movement q electon pair is opposite to chain growth whereas in anionic polymerization, it occurs in the same direction.

In case q anionic polymerization, the carbanion at the end q the chain remains active. Therefore, anionic polymerization is also known as living polymerization, and the polymers produced by anionic polymerization is known as living polymers.

Coordination polymerization

* Polymerization q olefins and dienes are done.
* Organometallic compounds are used as catalyst



* Coordination polymerization is also known as insertion polymerization because the monomer is inserted in between the metal ion and Carbon.

* Ziegler - Natta catalyst is commonly used for this polymerization ($AlEt_3$ + $TiCl_4$)

② Step polymerization

* The buildup is due to the reaction between functional groups of reactants.
* Again classified into three types
  - i) Polycondensation
  - ii) Poly addition
  - iii) Ring opening polymerization

i) Polycondensation

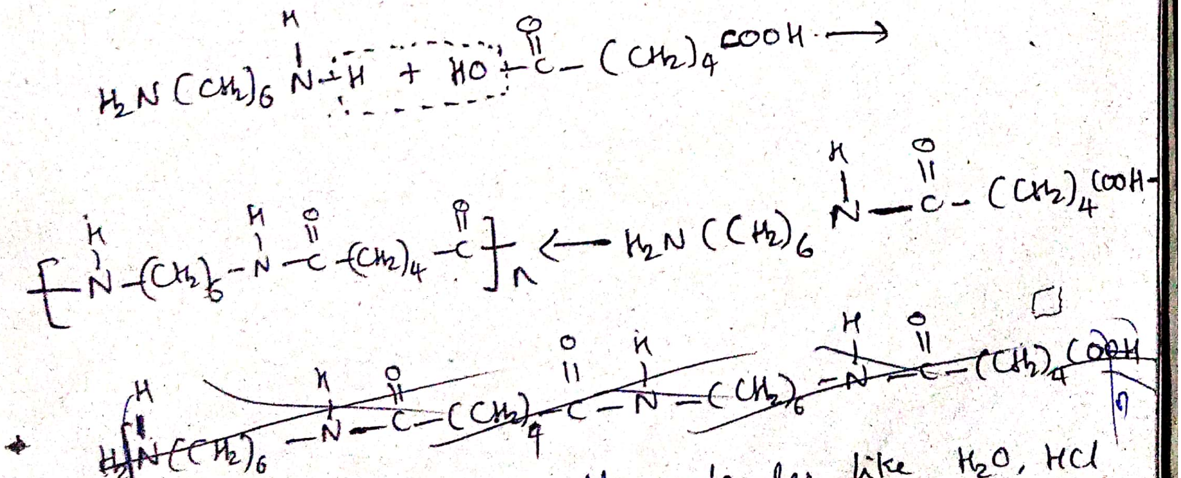
Eg :- Nylon 6,6 & Nylon 6,10

$H_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH$ → Nylon 6,6

Hexamethylene diamine + Adipic acid

$H_2N(CH_2)_6NH_2$ + $HOOC(CH_2)_8COOH$ → Nylon 6,10

Sebacic acid



$$H_2N(CH_2)_6\overset{H}{\overset{|}{N}}-H + HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4COOH \longrightarrow$$

$$H_2N(CH_2)_6\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4COOH$$

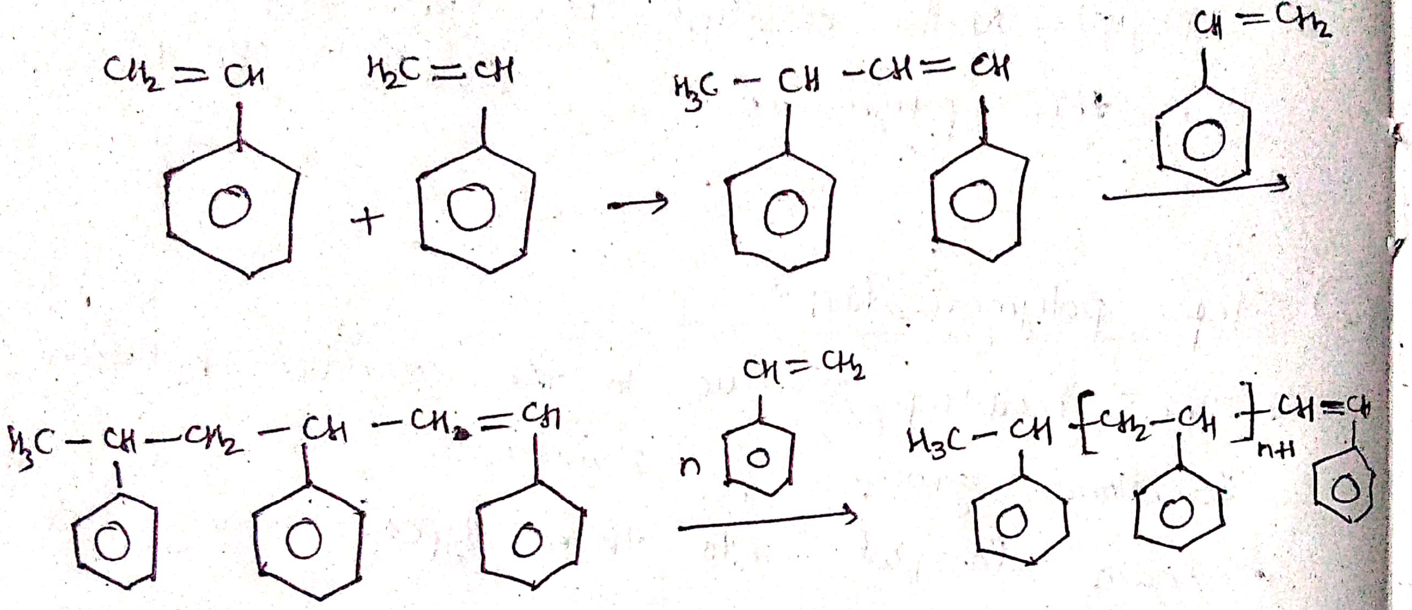
$$\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n \longleftarrow$$

$$H_2N(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4COOH$$

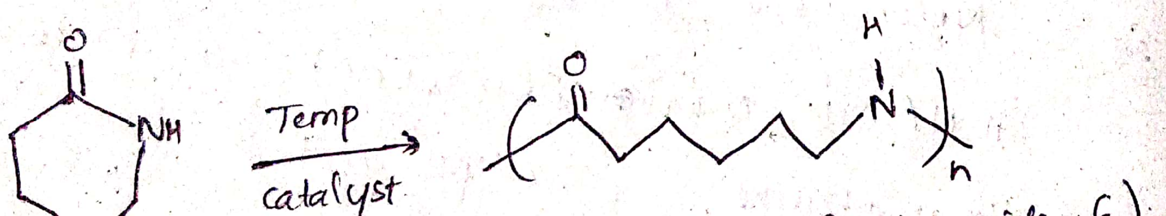
* In this, elimination of small molecules like H_2O, HCl takes place

ii) Polyaddition:

* In this, migration of atom from one monomer molecule to another monomer molecule occur.



iii) Ring opening polymerization



ε- Caprolactum

Nylon - 6 (polyamide - 6)