

# Polymer

Que :- 1 Give the classification of polymer with example.

- By origin
- By monomer
- By thermal response
- By mode of formation
- By structure
- By application & physical properties
- By tacticity

⇒ By origin :-

→ Natural polymer : Polymers which are isolated from natural material are called as natural polymer.

E.g. : Silk, wool, natural rubber, cellulose, starch, proteins etc.

→ Semi synthetic polymers (modified) : These polymer are mostly derived from naturally occurring polymers by chemical modification.

E.g. Cellulose acetate, cellulose nitrate

→ Synthetic polymers : polymers synthesized in laboratory from low molecular weight compounds are called as synthetic polymer.

E.g. : Nylon, Fevylene, polythylene, PVC, Teflon etc.

→ By monomer :

→ Homopolymer : A polymer consist of identical monomers is called homo polymer.

E.g. polyethylene, PVC, Nylon 6.

→ Copolymer : A polymer consist of monomers of different chemical structure is called co polymers.

E.g. : Nylon 6,6.

⇒ By thermal response

→ Thermoplastic polymer : They are easily moulded in diverse shapes by heating and subsequent cooling at room temp.

E.g. : PE, PVC, PS, PP

→ Thermosetting polymer : This polymer is hard and infusible on heating

E.g. Bakelite

⇒ By mode of formation :

→ Addition polymer : The polymers formed by the addition of monomers repeatedly without removal of by products are called addition polymer

E.g. Teflon, polyethylene, PVC

→ Condensation polymers : They are formed by the combination of two monomers by removal of small molecules like  $H_2O$ , alcohol or  $NH_3$ . Their molecular mass is not integral multiple of monomer units.

Eg : Polyamides ; polyesters (PET)

⇒ By structure

→ Linear polymers : In these polymers monomers are linked with each other and form a long straight chain.

E.g. HDPE, nylon

→ Branched polymers : They have straight long chain with different side chains  
Eg. : LDPE, LLDPE.

→ Cross linked polymers : In these monomeric units are linked together to constitute 3D network.

eg. : Bakelite, Melamine etc.

⇒ By tacticity : Tacticity simply means deposition of side group in space

→ If deposited on the same side of the chain then is called isotactic  
If deposited in alternating fashion it is called syndiotactic polymer

If the deposition of side group are at random around the main, it is called atactic polymer.

⇒ Other parameters :-

→ By crystallinity :-

Crystalline : Monomers arranged in ordered way  
Amorphous : Monomers arranged in random way

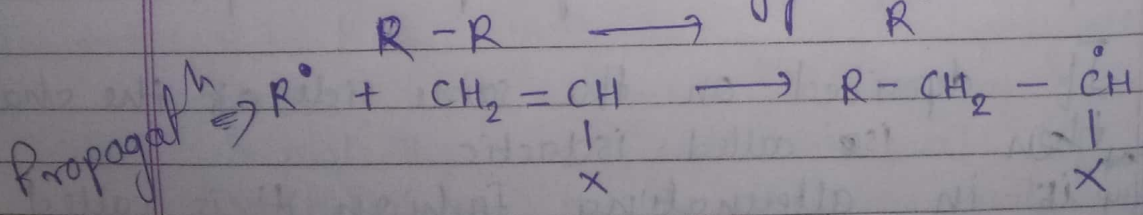
→ By Backbone atom :-

Organic : Polymer backbone is made up of carbon atom.

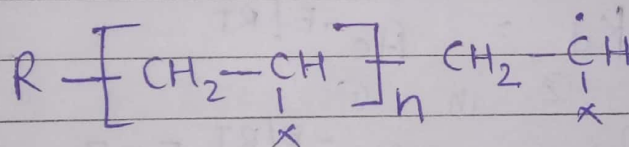
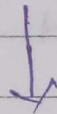
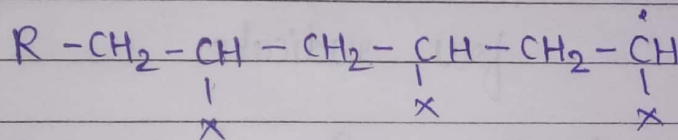
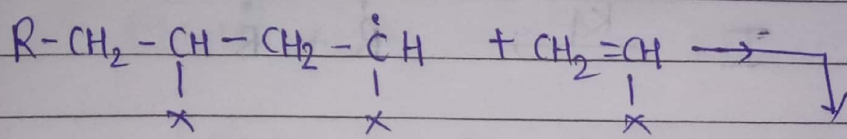
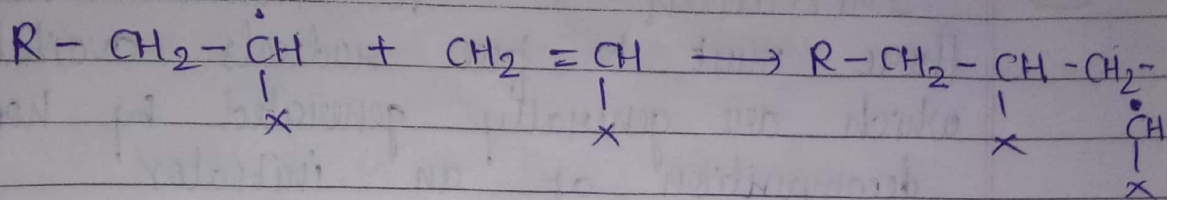
Inorganic : Polymer backbone is made up of other atoms.

Ques 2 Discuss the mechanism of free radical chain polymerisation.

Initiation :- The chain is initiated by free radicals,  $R_2$   $R^{\bullet}$  produced by reaction between some of the ethene and the oxygen initiator

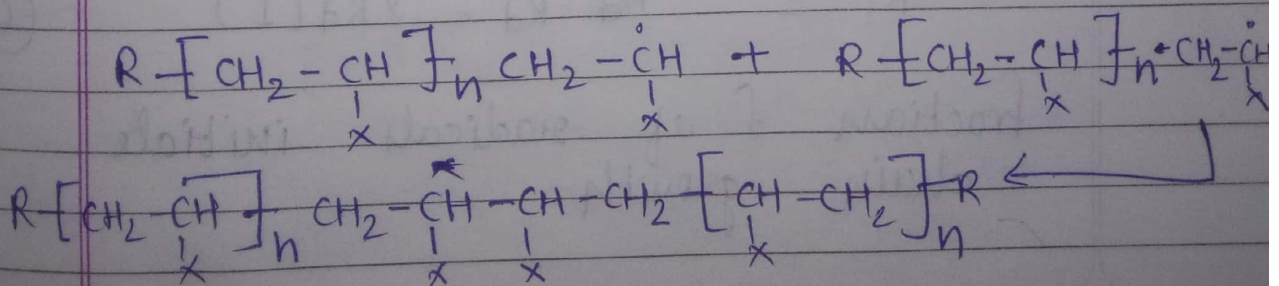


→ Propagation :- Each time a free radical hits an ethene molecule a new longer free radical is formed.



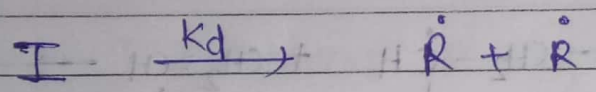
→ Termination :- Eventually two free radicals hit each other producing a final molecule. The process stops here because no free radicals are formed.

→ Chain combination :-



Que 3 Explain the kinetics of free radical chain polymerization.

⇒ Initiation :- To initiate the rxn there must be free radicals available, which are generally generated by homolytic decomposition of an initiator



I = initiator

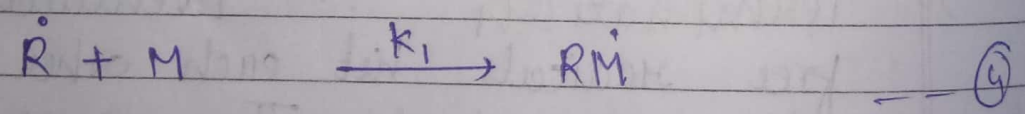
$\dot{R}$  = free radicals

$$-\frac{d[I]}{dt} = R_d = 2k_d[I] \quad \text{--- (1)}$$

$$k_d = A e^{-E/RT} \quad \text{--- (2)}$$

put eq<sup>n</sup> (2) in (1)

$$R_d = 2A e^{-E/RT} [I] \quad \text{--- (3)}$$



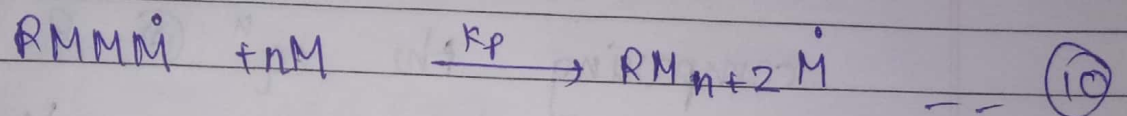
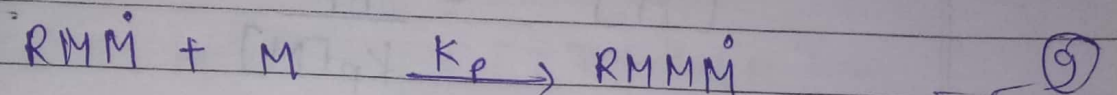
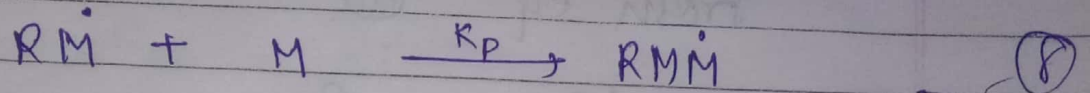
$$-\frac{d[M]}{dt} = R_i = k_i [\dot{R}][M] \quad \text{--- (5)}$$

$$R_i = R_d = 2k_d[I] \quad \text{--- (6)}$$

fraction f of radicals initiate chain growth.

$$R_i = 2fk_d[I] \quad (7)$$

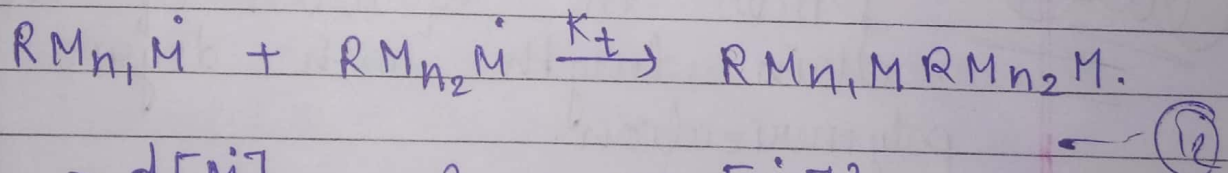
→ Propagation :-



$$\frac{-d[M]}{dt} - R_p = k_p [M][M\dot{M}] \quad (11)$$

$R_p =$  rate of propagation.

→ Termination.



$$\frac{-d[M\dot{M}]}{dt} = R_t = 2k_t [M\dot{M}]^2 \quad (13)$$

$$R_i = R_t \quad (14)$$

$$2k_d f[I] = 2k_t [M\dot{M}]^2 \quad (15)$$

$$[M\dot{M}]^2 = \frac{2k_d f[I]}{2k_t} \quad (16)$$

$$= \frac{k_d f[I]}{k_t}$$

$$[M] = \left( \frac{k_d f [I]}{k_t} \right)^{1/2} \quad (17)$$

From eq<sup>n</sup> (11)

$$[M] = \frac{R_p}{k_p [M]} \quad (18)$$

comparing the eq<sup>n</sup> (17) & (18)

$$\frac{R_p}{k_p [M]} = \left( \frac{k_d f [I]}{k_t} \right)^{1/2}$$

$$R_p = k_p \frac{k_d^{1/2}}{k_t^{1/2}} (f [I])^{1/2} [M]$$

Que 9 Discuss the equation of kinetic chain length with degree of polymerization.

→ Equation for kinetic chain length :

The average no. of monomer molecules consumed by each effective free radical generated by the initiator is called kinetic chain length.

The kinetic chain length can be expressed as,



$$v = \frac{\text{rate of propagation}}{\text{rate of termination}} = \frac{\text{rate of propagation}}{\text{rate of initiation}}$$

$$v = \frac{R_p}{R_t} = \frac{R_p}{R_i}$$

$$R_p = \frac{k_p k_d^{1/2}}{k_t^{1/2}} (f [I])^{1/2} [M]$$

$$R_i = 2k_d [I]$$

$$R_t =$$

$$v = \frac{k_p k_d^{1/2}}{k_t^{1/2}} (f [I])^{1/2} [M] \cdot \frac{1}{2k_d f [I]} = \frac{k_p [M]}{2(k_d k_t f [I])^{1/2}}$$

→ Degree of polymerization :  $D_p$  can be correlated as follows.

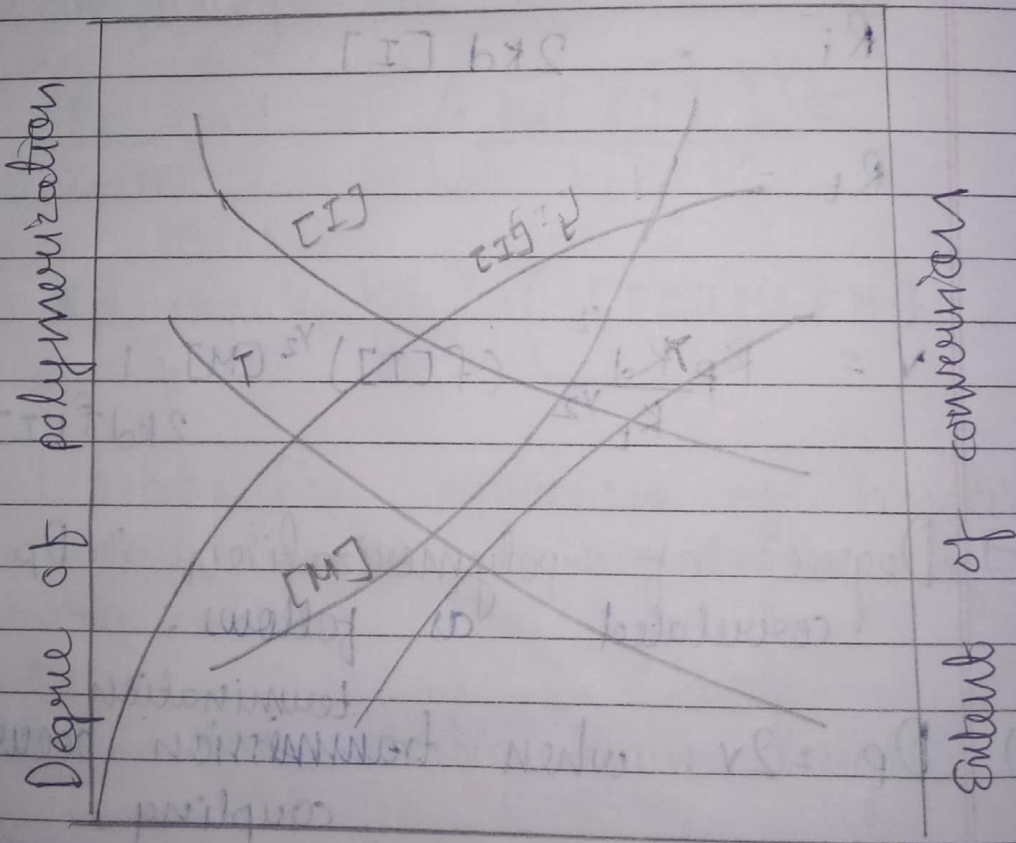
(1)  $D_p = 2v$ , when <sup>termination</sup> termination occurs by coupling.

(2)  $D_p = v$  when <sup>tran</sup> termination occurs by disproportionation.

(3)  $D_p = v/N$  where  $N$  has a value of 0.5 for termination by coupling and 1 for termination by disproportionation.

→ The degree of polymerization decreases with an increase of temperature and of initiator concentration and with a decrease of monomer concentration.

→ The extent of conversion increases with an increase of temp, polymerization time and initiator and monomer concn



Ques 5

Give an account on criteria of polymer solubility.

⇒ The solubi solution process :

The polymer dissolving occurs very slow and consists in 2 steps :

(1) solvent molecules slowly diffuse into the polymer → a swollen gel.

This process is very slow because of cross-linking, crystallinity or strong hydrogen bonding.

(2) The gel gradually ~~dis~~ disintegrates into a true solution. Agitation can speed up this process.

For very high molecular weight, the solution process takes days or weeks.

⇒ Polymer texture and its solubility  
Solubility relations in polymer systems are complex, because of

→ The size differences between polymer and solvent molecules.

→ The viscosity of the system

→ The effects of the texture

→ The molecular weight of the polymer.

→ Solubility depends on the nature of the solvent, the temperature of the solution the topology of the polymer and

the crystallinity.

→ Cross linked polymers do not dissolve, but only swell with the solvent when an interaction between the polymer and the solvent occurs.

→ Many non polar crystalline polymer do not dissolve, except at the temperatures near their crystalline melting points.

→ For Polymers, with the same chemical type and molecular weight the branched species are more soluble than their linear species.

⇒ Solubility parameters:

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G$  = free energy of mixing ( $< 0$ )

$\Delta H$  = heat of mixing

$T$  = temperature of mixing

$\Delta S$  = entropy of mixing ( $> 0$ )

For reasonably non polar molecules and in the absence of hydrogen bonding  $\Delta H$  is positive.

$$\Delta H = V_1 V_2 (\delta_1 - \delta_2)^2$$

$\Delta H$  = heat of mixing  
 $v_1, v_2$  = the fractions of solvent and polymer respectively.  
 $\delta^2$  is the cohesive energy density or the energy of vaporization for small molecules or solubility parameter.

→ In the absence of strong interaction such as hydrogen bonding  
 $(\delta_1 - \delta_2) < 3.5 - 4.0$

The structure of a polymer determines  $\delta_2$ .

$$\delta_2 = \frac{\rho \sum E}{M}$$

$\rho$  = density polymer

$E$  is the sum over the structural configuration of the repeating unit.

$M$  = repeat molecular weight

Solvents with high solubility have usually small and compact molecules.

Ques (6) Derive the general equations to determine the number average and weight average molecular weight.

⇒ Number average molecular weight:  
The most relevant average molecular weight is the weight of polymer divided by the number of polymer molecules. This average molecular weight follows the definition for the mean value of any statistical quantity. It is called the number average molecular weight -  $\bar{M}_n$

Here  $N_i$  is the number of polymers  
 $M_i$  is the molecular weight

Total weight =

$$\bar{M}_n = \frac{\sum_i f_i M_i}{\sum_i f_i} \quad \text{--- (1)}$$

$$f_i = \frac{N_i}{N_{\text{total}}} \quad \text{--- (2)}$$

$$N_{\text{total}} = \sum_i N_i \quad \text{--- (3)}$$

put the eq<sup>n</sup> (2) in eq<sup>n</sup> (1)

$$\bar{M}_n = \frac{\sum_i \left( \frac{N_i}{N_{\text{total}}} \right) M_i}{\sum_i \left( \frac{N_i}{N_{\text{total}}} \right)} = \frac{\sum_i N_i M_i}{N_{\text{total}}} \quad \text{--- (4)}$$

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

Total molecular weight of all the molecules,

$$= N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots$$

$$= \sum N_i M_i$$

Total no. of all the molecules

$$= N_1 + N_2 + N_3 + \dots$$

$$= \sum N_i$$

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}{N_1 + N_2 + N_3 + \dots} \quad \text{--- (6)}$$

$$\bar{M}_n = \frac{\sum_i \frac{N_i}{N} M_i}{\sum_i \frac{N_i}{N}} \quad \text{--- (7)}$$

$$N = N_1 + N_2 + N_3 + \dots + N_i$$

$$\bar{M}_n = \frac{\sum_i \frac{N_i}{N} M_i}{\frac{N}{N}}$$

$$\bar{M}_n = \sum_i X_{ni} M_i \quad \text{--- (8)}$$

dividing eq<sup>n</sup> (8) by  $N_A$ .

$$\bar{M}_n = \frac{\sum_i \frac{N_i}{N_A} M_i}{\sum_i \frac{N_i}{N_A}} = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad \text{--- (9)}$$

Weight average molecular

$$\overline{M_w} = \frac{\sum_i w_i M_i}{\sum_i w_i} \quad \text{--- (10)}$$

$$w = w_1 + w_2 + w_3 + \dots + w_i = \sum_i w_i$$

$$\overline{M_w} = \frac{\sum_i \frac{w_i}{w} M_i}{\sum_i \frac{w_i}{w}} \quad \text{--- (11)}$$

$$\overline{M_w} = \sum_i X_{wi} M_i \quad \text{--- (12)}$$

$$X_{wi} = \frac{w_i}{w}$$

$$w_i = \frac{N_i M_i}{N_A}$$

$$\overline{M_w} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \quad \text{--- (13)}$$

$$\overline{M_w} = \frac{\sum_i N_i M_i^2}{N_A} \div \frac{\sum_i N_i M_i}{N_A}$$

$$\overline{M_w} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad \text{--- (14)}$$

$$w_i = \frac{N_i (M_i / N_A)}{\sum_i [N_i (M_i / N_A)] M_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$



$$\bar{M}_w = \frac{\sum_i f_i M_i^2}{\sum_i f_i M_i} \quad \text{--- (16)}$$

Que 7 How to determine the molecular weight of polymer by viscosity method?

Ans Viscometry is an useful technique for determining the polymer molecular weight.

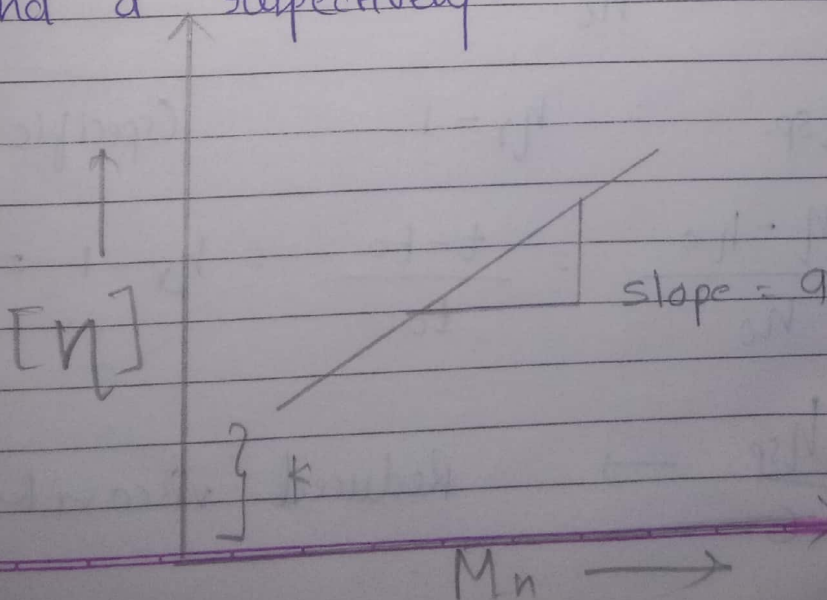
Mark - Houwink eq<sup>n</sup>.

$$[\eta] = k \bar{M}^a \quad \text{--- (17)}$$

$[\eta]$  = Intrinsic viscosity

$\bar{M}$  = molecular weight  
a and k are constant

A plot of  $[\eta]$  against  $\bar{M}_n$  gives a straight line. The ordinate intercept and slope of this line will give k and a respectively.



Acc. to poiseuille eq<sup>n</sup>.

$$\eta = \frac{3.14 p r^4 t}{8 v l} \quad \text{--- (2)}$$

v = volume of liquid

p = pressure head

r = radius of capillary.

t = flow time

l = length of capillary

$$t = \left( \frac{8 v l}{3.14 p r^4} \right) \eta \quad \text{--- (3)}$$

(polymer solution)

$$t_0 = \left( \frac{8 v l}{3.14 p r^4} \right) \eta_0 \quad \text{(solvent) --- (4)}$$

Taking the ratio of above eq<sup>n</sup>.

$$\frac{t}{t_0} = \frac{\eta}{\eta_0} = \eta_r \quad \text{(relative viscosity)}$$

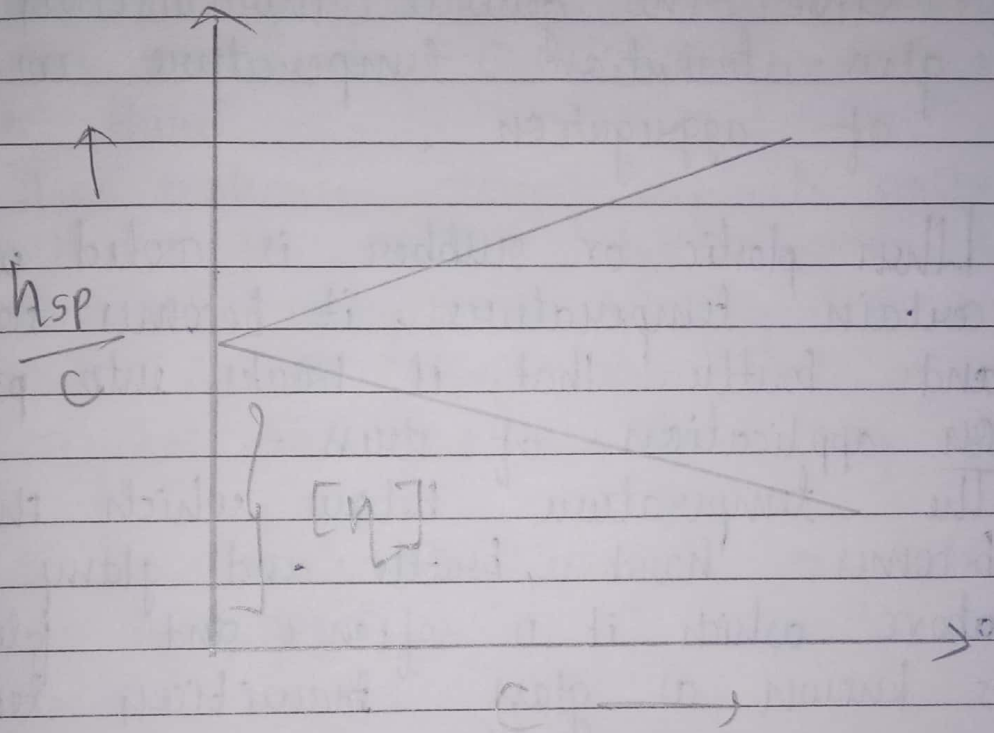
$$\star \quad \eta_{sp} = \eta_r - 1 \quad \text{(specific viscosity)}$$

$$\star \quad \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_r - 1 = \eta_{sp}$$

$$\star \quad \frac{\eta_{sp}}{c} \rightarrow \text{Reduced viscosity}$$

$$\frac{\ln \eta_r}{c} = \text{Inherent viscosity}$$

$$\left( \frac{\eta_{sp}}{c} \right)_{c \rightarrow 0} \rightarrow [\eta] = \text{Intrinsic viscosity}$$



# Que Numericals

(from the G.C.)

Que (8)

Give the general introduction on glass transition temperature with states of aggregation.

Ans

When plastic or rubber is cooled up to certain temperature, it becomes so hard and brittle that it breaks into pieces on application of stress.

→ The temperature below which the polymer becomes hard, brittle and glassy and above which it is softer and flexible is known as glass transition temperature.

→ The glass transition is a property of only ~~amorphous~~ amorphous portion of a semi-crystalline solid. The crystalline portion remains crystalline during the glass transition.

Glassy state (Brittle plastic)	Rubbery state (Tough plastic)	visco fluid state (polymer melts)
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Temp.  $T_g$   $T_m$

## → States of Aggregation :

→ Low mol. wt. compounds have three states of aggregation solid, liquid, gas.  
polymers have only two : solid, liquid.

→ In a crystalline solid there is no brownian movement. Only vibrational motion is there.

→ The molecules occupy definite positions within the crystal lattice and this well defined arrangement is repeated several times in all three dimensions of the crystal and give rise to long range order.

→ A low molecular weight crystalline solid is defined by :

- (1) position & condition of individual molecules
- (2) geometry of the crystal lattice.
- (3) response to an external force.

→ As the temp is raised, more energy is added and vibrational motion increases sufficiently to cross the energy barrier. Brownian movement is activated and becomes vigorous at high temp.

→ The molecules are diffused all over randomly. This state is called liquid state.

→ The temp at which this change of state occurs is called melting point.

→ In polymer, as we increase temp. localized units within the long chain molecule are first mobilized before the whole molecule start moving.

→ At this stage, we have two kinds of movements.

(1) localized mobility of chain segments. TBM

(2) The total mobility of the molecule as a whole: EBM.

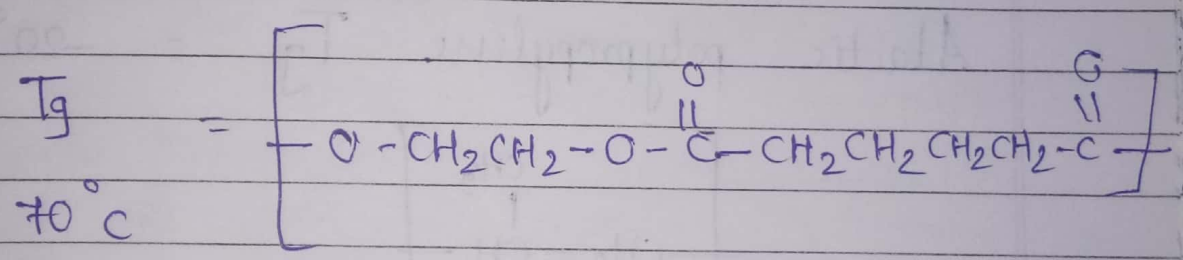
Ques 40

Discuss the factors influencing glass transition temperature.

⇒ Factors affecting glass transition temp. are

(1) Chain flexibility

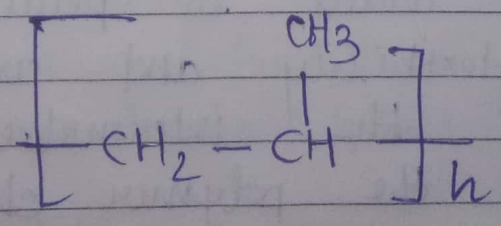
(1) Chain flexibility : In the polymer chain reduce the flexibility of the chain and raise the value of  $T_g$ .



poly (ethylene terephthalate)  $T_g = 69^\circ\text{C}$

(2) Intermolecular forces : Strong intermolecular forces lead to a higher  $T_g$ . PVC has stronger intermolecular forces than polypropylene because of the dipole-dipole forces from the C-Cl bond.

Atactic polypropylene  $T_g = -20^\circ\text{C}$

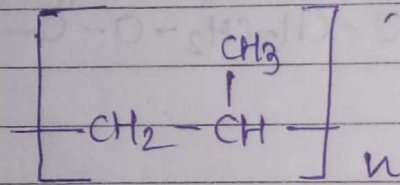


### 3) Pendant Group Groups :

The influence of pendant groups on the glass transition temperature is somewhat more complicated.

Bulky pendant groups, such as a benzene ring can catch on neighbouring chains like a "fish hook hook" and restrict rotational freedom. This increases  $T_g$ .

Atactic polypropylene  $T_g = -20^\circ\text{C}$



### 4) Cross linking :

The presence of cross linking between chains restricts rotational motion and raises  $T_g$ .

### 5) Plasticizers :

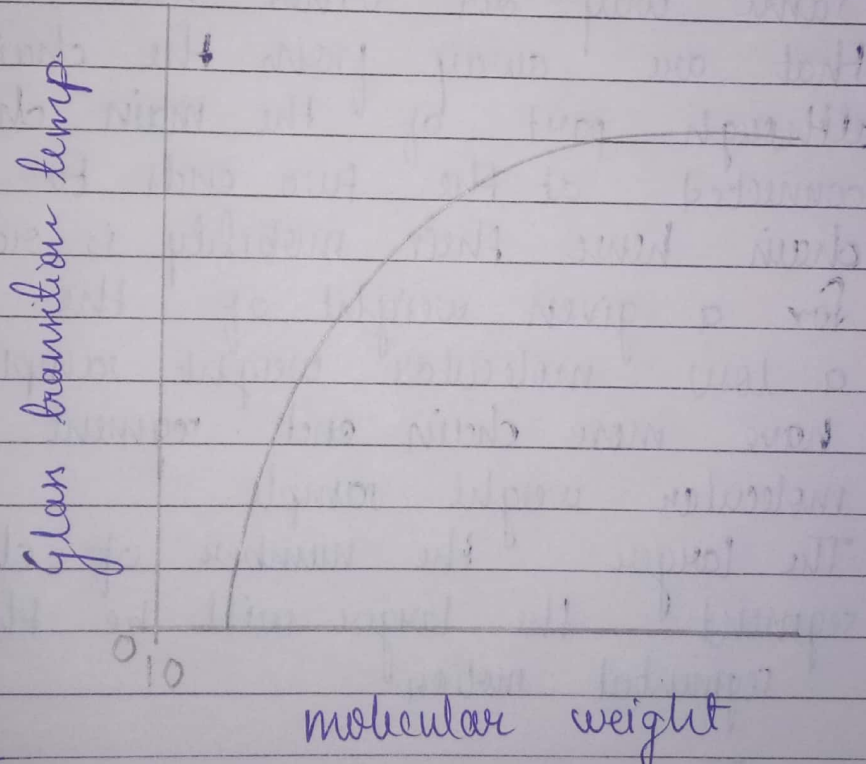
Plasticizers are low molecular weight compounds added to plastic to increase their flexibility and workability. They weaken the intermolecular forces between the polymer chains and decrease  $T_g$ .



(11) Explain the relation between glass transition temperature and molecular weight with importance of glass transition temperature.

→ The glass transition temperature of a polymer is influenced by its molecular weight at least up to around a value of 20,000.

→ Beyond this, the effect of the MW. is not pronounced.



→ The Flory Fox equation relates the number average molecular weight,  $M_n$  to the glass transition temperature  $T_g$ , as shown below.

$$T_g = T_g^\infty - \frac{K}{M_n}$$

$$\frac{1}{T_g} = \frac{1}{T_g^\infty} + \frac{A}{M_n}$$

→ Polymer chains made of hundreds of monomeric unit comprise several segments each made of a few tens of monomeric units.

→ Thus the mobility of chain segments influences the glass transition temperature. At the end of chain, chain ends have more freedom for motion.

→ Same way on other hands the segment that are away from the chain ends although part of the main chain, is connected at the two ends to the main chain hence their mobility is rather restricted.

→ For a given weight of the polymer a low molecular weight sample will have more chain end segment than a high molecular weight sample.

→ The larger the number of chain end segment the larger will be the effective segmental motion.

## ⇒ Importance

→ It is used to know whether a polymer molecule is flexible or rigid and brittle.

- $T_g$  is used to measure the type of response of the polymer whether it exhibits mechanical stress
- Glass transition temperature gives an idea about the polymeric material whether it will behave like plastic or rubber
- $T_g$  informed about a right processing temperature.