Molecular weight of polymer Sample

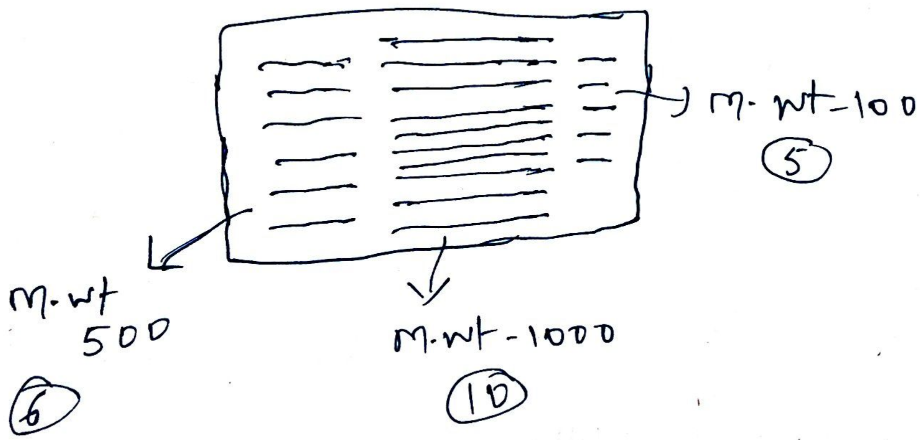
Discrete molecule

CH_3OH — m.wt - 32

C_2H_5-OH — m.wt = 46

Polymer

no of monomers - unpredictable
un controllable



In terms of Averages

$\overline{M}_n$ - number average $\dfrac{5\times100+6\times500+10\times1000}{5+6+10}$

$\overline{M}_w$ - weight average

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3}$$

$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \qquad \left[\underbrace{\frac{\sum N_i M_i}{\sum N_i}}_{\overline{M_n}} \times \frac{M_i}{M_i} \right]$$

N_1 is the number of macromolecules having m. wt M_1

N_2 ,, m. wt M_2

$\overline{M_n} = ?$

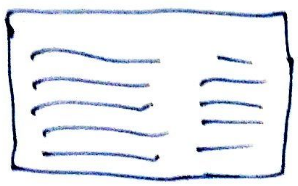
N	M
5	100
6	500
10	1000

$$= \frac{5 \times 100 + 6 \times 500 + 10 \times 1000}{5 + 6 + 10}$$

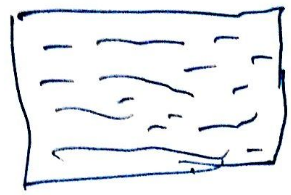
$$= \frac{13500}{21} \simeq 643$$

$$\overline{M_w} = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 \ldots}{N_1 M_1 + N_2 M_2 + N_3 M_3 \ldots}$$

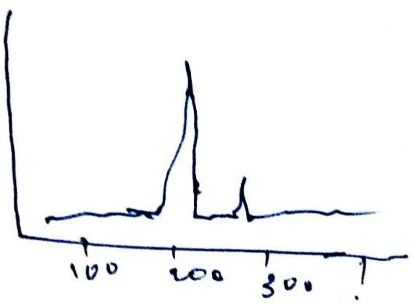
sample A



Sample B

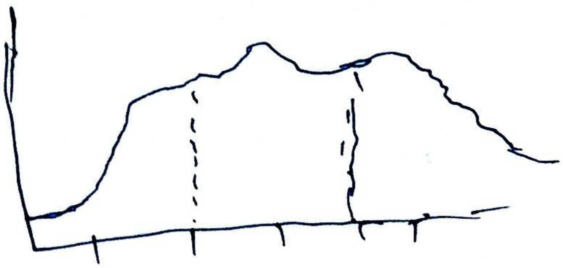


NO



m. wt

NO



m. wt

Limited types

Many Type

Homogeneous

Heterogeneous

$$\text{Poly Dispersity Index (PDI)} = \frac{\bar{M}_n}{\bar{M}_w}$$

$PDI = 1 \rightarrow$ Homogeneous.

$PDI \neq 1 \rightarrow$ Heterogeneous

Deviation

Ex:

A polymer sample consists of three different types of macro molecular species namely A, B and C. The molecular wt of A, B and C is 100, 1000 and 10000 respectively. The total number of A, B and C presented in the polymer sample is 100, 200 and 300, respectively

Find $\overline{M}_n$, $\overline{M}_w$ & PDI

$\overline{M}_n = 5.35 \times 10^3$ PDI $= 1.757$

$\overline{M}_w = 9.4 \times 10^3$

5 molecules → m. wt 100

$$\overline{M}_n = \frac{N_1 M_1}{N_1} = \frac{5 \times 100}{5} = \frac{500}{5} = 100$$

$$\overline{M}_w = \frac{N_1 M_1^2}{N_1 M_1} = \frac{5 \times 100^2}{5 \times 100} = \frac{50000}{500} = 100$$

PDI = 1

ADDITION. Polymerization

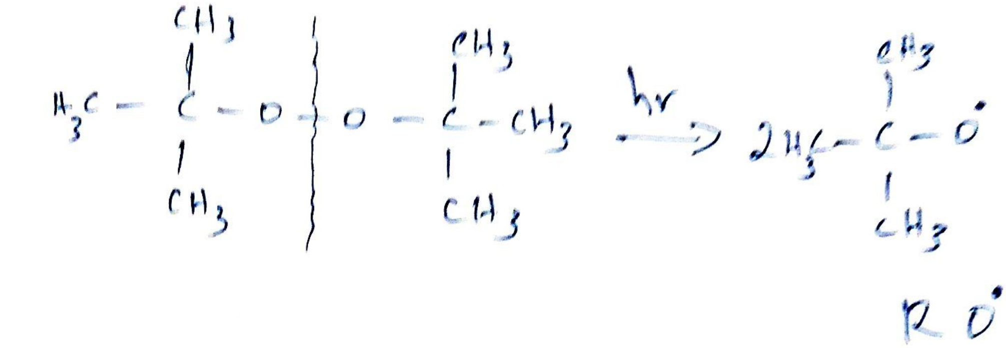
Free radical mechanism

3 - steps
1. Initiation
2. Propagation
3. Termination
   - → Coupling
   - → Disproportionation
   - → chain Transfer

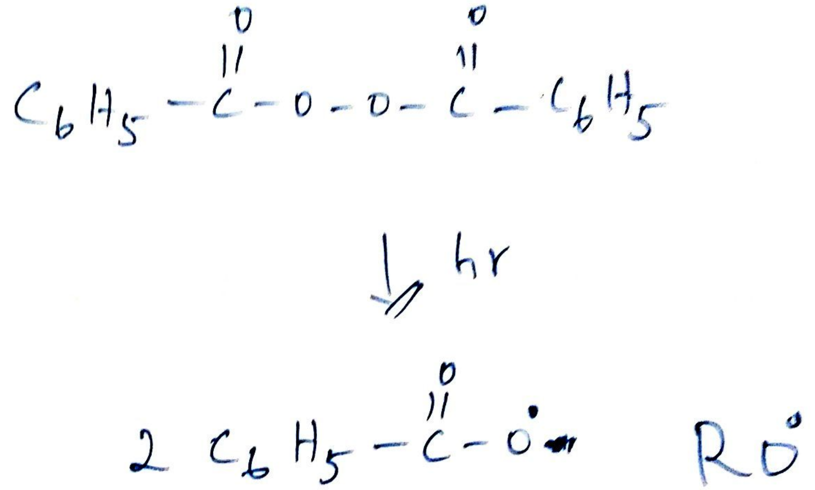
Initiation - Different types of Initiators

Thermally Photochemically unstable

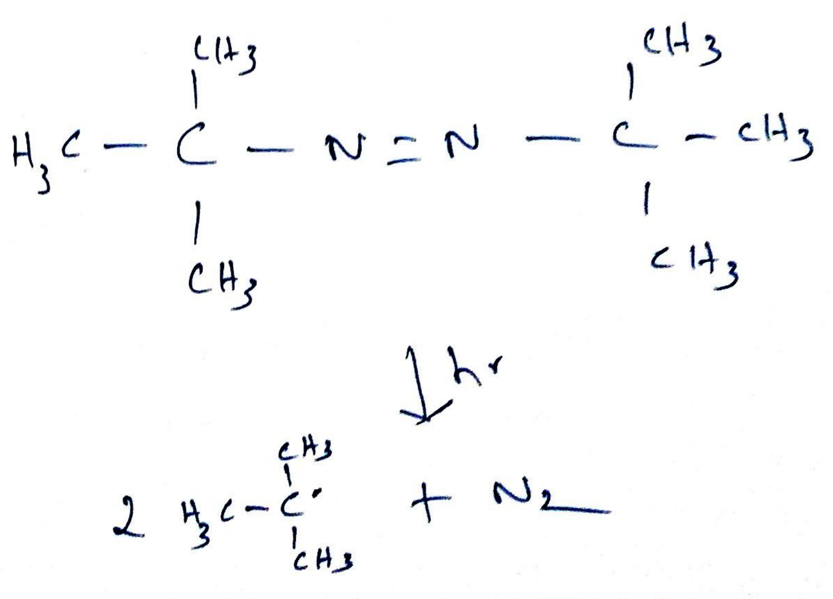
n-Butyl Peroxide



Benzoyl Peroxide



Azobis (isobutyronitrile)



$$H_2O_2 \longrightarrow H-O-O-H \longrightarrow HO^{\cdot} \longrightarrow RO^{\cdot}$$

① Initiation

$$R-O-O-R \xrightarrow{h\nu} 2R-O^{\cdot}$$

$$RO^{\cdot} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow R-O-CH_2-\overset{H}{\overset{|}{\underset{X}{\underset{|}{C^{\cdot}}}}}$$

$X = Cl, H, OH, CH_3, C_6H_5$

② Propagation

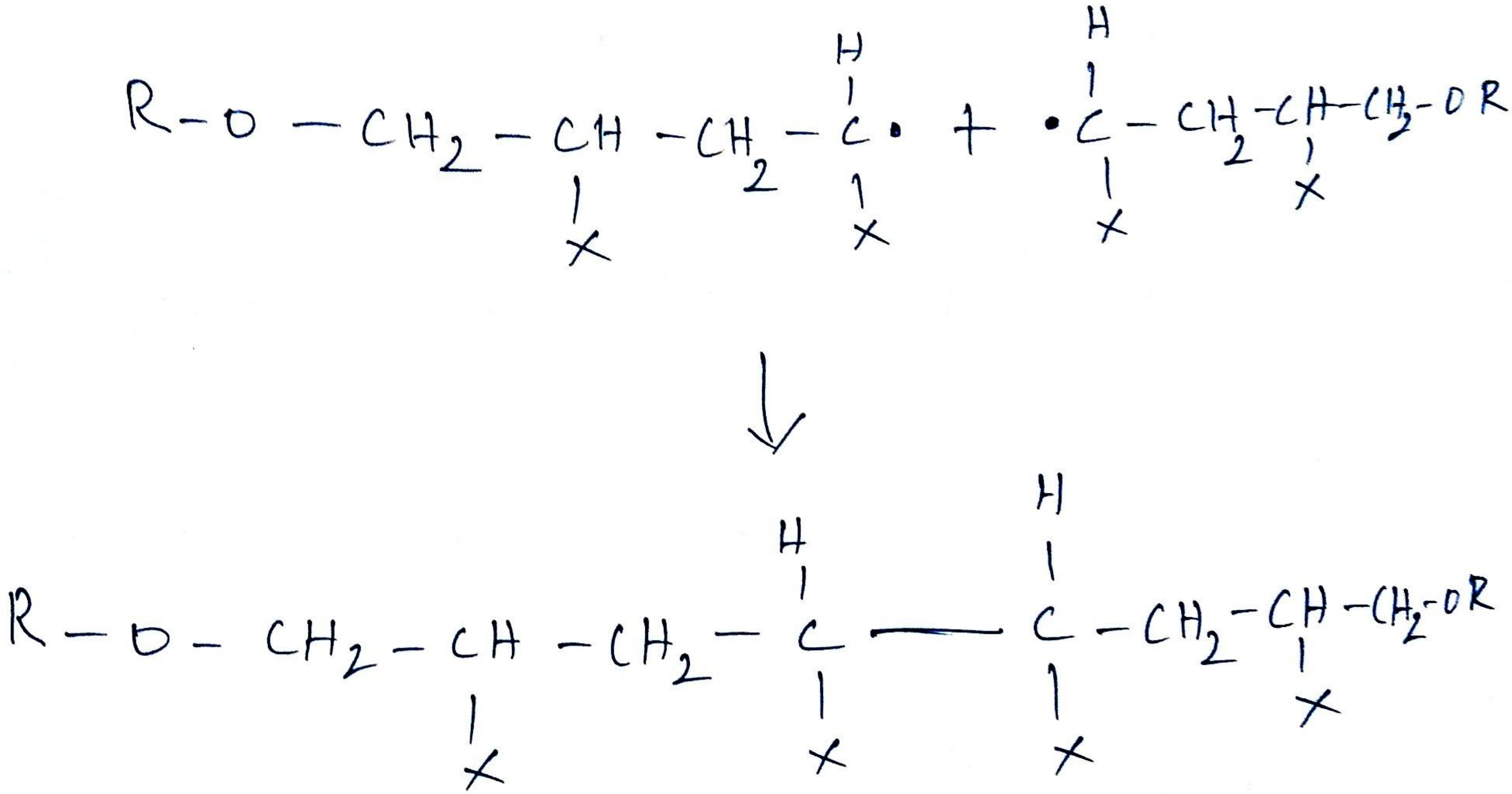
$$R-O-CH_2-\overset{H}{\overset{|}{\underset{X}{\underset{|}{C^{\cdot}}}}} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow R-O-CH_2-\overset{H}{\overset{|}{\underset{X}{\underset{|}{C}}}}-CH_2-\overset{H}{\overset{|}{\underset{X}{\underset{|}{C^{\cdot}}}}}$$

$$\downarrow$$

$$R-O\left(CH_2-\overset{H}{\overset{|}{\underset{X}{\underset{|}{C}}}}\right)_n CH_2-\overset{H}{\overset{|}{\underset{X}{\underset{|}{C^{\cdot}}}}}$$

③ Termination

ⓐ Coupling



Crystallinity

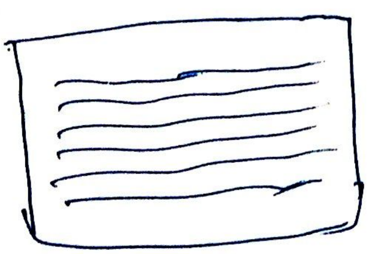
Crystalline - Regular Arrangement of atoms

- High Degree of order
- Regid
- High m. pt

Polymer → Never - 100% Crystalline

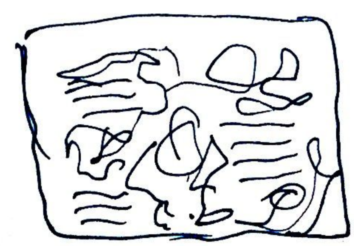
Partially - Regular

Crystalline → empedded in Amorphous



Crystalline

Amorphous



Semi crystalline

At lower Temp

Amorphous region – Frozen liquid
can not move/rotate
- called glassy state

Upon Heating up

intermolecular Forces } goes away

↓

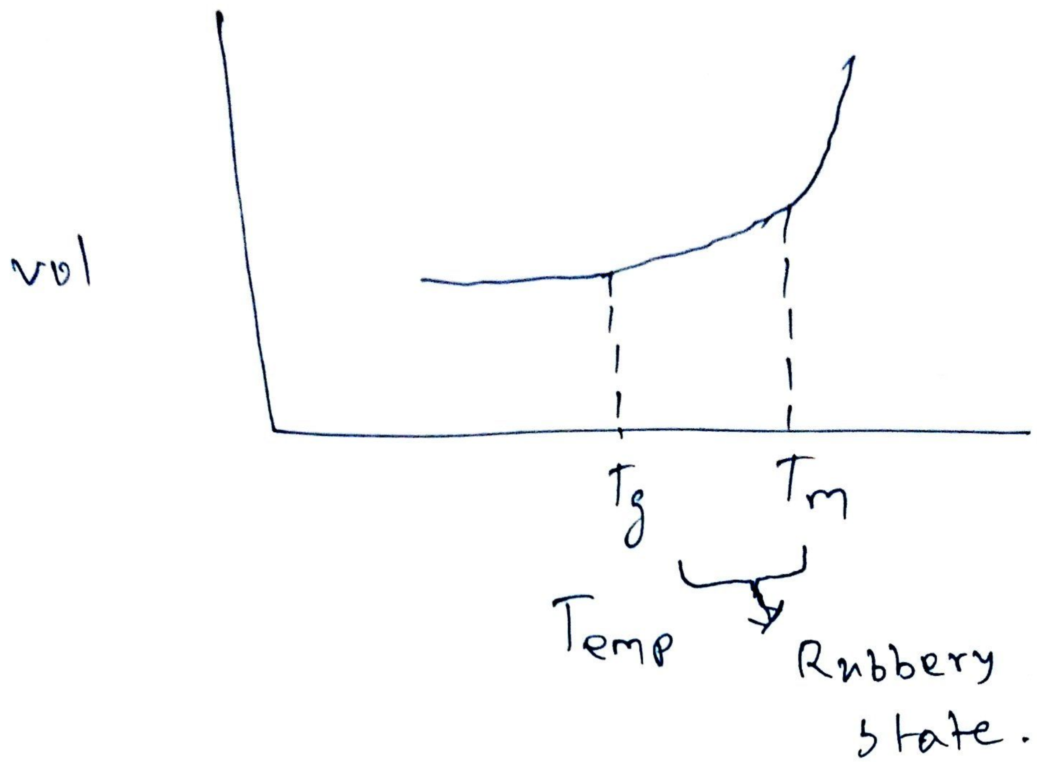
molecules Free to rotate & move

↓

Soft, Flexible, Rubbery

Intermolecular Forces

crystalline > Amorphous



T_g - Glass Transition
Temp.

- The Temp at which the polymer
Solid $\xrightarrow{\text{into}}$ rubbery state

T_g - important for Engineering Applicat

Glass (or) Rubbery ? Depends on T_g

→ At R.T

T_g is crossed

R.T > T_g

T_g of rubber is -20°c

Exist as soft & Rubbery

Polystyrene - Regid at R.T

→ T_g = 100°c > R.T