MODEL ANSWER

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Polymer Chemistry

Section A:

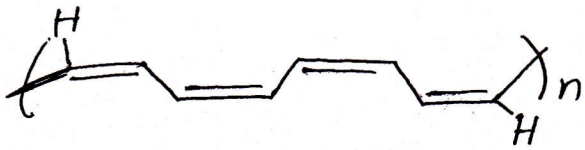
Q1 (i): Why thermoplastic polymers are soft and thermosetting polymers are hard?

Ans: Thermoplastic polymers are soft because adjacent polymer chains are held together by either Vander Waals forces or by dipole-dipole interactions or by H-bonds.
Thermosetting polymers are hard because adjacent polymeric chains are held together by strong covalent bonds that result in formation of cross-linked structures.

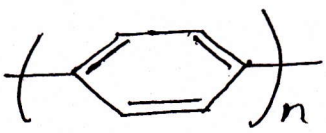
Q1 (ix): Define conducting polymers. Give the name and structure of any two conducting polymers.

Ans: Polymers with conjugated p-electron systems display unusual electronic properties. Such polymers are easily oxidized or reduced by charge-transfer agents (dopants) that act as electron acceptors or electron donors, respectively. This could result in poly(radical–cation)- or poly(radical–anion)-doped conducting materials (p-type and n-type, respectively) with near-metallic conductivity in some cases. Electrons are removed from or added to the conjugated p-electron system to form extra holes or electrons, respectively, which carry current through the polymer chain. The dopant plays an additional role other than bringing about oxidation or reduction. It acts as the bridge or connection for carrying current between different polymer chains. Oxidative dopants include AsF_5, I_2, $AlCl_3$, and $MoCl_5$. Sodium, potassium, and lithium naphthalides are reductive dopants.

Example: Polyacetyelene, Poly-p-phenylene



Polyacetylene



Poly-p-Phenylene

Section - A

Qu.(ii) Write the factors affecting microstructure of polymer?

Ans: Many factors affecting microstructure of polymer intermolecular and intramolecular ~~intermolecular~~ action of polymer chains in aggregated state. Such interaction are caused by forces, such as dispersion force, induction force, dipole interaction and hydrogen bonding, acting within various parts of the same molecule as well as between the neighbouring molecule The nature and the magnitude of such interaction forces depend, apart from the chemical characteristics of the monomer on the manner in which these monomeric units are linked with each other in polymer, whereas the number and chemical nature of monomeric units forming the macromolecules gives an overall picture of the polymer chain.

- Microstructure Based on the chemical structure
  - Organic and Inorganic polymer
  - Homochain and Heterochain
  - Homopolymer and Copolymer

- Microstructure Based on the Geometrical structure - chemical structure of a macromolecules depends on the chemical nature of monomeric units. the geometrical structure depends on the spatial arrangement of the monomeric units with respect to each other. polymer having the same chemical structure can have different geometrical structure.

Qu: (iii) What is reinforcing? Why it is used in polymer?

Ans: "Reinforcing a plastic matrix with a high-strength fibre material results in the formation of what are called fibre-reinforced plastics."

It is used in polymer because outstanding properties such as high strength to weight ratio and excellent corrosion resistance and are easy to fabricate.

A wide variety of articles are made by the fibre reinforcing process. A remarkably high strength-to weight ratio is the main feature attracting spacecraft designers to use reinforced plastics in satellites. Elegance, light weight and corrosion resistance qualifies reinforced plastics for use in boat hulls which are required to rough through marine salt water. The corrosion resistance property of reinforced plastics is fully utilized when they are employed as huge storage thanks for storage acids.

Qu(iv) Above ceiling temperature, depolymerization is favorable process. why?

Ans: The ΔG for polymerization is negative as long as ΔH (exothermic, $\Delta H = -ve$) is greater than $T\Delta S$ ($\Delta G > 0$) at higher temperature and thus the reverse (depolymerization) process becomes favourable.

Qu:(v) What is glass transition temperature? Give the name of the experimental method used for its determination?

Ans: The glass transition temperature (T_g) is defined as the temperature, below which a polymer is hard and above which it is soft. The hard and brittle state is known as glassy state and the soft flexible state as the rubbery or viscoelastic state. Further heating of polymer above glass transition temperature, if polymer is uncrosslinked then it becomes

a highly viscous liquid and starts flowing. this state is termed viscofluid state. The transition taking place at its is flow temperature T_f. All these state are shown by following figure.

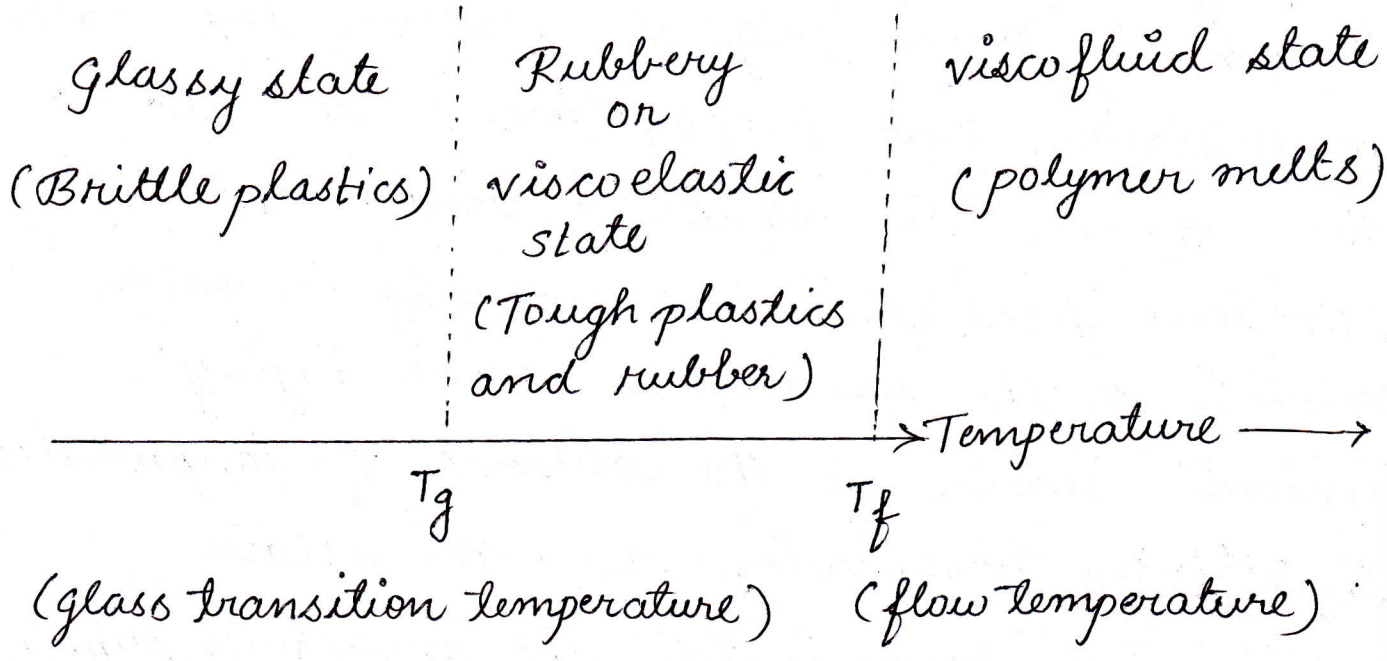


Fig: change of state with temperature in polymeric materials.

Method used for Determination of Glass Transition temperature.

1) Dilatometric method.
2) Thermomechanical method.
3) Calorimetric method.

Qu(vi) Why anionic polymers are known as living polymers?

Ans: Anionic polymerization has tremendous commercial importance because of its ability to control molecular structure during polymerization. anionic polymers are known as living polymers because the rates of initiation and propagation vary with the monomer, ion and solvent. The reactions proceed more rapidly in polar solvents as the species are more highly ionized. Second in the absence of impurities there is no termination step. The chain continue to grow untill the monomer supply is exhausted. In this case, while there is no more monomer left to be polymerized, the carbanions at the chain ends remain potentially active. If a fresh quantity of monomer is added the polymerization again goes on untill all the freshly added monomer is consumed Therefor the anionic polymers are known as living polymers.

Qu(vii) What information can be deduced from molecular weight distribution? How can you generate this curve?

Ans: Many properties of a polymer material like solubility, melt, viscosity etc. depends on its molecular weight. A polymer can have low molecular weight or high. i.e. it contains molecules of different sizes and never has a fixed value of molecular weight. Thus for such dispersed polymers, it is necessary to describe their molecular weight as relative molecular weight or an average molecular weight.

- Depending upon the method of determination there are three types of average molecular masses of polymer:

(i) Number average molecular mass ($\bar{M}_n$)

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

(ii) Mass average molecular mass ($\bar{M}_m$)

$$\bar{M}_m = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

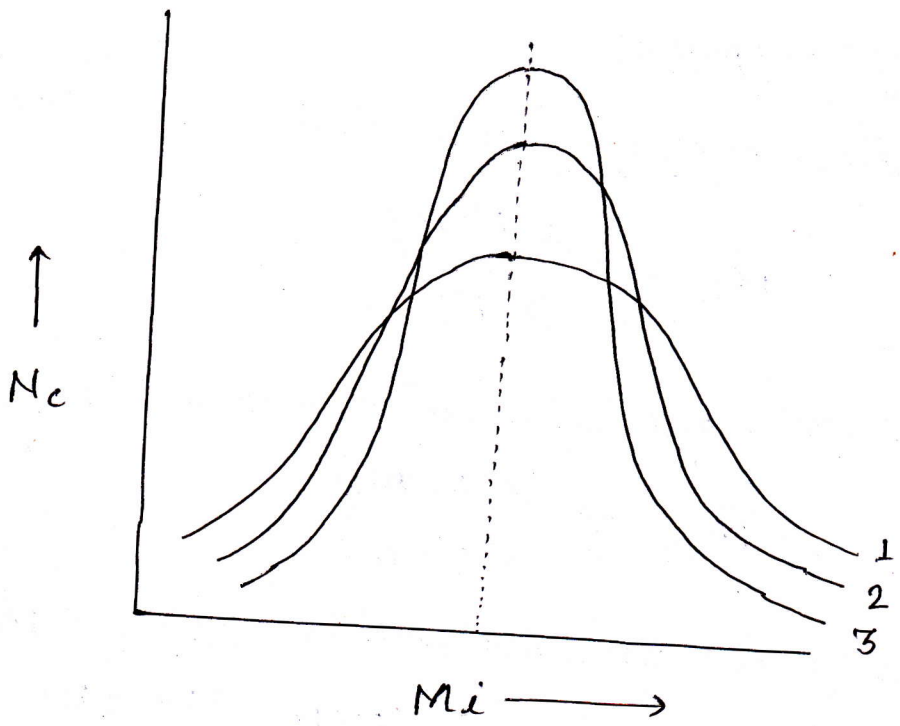
(iii) Viscosity average molecular weigh ($\bar{M}_v$)

$$\bar{M}_v = \left[\frac{\sum (N_i M_i)^{1+\alpha}}{\sum N_i M_i} \right]^{1/\alpha}$$

Molecular Weight distribution curve

Molecular weight distribution is of great practical as well as fundamental importance. For example a small amount of a fraction of either very High or very low molecular weight can greatly change the solid and solution state properties, and thus affects the processing characteristics of a polymer. It is therefore necessary to develop quantitative ways to obtain molecular weight distribution

The figure given below shows the molecular weight distribution of three polymer samples with almost same number average molecular weight.



It can be seen from the curves that polymer sample 1 is highly polydispersed than polymer 2. while polymer sample 3 is less polydispersed than the other two. The polydispersity index P.I. for polymers is defined as the ratio = $\bar{M}_w / \bar{M}_n$. The polydispersity of the molecular weight is the polymer fractions is mainly due to variation of degree of polymerization process. Hence the value of P.I. are highly dependent on the type of polymer process. For a monodispersed polymer P.I. value is unity.

Qu: (viii) Equal numbers of molecules with $M_1 = 10,000$ and $M_2 = 1,00,000$ are mixed. calculate number average and weight average molecular mass of polymer.

Solution: Let $n_1 = n_2 = 10$ (suppose)

then $$\boxed{\overline{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}}$$

$$= \frac{10 \times 10,000 + 10 \times 1,00,000}{(10+10)}$$

$$= \frac{10^5 + 10^6}{20} = \frac{10^5(1+10)}{20}$$

$$\frac{11 \times 10^4}{2} = \frac{110000}{2} = 55,000 \text{ g mol}^{-1}$$

$$\boxed{\overline{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2}{n_1 M_1 + n_2 M_2}}$$

$$= \frac{[10 \times (10,000)^2] + 10 \times (1,00,000)^2}{10 \times 10,000 + 10 \times 1,00,000}$$

$$= \frac{10^9 + 10^{11}}{10^5 + 10^6} = \frac{10^9(1+100)}{10^5(1+10)} = \frac{10^9 \times 101}{10^5 \times 11}$$

$$= \frac{10^4 \times 101}{11} = \frac{1010000}{11} = 91.818$$

$\simeq 92,000$ g mol^{-1} Ans.

Qu. (x) Explain Flory's Theta temperature?

Ans: Different types of interaction forces exist in solution of polymer, such as cohesive forces act between the polymer chain segments and, as a consequences, the segments try to come closer and tighten the coil. Inspite of this strong interaction as well as dispersion forces act between the polymer segments and solvent molecules, pushing the segments apart and loosening the coil. The actual dimension of the polymer chain suspended in a solvent will, therefore, depend on the net result of these opposing forces and will be different from the, unperturbed dimention. In thermodynamically good solvents, strong interaction forces are developed between the chain segment and the solvent. The polymer coil, therefore, opens up considerably increasing the coil dimension. If we can denote the end-to-end distance of a chain in a solvent as (r) the same can be related with (r_0) through an expansion factor α which

discribes the increase in size of the polymer coil in solution over the unperturbed dimension.

$$\boxed{(\bar{r}^2)^{1/2} = \alpha (\bar{r}_0^2)^{1/2}}$$

α will be large in case of polymer molecules in a good solvent. In a thermodynamically poor solvent, where there are no strong interaction forces. but only dispersion forces ~~interaction forces~~. acting between the solvent and polymer segments, the chain expansion is relatively less and the value of α is also low. For a given polymer and solvent, the temperature at which α becomes unity is called Flory's theta temperature (θ) and the solvent at that temperature is called the theta solvent for that polymer.

Section - B

Ans(2a) and (2b) :— Mechanism of Free Radical Polymerization & Kinetics of polymerization without chain transfer reaction

Free radical chain polymerization

We can understand the kinetics of free radical addition polymerization under three steps

(i) Initiation
(ii) Propagation
(iii) Termination

To initiate the reaction, there must be free radicals available, which are usually generated by the homolytic decomposition of an initiator as shown

$$I \xrightarrow{Kd} \dot{R} + \dot{R} \quad \text{——} \quad (1)$$

Here, I is the initiator, $\dot{R}$ the free radical formed and Kd the initiator decomposition rate constant. The rate of decomposition (Rd) of the initiator is related to the concentration of the initiator (I) by the following equation :

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

A factor of 2 is used in equation (2) as a pair of radicals is produced by decomposing one molecule of the initiator. From the Arrhenius equation, we know that the rate constant is related to temperature as follows —

$$Kd = A e^{-E/RT} \quad \text{——} \quad (3)$$

where A is a constant called the frequency factor, E the activation energy term, R the gas constant and T the temperature in the absolute scale

Sutituting ~~the~~ Kd from equation (3) in (2). Equation (2) can be rewritten as

$$R_d = 2A\, e^{-E/RT}\, [I] \quad \text{——— (4)}$$

This equation tells us that rate of decomposition of an initiator increases with the temperature and concentration of the initiator.

Initiation

The free radicals generated by the decomposition of the initiator can attack the monomer to give a new free radical as shown

$$R^{\cdot} + m \xrightarrow{k_i} Rm^{\cdot} \quad \text{——— (5)}$$

where m is the monomer and k_i is the initiation rate constant. The rate of initiation denoted by R_i may then be written as

$$-\frac{d[M]}{dt} = R_i = k_i [R^{\cdot}][M] \quad \text{——— (6)}$$

The free radicals have such a high reactivity that as soon as they are formed by the decomposition of the initiator, they attack the monomer and start the initiation process. We can assume, therefore, that the rate of formation of free radicals is equal to the rate of the disappearance of the same, according to equation (5). We can, therefore, visualise that R_i is equal to R_d. R_i can now be written as ($R_i = R_d$) due to high reactivity

$$R_i = 2k_d [I] \quad \text{——— (7)}$$

This equation holds good when all the free radicals produced are effective in initiating the polymer growth. In actual practice, some of them are not effective since they are lost as side products by way of processes such as

recombination. If we denote by f, the fraction of the free radicals produced that is effective in initiating the chain growth, then R_i can be further modified as

$$R_i = 2 f k_d [I] \quad \text{——— (8)}$$

The value of f, which is usually between 0.6 and 1.0 gives us the efficiency of the initiator. A value of 0.6 indicates that only 60% of the radicals generated have effectively initiated chain growth, the remaining 40% being lost as side products.

Propagation

Initiation is followed by a propagation step which can be represented as:

$$R\dot{M} + M \xrightarrow{k_p} RM\dot{M} \quad \text{——— (9.1)}$$

$$RM\dot{M} + M \xrightarrow{k_p} RMM\dot{M} \quad \text{——— (9.2)}$$

$$RMM\dot{M} + nM \xrightarrow{k_p} RM_{n+2}\dot{M} \quad \text{——— (9.3)}$$

where k_p is the propagation rate constant

The rate of propagation (R_p) is represented by

$$-\frac{d[M]}{dt} = R_p = k_p [\dot{M}] [M] \quad \text{——— (10)}$$

From equation (10) we understand that the propagation rate is proportional to $[\dot{M}]$, the concentration of reactive free radical sites (i.e., concentration of growing chains) as well as $[M]$, the concentration of the monomer.

Termination.

The final step in polymerization is termination. If termination occurs by the combination of two growing chains (i.e. coupling), it can be represented as

$$RM_{n_1}\dot{M} + RM_{n_2}\dot{M} \xrightarrow{k_t} \underset{\text{for different}}{RM_{n_1}MMM_{n_2}R} \text{ or } \underset{\text{for similar}}{RM_{n_3}R} \quad \text{—— (11)}$$

where k_t is the termination rate constant.

The corresponding rate equation for the termination process is given by

$$-\frac{d[\dot{M}]}{dt} = R_t = 2k_t[\dot{M}]^2 \quad \text{—— (12)}$$

However, when the steady state prevails (i.e., when the number of chain growths initiated equals the number of chain growth arrested), the rate of initiation is equal to the rate of termination, i.e.,

$$R_i = R_t \quad \text{—— (13)} \quad \text{(steady state)}$$

From equations (8) and (12), we can write

$$2k_d f[I] = 2k_t[\dot{M}]^2$$

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

$$[\dot{M}] = \left(\frac{k_d f[I]}{k_t}\right)^{1/2} \quad \text{—— (14)}$$

From equation (10), we get the value of $[\dot{M}]$ as

$$[\dot{M}] = \frac{R_p}{k_p [M]} \quad \text{———} \quad (15)$$

On substituting this value of $[\dot{M}]$ in eq (14), we get

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

or

$$\boxed{R_p = k_p \frac{k_d^{1/2}}{k_t^{1/2}} (f[I])^{1/2} [M]} \quad \text{—} \quad (16)$$

This equation states that the rate of polymer formation is proportional to the first power of monomer concentration and also to the square root of the initiator concentration.

Equation for kinetic chain length

The kinetic chain length (ν) can be defined as the average no. of monomer molecules consumed by each effective free radical generated by the initiator. It, thus, expresses the number of monomer molecules added to a growing chain from its initiation up to termination. The kinetic chain length can be expressed as

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

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad \text{———} \quad (17)$$

Substituting the value of R_p and R_t from eqn. (16) equations (16) and (8) in eq. (17), we get

$$\nu = K_p \frac{K_d^{1/2}}{K_t^{1/2}} \left(f[I]\right)^{1/2} [M] \frac{1}{2 K_d f[I]}$$

$$\nu = \frac{K_p [M]}{2 \left(K_d K_t f[I]\right)^{1/2}} \quad \text{—— (18)}$$

Degree of polymerization

As the kinetic chain length gives the average number of monomer molecules present in a growing chain at the time of termination, the average degree of polymerization, $\bar{D}_p$ can be correlated as follows :-

(i) $\bar{D}_p = 2\nu$, when termination occurs by coupling

(ii) $\bar{D}_p = \nu$, when termination occurs by disproportionation

(iii) $\bar{D}_p = \nu / N$, where N has a value of 0.5 for termination by coupling and 1 for termination by disproportionation.

From an overall study of the kinetics, we can put following generalisation about radical polymerization.

(a) The degree of polymerization decreases with an increase of temperature and

The results are shown by fig. 1

DP decreases with increasing the T and I but increases with increasing mono conch

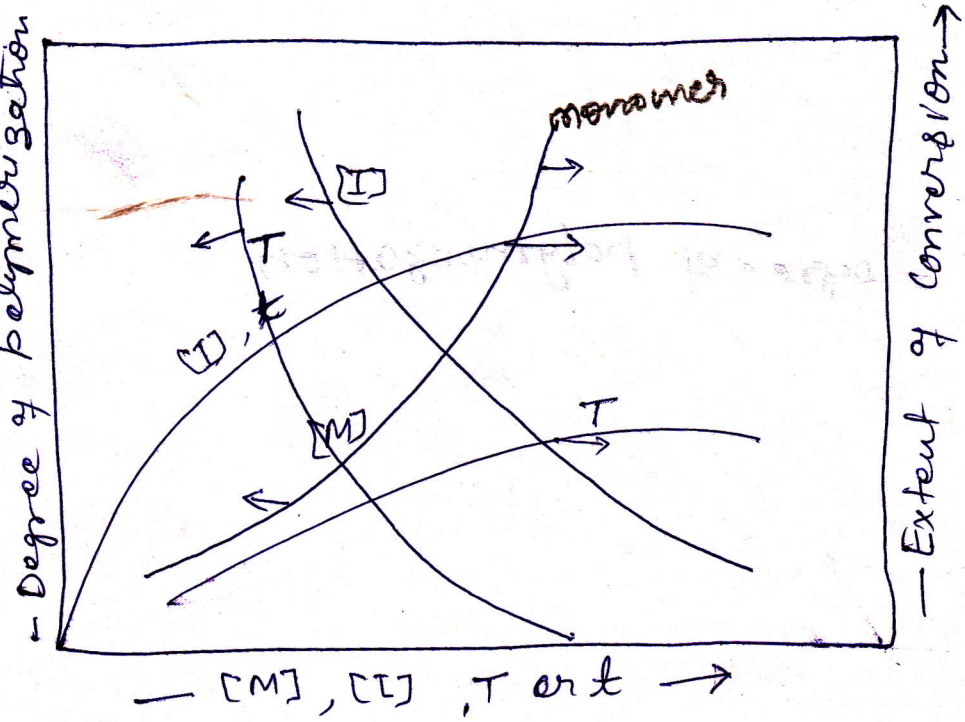


Fig. 1 Dependence of degree of polymerization and extent of conversion:
(i) monomer concentration, [M]
(ii) Initiator Concentration, [I]
(iii) Temperature of polymerization, T or
(iv) Polymerisation time, t - in radical polymerisation.

of initiator concentration and with a decrease of monomer concentration.

(b) The extent of conversion increases with an increase of (i) temperature (ii) Polym time and (iii) Initiator and monomer conch.

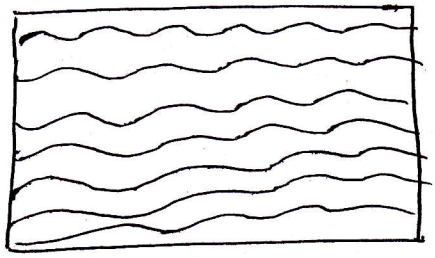
Section B:

Q3: What are polymers? Explain their classification based on structure, and the modes of polymerization.

Ans: Poly meaning 'many' and mer meaning 'part' (in Greek). Polymer is made up of many small units as monomers which have linked to each other to form a long or large molecule. Polymers are complex and giant molecules and they are different from low molecular weight compounds. The process by which the monomer molecules are linked to form a polymer is called polymerization.
On the basis of structure, polymers are classified into following categories.
Linear chain polymers: The monomers react to each other and form a straight long chain. Linear polymers are well packed and therefore the possess:

(a) High crystallinity,
(b) Tensile strength,
(c) High densities,
(d) High melting point

Example: HDPE, Amylose

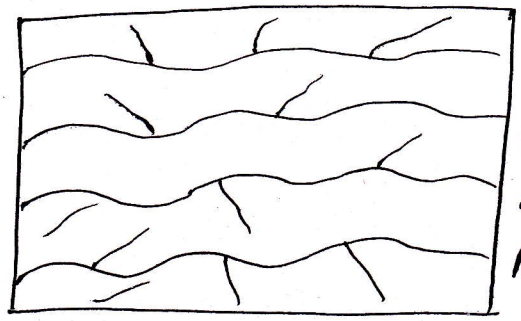


Linear chain Polymer

Branched chain polymers: Polymers which have side chains attached to side chains attached to the linear chain. The branched chain polymers are irregularly packed and they have:

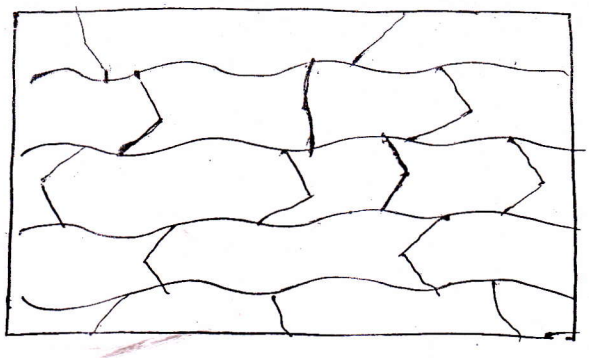
(a) Lower tensile strength
(b) Lower melting point
(c) Lower density
(d) Lower crystallinity

Example: LDPE, Amylopectin etc.



Branched chain Polymers.

Cross-linked polymers: Polymers in which adjacent polymeric chains are linked to each other directly or through side chains are called cross-linked polymers.
The crosslinking of polymeric chains forms a network type structures. When heated in a mould, cross-linked polymers become infusible and form an insoluble hard mass. As a result once molded, these polymers can not be reshaped or remelted by heating.
Example: Bakelite , urea formaldehyde resin, vulcanized rubber



~~Cross-linked~~

Cross-linked polymers.

On the basis of modes of polymerization, there are two modes of polymerization

A) Addition polymerization
B) Condensation polymerization

<u>Addition polymerization or chain growth polymerisation</u>: The repeated addition of monomers to the growing polymer chain is called addition polymerization. It is performed using the molecules containing double or triple bonds (unsaturated monomers). The monomer units combine in a head to tail manner to give the polymer chain. The polymers have the same empirical formula as their monomers.

Examples:

(i) $nCH_2=CH_2 \xrightarrow{\text{Polymerization}} \left[CH_2-CH_2\right]_n$

PE

(ii) $nCH_3-CH=CH_2 \xrightarrow{n} \left[CH_2-\underset{\underset{CH_3}{|}}{CH}\right]_n$

PP

(iii) $nCH_2=CHCl \xrightarrow{n} \left[CH_2-\underset{\underset{Cl}{|}}{CH}\right]_n$

PVC

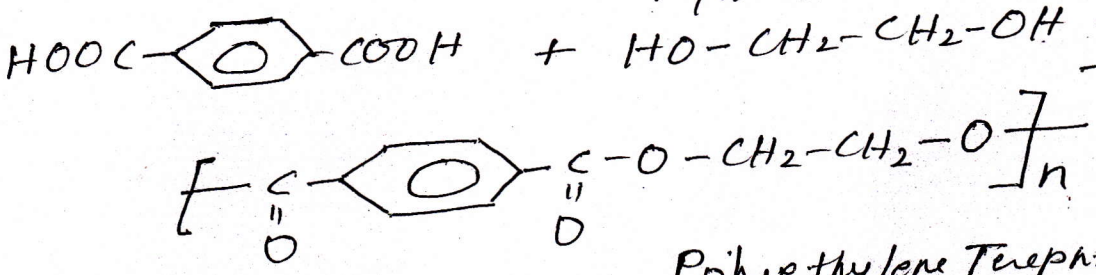
<u>Condensation polymerization or step-growth polymerisation</u>:
This polymerization is carried out by monomers containing two or more reactive functional groups such as –OH, -COOH, -NH_2 react with each other with a loss of small molecules like H_2O, NH_3 and HCl. Some typical examples are given below.

Examples:

(i) $nHOOC-(CH_2)_4-COOH + nH_2N-(CH_2)_6-NH_2 \xrightarrow[-H_2O]{\text{Polym.}}$

$$\left[\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_6-NH\right]_n$$

Nylon 6,6

(ii) 

Polyethylene Terephthalate (PET)

Ans(4) :- The Flory-Huggins theory of Polymer Solutions

The polymer obey the Raoult's Law only at extreme dilution otherwise they show considerable departure from Raoult's Law. In order to understand the reason for this departure, we have to look into structure of polymer and low molecular solutions as shown in Fig. 1 based on quasi crystalline lattice model for solns

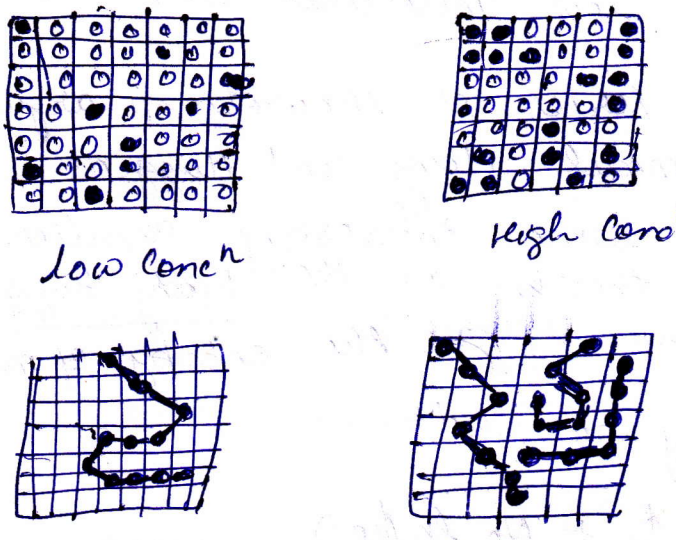


Fig. 1 Two dimensional quasicrystalline lattice model for solutions of low molecular weight compounds and Polymers

This figure shows a two dimensional lattice model (two component system)

According to the Boltzmann equation the no of ways the solute and solvent molecules can be arranged (W) is defined by the following equation:

$$\Delta S_m = K \ln W \quad \text{——— (1)}$$

where ΔS_m = Entropy of mixing

K = Boltzmann constant.

In the lattice model concept, it is assumed that the sizes of the polymer chains segments are comparable to those of the solvent molecules as well as of lattice sites and that the segments can occupy the lattice sites as shown in figure. 1. owing to the large size of the polymer molecules, it is evident that the number of ways of arranging the polymer segments will be relatively small. That is to say, the entropy of mixing for polymer dissolution is much less compared to that for low molecular weight solutes.

~~Though~~ Through a series of theoretical arguments based on the lattice model, Flory and Huggins independently arrived at some interesting equations which later came to be known as the Flory Huggins theory. According to this theory the entropy of mixing for polymer solution may be written as

$$\Delta S_m = -k\,(N_s \ln \phi_s + N_p \ln \phi_p) \qquad (2)$$

where the subscript S stands for the solvent and P for the polymer.

The volume fraction ϕ_s and ϕ_p in the foregoing equation are given by

$$\phi_s = \frac{N_s}{(N_s + nN_p)} \qquad (3)$$

no of segments in polymer molecule

$$\phi_p = \frac{nN_p}{(N_s + nN_p)} \qquad (4)$$

where N_s = no. of solvent molecules
N_p = no. of polymer molecules
n = the no of segments in a polymer molecule

The heat of mixing of polymer solutions could be ~~given as~~ written as measure the solvent power

$$\Delta H_m = KT\chi N_s \phi_p \quad \text{——} \quad (5)$$

where χ = Flory Huggins interaction parameter, which, in essence, measures the solvent power of the system and enables us to distinguish between a good solvent and poor solvent.

A low value of χ is indicative of a good solvent whereas a ~~low~~ high value of χ means a poor solvent.)

The free energy of mixing of polymer solutions is given in terms of χ as follows.

$$\Delta F_m = \Delta H_m - T\Delta S = KT\chi N_s\phi_p + TK(N_s \ln\phi_s + N_p \ln\phi_p)$$

$$\Delta F_m = kT(\chi N_s \phi_p + N_s \ln\phi_s + N_p \ln\phi_p) \quad \text{——} \quad (6)$$

The Flory Huggins theory suggested a equation for total free energy of dilution on the basis of following thoughts.

- There are two entropy factors which contributes to the free energy of dilution: one arising from contact between polymer segments and solvent molecules, and the other is called conformation entropy. Thus, the overall free energy of dilution will be the sum of the two terms as follows:

$$\Delta F_m = \Delta F_{conform} + \Delta F_{contact} \quad \text{——} \quad (7)$$

It is shown that

since $Nx = R$

$$\Delta F_{conform} = RT\left[\ln(1-\phi_p) + \left(1-\frac{1}{n}\right)\phi_p\right] \quad \text{——} \quad (8)$$

and

$$\Delta F_{contact} = RT\left[\chi\phi_p^2\right]$$

so that

$$\Delta F_m = RT\left[\ln(1-\phi_p) + \left(1-\frac{1}{n}\right)\phi_p + \chi\phi_p^2\right] \quad \text{——} \quad (9)$$

This equation is derived for monodisperse polymer. Further it has been shown that for a polydisperse system the n factor in the equation (10) has to be replaced its average value denoted as $\bar{n}$.

In that case, for a polydisperse system, equ (10) becomes

$$\Delta f_m = RT\left[\ln(1-\phi_p) + \left(1-\frac{1}{n}\right)\phi_p + \chi\phi_p^2\right] \quad -(11)$$

In Equation (11), if the value of χ exceeds some critical value denoted as $(\chi)_c$, the system will tend to separate into two phases. In that cases, the corresponding values in terms of n are mathmatically shown to be as follows:

$$(\chi)_c = \frac{1}{2}n + \frac{1}{\sqrt{n}} + \frac{1}{2} \quad \text{——— (12)}$$

$$(\phi_p)_c = \frac{1}{1+\sqrt{n}} \quad \text{——— (13)}$$

Two phase occur at critical value.

Here $(\phi_p)_c$ represents the critical composition (i.e. critical volume fraction of the polymer) corresponding to the critical value $(\chi)_c$.

Equation (11) has been derived based on many theoretical thoughts or reservations. Therefore, attempts have been made to rectify the shortcomings of the theory. The most important correction has been done with respect to the term $\Delta f_{contact}$. For instance, Orofino and Flory argued that this term would be better represented by the equation

$$\Delta f_{contact} = RT\left[\chi\phi_p^2 + \chi'\phi_p^3 + \chi''\phi_p^4 + \cdots\right] \quad \text{——— (14)}$$

where as in equation (9) only the first term is taken into account, neglecting the other terms. Hence, the ultimate free energy of dilution Δf_m has also to be corrected accordingly by using eq (14) in place of equation (10)

$\pi V = nRT$

The osmotic pressure (π) is related to the free energy of dilution through the following equation

$$\pi \bar{V}_s = -\Delta F_m \quad \text{——} \quad (15)$$

since $-\Delta F_m = \pi \bar{V}_s$
so $\Delta F_m = -\pi V_s$

where $\bar{V}_s$ is the partial molar volume of the solvent.

On substituting the value of ΔF_m from above equation in equation (11), we have

$$-\pi \bar{V}_s = RT\left[\ln(1-\phi_p) + \left(1-\frac{1}{n}\right)\phi_p + \chi\phi_p^2\right] \quad (16)$$

$$\pi = \frac{-RT}{\bar{V}_s}\left[\ln(1-\phi_p) + \left(1-\frac{1}{n}\right)\phi_p + \chi\phi_p^2\right] \quad (17)$$

In dilute solutions, the value of ϕ_p will be far less than unity and hence, $\ln(1-\phi_p)$ may be written as follows – series expansion for low value

$$\ln(1-\phi_p) = -\left[\phi_p + \frac{\phi_p^2}{2} + \frac{\phi_p^3}{3} + \cdots\right] \quad (18)$$

Now, Equation (17) may be rewritten as

how

$$\pi = \frac{RT}{\bar{V}_s}\left[\frac{\phi_p}{n} + \left(\frac{1}{2}-\chi\right)\phi_p^2 + \frac{1}{3}\phi_p^3 + \cdots\right] \quad (19)$$

or

$$\pi = RT\left[\frac{\phi_p}{n\bar{V}_s} + \left(\frac{1}{2}-\chi\right)\frac{\phi_p^2}{\bar{V}_s} + \frac{1}{3}\left(\frac{\phi_p^3}{\bar{V}_s}\right) + \cdots\right] \quad (20)$$

On appropriate substitutions, equation (20) will take the following form (where in the osmotic pressure is related to molecular weight ($\bar{M}_n$) and concentration (c) of the solution).

$\frac{\phi_p}{V_s} = c$

$$\pi = RT\left[\frac{c}{\bar{M}_n} + \frac{\bar{v}_p^2}{\bar{V}_s}\left(\frac{1}{2}-\chi\right)c^2 + \cdots\right] \quad (21)$$

$\bar{n} = \bar{M}_n$

$\phi = c \cdot v$

Here v_p is the partial specific volume of the polymer.

Equation (21) may also be rewritten as

$$\pi = \left[\left(\frac{RT}{\bar{M}_n}\right)c + RT\left(\frac{\bar{v}_p^2}{\bar{v}_s}\right)\left(\frac{1}{2}-\chi\right)c^2 + \cdots\right] \quad \text{— (22)}$$

take common c

$$\text{or} \quad \frac{\pi}{c} = RT\left(\frac{1}{\bar{M}_n} + Bc\right) \quad \text{— (23)}$$

where B is termed as second virial coefficient. The force of interaction between the polymer molecules and the solvent is measured by this term.

Equation (23) demonstrates the need to extrapolate the experimental osmotic pressure data to zero concentration at which the higher power concentration terms may be neglected and the equation gets reduced to:

$$\boxed{\left(\frac{\pi}{c}\right)_{c\to 0} = \frac{RT}{\bar{M}_n}} \quad \text{— (24)}$$

The term on the left hand side of equation (24) indicates $\frac{\pi}{c}$ at zero concentration or infinite dilution.

Section - B

Ans (5) :-

Definition of Polymer degradation :- Polymeric materials undergo decrease in their molecular weight during fabrication and / or long term use, by chemical and/ or radiation attack. The loss of molecular weight is mostly undesirable and is called polymer degradation. The degradation is caused by the scission of the backbone by certain agents like heat, light and other ionizing radiations, water and bacteria etc.

or

The deterioration in properties like strength, lustre, elasticity etc in the presence of rain, sun and other physical factor is due to a phenomenon called polymer degradation.

Polymer degradation process is some time useful like for protecting the spacecraft from explodation

Mechanism of degradation process

The degradation takes place in two different ways

(i) chain end degradation or unzipping or depolymerization

(ii) Random degradation

(i) **chain end degradation**

(unzipping with example)

In this process chain begins to break from its ends so slow decrease in molecular weight occured and monomers are liberated therefore it is called as depolymerization. Propagation is "closing of zip" and depolymerization "opening of zip" so also termed as unzipping.

In this case large no. of monomer unit is liberated. The unzipping polymer degradation process occurred in the following manner.

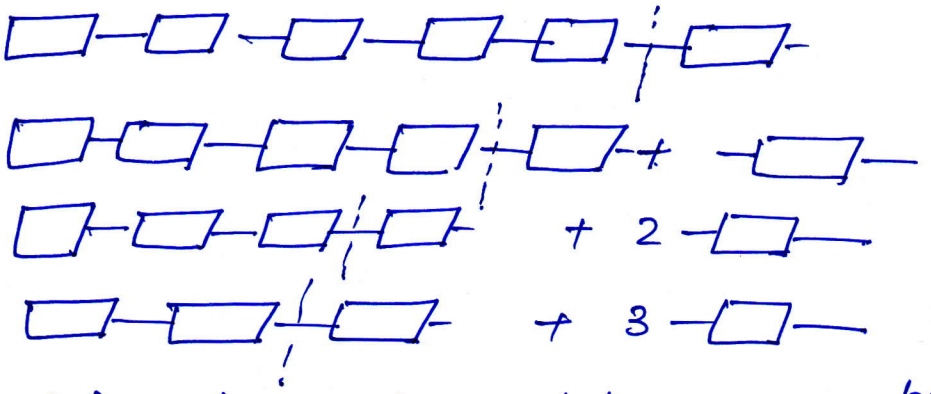


Fig. 1 :- Schematic representation of a polymer molecule undergoing chain-end degradation (Each block in the diagram represents one monomeric unit)

Example:- A good example of unzipping or chain end degradation is provided by the thermal depolymerization of non-terminated (i.e. living) poly α-methylstyrene synthesized through the anionic mechanism. This polymer in a solvent such as anhydrous tetrahydrofuran (THF) upon heating from −70°C to 60°C, undergoes degradation from the chain end carrying the active carbanion in such a manner that, at 60°C, the entire polymer is converted into the monomer. The important precaution to be taken is that the system should be kept free from moisture and other impurities such as oxygen and carbon dioxide. The process is, interestingly enough, reversible. Hence, by simply cooling the system back to −70°C, the polymer can be obtained qualitatively

(ii) <u>Random degradation</u>:- The Random degradation occurs at any random point along the polymer chain instead of at the chain ends and hence known as Random degradation. This type of degradation could be thought of as the reverse of the polycondensation process as illustrated by the following equation:

$$M_n \rightarrow M_x + M_y$$

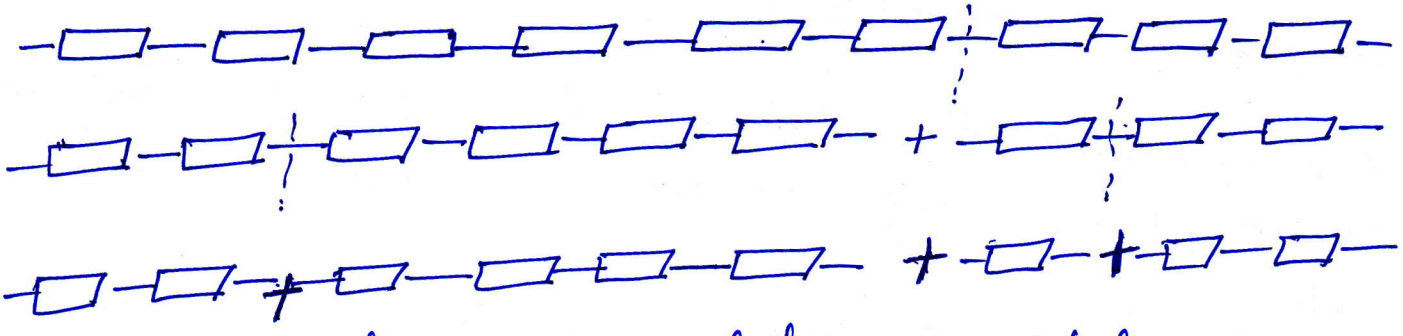
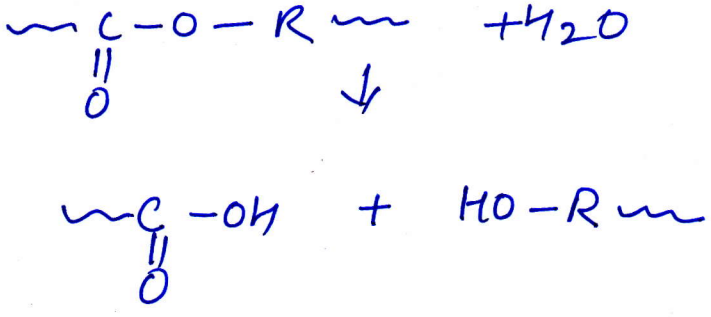


Fig. 2: Schematic representation of a polymer molecule undergoing random degradation (Each block in the diagram represents one monomeric unit)

- Here, the polymer degrades to lower molecular weight fragments but (unlike in chain-end degradation) practically no monomer is liberated.

- Almost all polymers can undergo random degradation.

Example:- Polyesters undergo hydrolytic degradation, resulting in chain scission



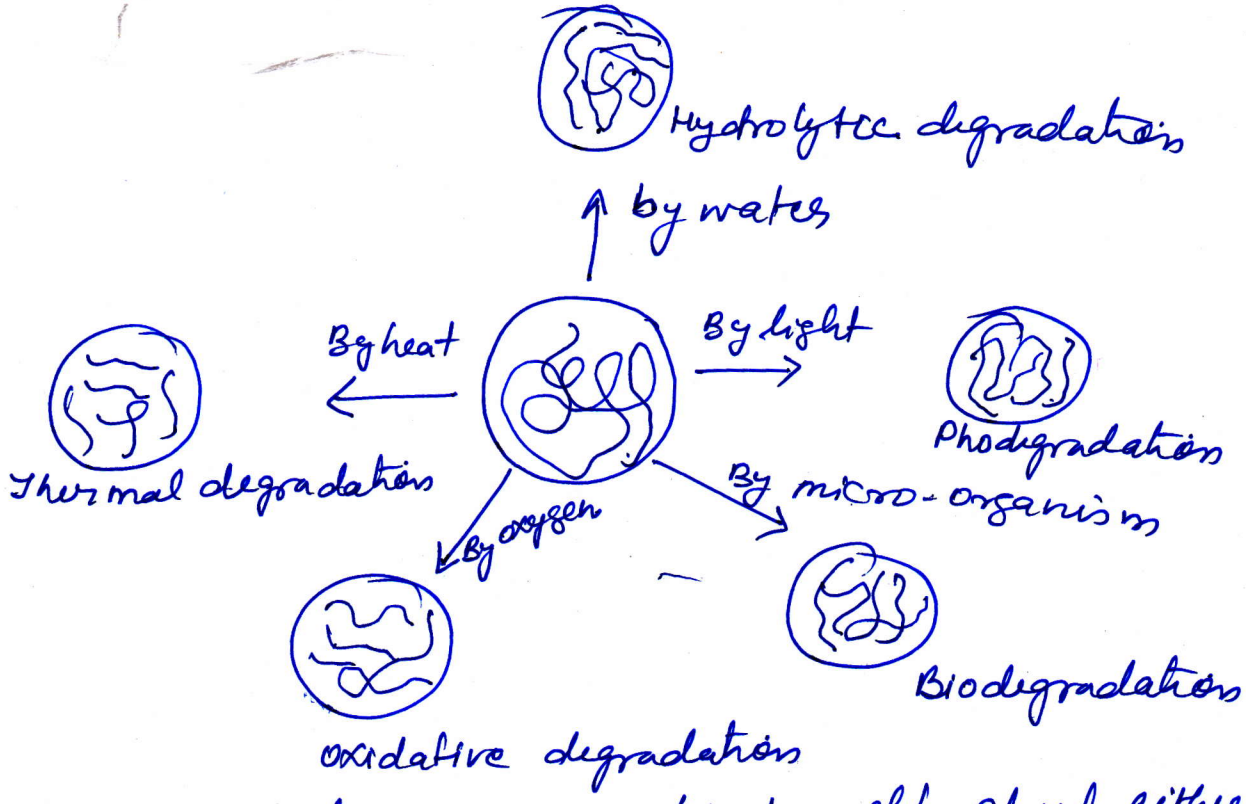
Further, in random degradation of polyethylene for instance, a hydrogen atom may migrate from one carbon to another and yield two fragments, as follows

$$\sim CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2\sim$$

$$\sim CH_2-CH_2-CH_2-CH_3 + CH_2=CH-CH_2-CH_2-CH_2\sim$$

- For random degradation to occur, the polymer chain need not necessarily carry any active site
- In Random degradation, sudden drop in mol. wt. occurred with little or no release of the monomer.

several possible types of degradation are schematically represented in fig. 3



Degradation of polymers may be brought about either by physical factor such as heat, light, mechanical stress or by chemical agents like oxygen, ozone, acids, alkalies or by micro organism. Therefore on the basis of above factor we can classify the polymer degradation process as follows:—

1. Thermal degradation
2. Mechanical degradation
3. Degradation by ultrasonic waves
4. Photodegradation
5. Degradation by high energy radiation
6. Oxidative degradation
7. Hydrolytic degradation
8. Biodegradation.

It is caused by heating of polymers.
Example – Teflon, Polyethylene etc.

② Mechanical degradation

There are some polymers such as polystyrene, rubber (polyisoprene) dissolved in a solvent, when subjected to vigorous stirring or heating undergoes considerable molecular degradation or fragmentation. As such types of degradation called as mechanical degradation. Mechanical degradation can reduce the average molecular weight, give a narrow molecular weight distribution and make the polymer easily processable.

Example :- Degradation polyisoprene, rubber

③ Degradation by ultrasonic waves

When a dilute solution of high molecular wt. polymer is subjected to ultrasonic waves, the polymer begins to degrade, thereby reducing its molecular weight. A close look at the process taking place at a molecular level shows that ultrasonic degradation is a special case of mechanical degradation as the polymer here is subjected to very high vibrations, which are only mechanical forces. As ultrasonic waves pass through the solution, the localised shear gradients produced tear off the polymer molecules leading to chain scission. As a result average mol. wt of the sample goes down.

Dilute solution of high molecular weight polymers are degraded by the action of ultrasonic waves

④ Photodegradation

When a molecular degradation process brought about by ultraviolet light called as photodegradation. For e.g. → photodegradation of polymethylmethacrylate.

⑤ Degradation by High Energy radiation

Degradation caused by X-rays, gamma rays, alpha rays, and β-rays which are high energy radiations in comparison to UV rays is called high energy radiation degradation. Such type of degradation is more massive than that by low energy radiation. High energy radiation smash a polymer molecule to tiny fragments.

Example:- Polyisobutylene, polyethylene, polystyrene

⑥ Oxidative degradation

Oxidative degradation is caused by O_2, O_3 or by some free radicals.

Example:- Polystyrene, polyisoprene, polybutadiene

⑦ Hydrolytic degradation

Polymer chains containing ester functional groups in their backbone undergoes degradation by hydrolysis. Also, polymer chains containing amide and acetal groups can undergo hydrolytic degradation. Acidolysis and aminolysis of these polymers also lead to random degradation of the polymer chain.

⑧ Biodegradation:-

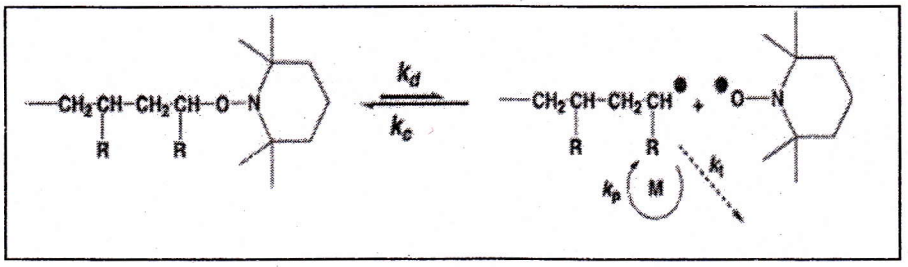
The natural polymers like starch, cellulose, gums proteins etc are degraded by the attack of microorganism present in soil, water, human organs etc.

Q6: Explain Nitroxide Mediated Polymerization (NMP) mechanism giving a suitable example. How is it different from atom transfer radical polymerization (ATRP)?

Nitroxide Mediated polymerization:

A controlled polymerization of styrene in the presence of benzoyl peroxide and the mediating stable free radical TEMPO (2, 2, 6, 6-tetramethyl-1-piperidynyl-N-oxy) was the first example of a successful CRP utilizing a nitroxide-based system.
Control in NMP is achieved with dynamic equilibration between dormant alkoxyamines and actively propagating radicals (Scheme 1).
In order to effectively mediate polymerization, TEMPO (and other stable free radicals) should react neither with itself nor with monomer to initiate the growth of new chains, and it should not participate in side reactions such as the abstraction of **β-H atoms.**
These persistent radicals should also be relatively stable, although their slow decomposition may help maintain appropriate polymerization rates.

Scheme 1: Dynamic equilibration between dormant alkoxyamines and actively propagating radicals



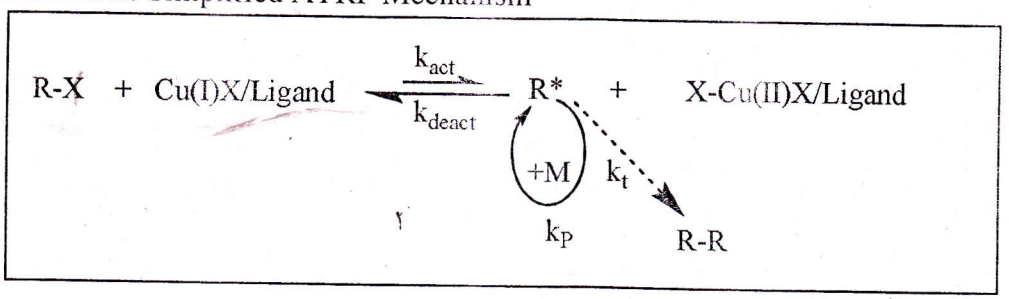
TEMPO and its derivatives form a relatively strong covalent bond in alkoxyamines.
The SFRP equilibrium constant [ratio of dissociation (kd) to cross-coupling/association (kc) rate constant] is generally very small.
The values of Keq are often so low that in the presence of excess TEMPO, the equilibrium become very strongly shifted towards the dormant species and significantly reduces the polymerization rate.

Atom Transfer Radical Polymerization:

Polymerisation of styrene, acrylates, methacrylates, and acrylonitrile by using various transition metal complexes, including nickel, iron, palladium, and rhodium have been performed via ATRP.
The name ATRP comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of polymeric chains.
ATRP originates in atom transfer radical addition (ATRA) reactions, which target the formation of 1:1 adducts of alkyl halides and alkenes, which are catalyzed by transition metal complexes.
In copper mediated ATRP, the carbon-halogen bond of an alkyl halide (RX) is reversibly cleaved by a Cu(I)X/ligand system resulting in a radical (R*) and Cu(II)X_2/ligand.

The radical will mainly either reversibly deactivate or irreversibly terminate [Scheme 2].

Scheme 2: Simplified ATRP Mechanism

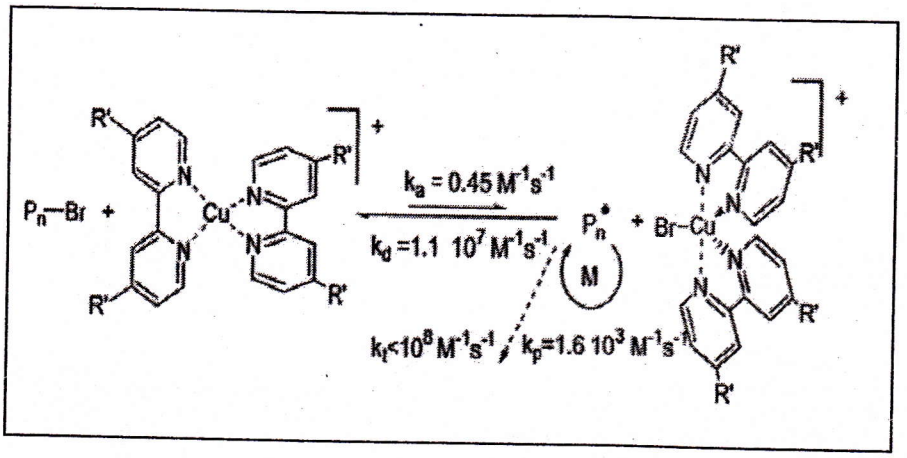


The rate coefficients of termination decrease significantly with the progress of the polymerization reaction due to the increase in the chain length and increased viscosity of the system.

In fact, the progressive reduction of kt is one of the most important features of many controlled radical polymerizations.

The role of the different ingredients like monomers, alkyl halide initiators, catalyst, ligand and solvent employed during ATRP is of paramount importance.

Scheme 3: Values of the rate constant for activation (ka), deactivation (kd), propagation (kp) and termination (k) for a bulk styrene polymerization at 110°C.



Scheme 3 shows such a system with the values of the rate constant for activation (ka), deactivation (kd), propagation (kp) and termination (kt) for a bulk styrene polymerization at 110°C.

Q7: How are polymer nanocomposites formed? Discuss the types of polymer nanocomposites. What are their potential applications?

Ans; Nanocomposites are new materials made with fillers which have nanosoze.
The nanosized inclusions are defined as those have at least one dimension in the range of 1-100 nm.

Polymer nanocomposites are polymers (thermoplastic, thermosets) that have been reinforced with small quantities (less than 5% by weight) of nano sized particles.
Polymer nanocomposites represent an alternative to a filled polymer or polymer blend.
In contrast to conventional composites, where the reinforcement is on the order of microns. PNCs consist of discrete constituents on the order of few nanometers.
There are three main material constituent in any composite: the matrix, the reinforcement (Fiber) and the interfacial region.

Many methods have been devised to prepare polymer/clay nanocomposites. In general, these methods (as shown in *Figure* 1) achieve molecular level incorporation of the layered silicate (e.g. montmorillonite (MMT) clay, or synthetic layered silicate) into the polymer by addition of a modified silicate during the polymerization (*in situ* polymerization).

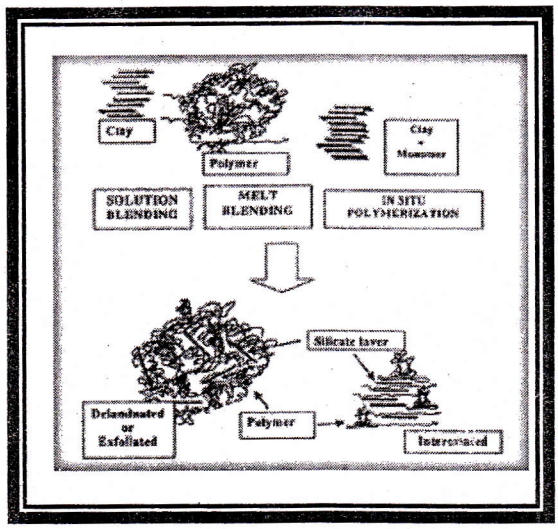


Figure 1: *Various methods used to prepare polymer layered-silicate nanocomposites*

Most of the studies have been performed on polymers/polymer blends like polystyrene (PS), polypropylene (PP), epoxy resins, polyamides, PVC, PET, polysiloxanes, polyesters, polyurethanes, polyamide 6-PP blends, polyisoprene-PEO blends etc. These novel materials have shown drastic enhancements in the mechanical, electrical, optical and thermal properties. For example, dramatic improvements in the stiffness and strength, increased dimensional stability, improved flame retardancy, improved solvent and UV resistance, and reduction in permeability of gases have been reported.
Rheological properties of nanostructured polymer/clay nanocomposites are strongly influ-enced by the morphology of the materials, which depends on the clay dispersion in the polymer matrix as shown in *Figures* 2a and 2b.

If the extended chains are inserted in the self-assembled, well ordered gallery spaces, it is termed as intercalated structure as illustrated in *Figure* 2a. If the individual silicate layers are no longer close enough to interact with adjacent layers it is termed as delaminated or exfoliated structure as explained in *Figure* 2b.

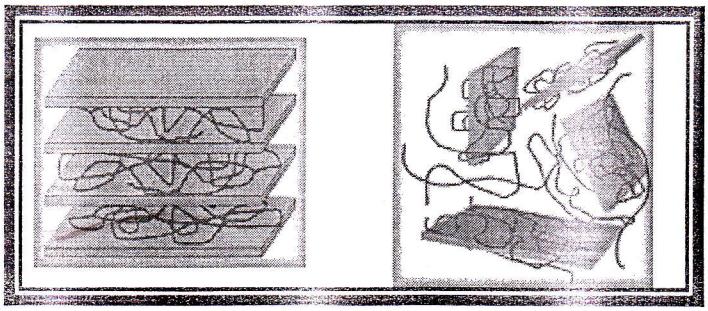


Figure 2a. Intercalated structure *Figure 2b. Exfoliated structure*

Polymerization of caprolactum, along with modified MMT (montmorillonite), resulted in the first synthesis of an exfoliated Nylon-6 polymer/clay nanocomposite prepared with just 5%(by weight) loading of clay. They reported 40% higher tensile strength, 68% higher tensile modulus, 60% higher flexural strength, 126% higher flexural modulus and increase of heat distortion temperature from 65*C to 152*C.
As the size of the particle is reduced, the number of defects per particle is also reduced and mechanical properties rise proportionately.

New polymer/clay nanocomposites have been developed like polyurethane, PVC, polyesters, polystyrene and polypropylene. Also, some biocompatible polymers like PLA, poly (ε-caprolactone) have been synthesized by varying methods and with different clay loadings (%by weight).

These materials have applications in the following industries and more.

1. Automotive
2. Aerospace
3. Construction
4. Electrical application
5. Food packing

In addition, polymer nanoparticle compounds have very interesting functional applications. For instance, γ-Fe_2O_3/ polymer nanocomposites are used as advanced toner materials for high quality colour copiers and printers and as contrast agents in NMR analysis, memory devices.
These nanocomposites are being used commercially in making tough, heat resistant, nylon timing belt covers.
Recently, considerable efforts have been devoted to the development of methods for the preparation of composite particles consisting of polymer cores covered with shells of different chemical composition. These particles covered with magnetic materials have been used as beads for gas separation, or as pigments, catalysts, coatings, flocculents, toners, raw materials recovery, drug delivery and anticorrosion protection.

Ans:- 8(a)

Section - B

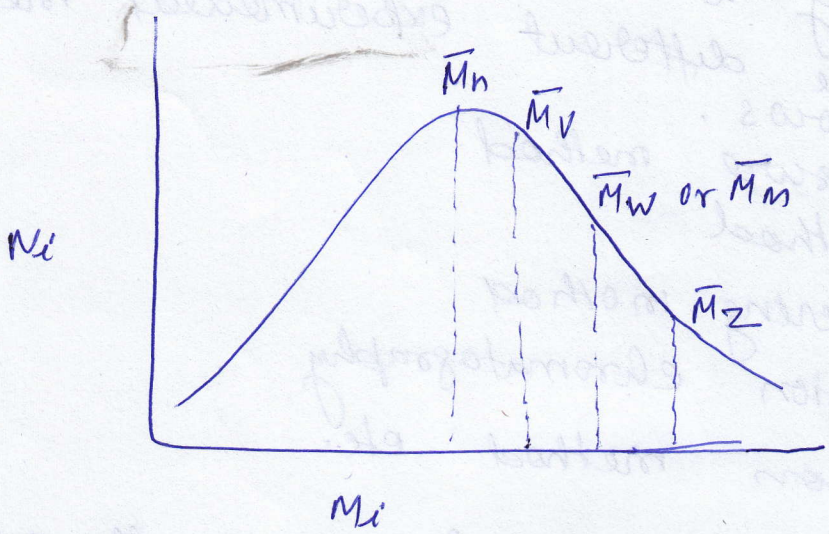
molecular weight distribution

The molecular weight of polymer is not a absolute quantity and the value of a given polymer may vary with the method of its determination. The different experimental method are used as follows.

1. osmotic pressure method
2. viscosity method
3. light scattering method
4. size exclusion chromatography
5. sedimentation method etc.

Each method or group of methods defines the molecular weight depending upon the statistical weight that is measured. Suppose that the molecular weight of two polymers of same chemical constitution is determined to be same, but both of them may possess different properties. This is because the two samples might consist fractions that are not identical in terms of number of molecules / moles, weight of molecules and of course in mol. wt. But still, the averaging of all the fractions yield same final value. That is why not only the averaged molecular weight but the dispersity of molecular weight from smaller to larger fraction is to be known. Such an analysis is normally done by expressing or mapping the molecular weight distribution curve. Such a curve is developed easily from the experimentally derived data and simply is a plot showing the variation of number (or mole fraction) N_i molecule (having a molecular weight M_i)

against the corresponding molecular weight M_i. Such a curve for polymer having a hypothetical distribution of fractions with different molecular weight is shown in given figure below.



From the figure, it can be seen that the number of molecules (or moles) having particular molecular weight passes through a maximum i.e. it increases initially with respect to molecular weights. This means the statistical weighing factor predominantly shifts to weight and size of fraction at high molecular weights. So this explains that the experimental methods need to be changed for determination of molecular weight of a same type of polymer but differing in molecular weight. The pattern shown in the above figure also reveals that

$\bar{M}_n < \bar{M}_v < \bar{M}_w$ or $\bar{M}_m < \bar{M}_z$

Ans:- 8(b)

Osmotic pressure method or osmometry

Macromolecular substances or polymers in general have very high molecular weights. Thus solutions of these substances show much smaller magnitudes of colligative properties. The magnitudes of lowering of vapour pressure or depression of freezing point of solvent on dissolving such substances into it are not measurable and not significant. However osmotic pressure of solutions are significant and easily measurable, Thus measurement of osmotic pressure is a convenient method for determination of molecular weights of polymers.

Membrane osmometry is based on the phenomenon of osmosis, which can be described as follows. If a pure solvent is separated from the solution by a semipermeable membrane on account of the difference in chemical potentials between the solvent and the solution, the solvent molecules diffuse into the solution through the membrane till the solution is rendered infinitely dilute. The flow of solvent into the solution, could nevertheless be practically stopped by applying an appropriate pressure on the solution side.

Osmotic pressure of a solution can thus be defined as the pressure that must be applied to the solution so as to totally prevent the flow of solvent through the semipermeable membrane into the solution.

The solution of a polymer in a suitable solvent can be subjected to the phenomenon of osmosis because the size of the polymer molecules in the

solution is large enough not to pass through the semipermeable membrane while the solvent molecules can easily pass through. If the solution were dilute, the osmotic pressure is given by the Van't Hoff equation, viz.

$$PV = nRT$$

$$\text{or } P = \frac{n}{V} RT \qquad \text{——— (1)}$$

molar conc^n

where P = osmotic pressure of solution

$\frac{n}{V}$ = number of moles of the polymer dissolved / litre i.e., it is the molar ~~solution~~ concentration.

T = absolute temperature at which measurements are made

R = Solution constant or gas constant

Putting $n = \frac{w}{M} = \frac{\text{Mass in gm}}{\text{Molecular mass}}$

Therefore the equation (1) becomes

$$P = \frac{w}{M} \times \frac{1}{V} RT$$

$$P = \frac{w}{V} \frac{RT}{M} = c \frac{RT}{M} \qquad \text{——— (2)}$$

where $c = \frac{w}{V}$ is the concentration of the solution in gm / litre and M is the gram molecular weight of the polymer.

Equation (2) may be rewritten as

$$\frac{P}{c} = \frac{RT}{M} \qquad \text{——— (3)}$$

According to this equation, $\frac{P}{C}$ should be constant at constant temperature i.e., a plot of $\frac{P}{C}$ vs. C should be a straight line.

However this result is found to hold good only for dilute solutions of low molecular mass polymers. For high polymer solutions, it has been derived thermodynamically that the osmotic pressure varies with concentration according to the following relationship

$$\frac{P}{C} = \frac{RT}{M} + AC + BC^2 + \cdots \quad \text{—— (4)}$$

P - reduced o.p.

$$Y = c + mX$$

where A, B etc. are constant

The quantity P/C is called reduced osmotic pressure

when C approaches zero, i.e. C=0 then from (4), we get

$$\text{limit}\left(\frac{P}{C}\right)_{C\to 0} = \frac{RT}{M} \quad \text{—— (5)}$$

Thus, if $\frac{P}{C}$ values are plotted against C and the graph is extrapolated to C=0, then the intercept on the Y-axis is ~~equalle~~ equal to $\frac{RT}{M}$, from which the value of M can be calculated, i.e.

$$M = \frac{RT}{(P/C)_{C\to 0}} \quad \text{—— (6)}$$

Further, it may be pointed out here that as osmotic pressure is a colligative property i.e.

it depends upon the number of particles present therefore the molecular mass obtained by this method is the number-average molecular mass. Hence the equation (6) can be written as

$$\boxed{\bar{M}_n = \frac{RT}{\left[\frac{P}{c}\right]_{c \to 0}}}$$

Thus to determine the molecular mass of a polymer, it is required to measure the osmotic pressure of solutions of several concentrations and plot a graph between P/c versus c and extrapolate the resulting line to zero concentration.

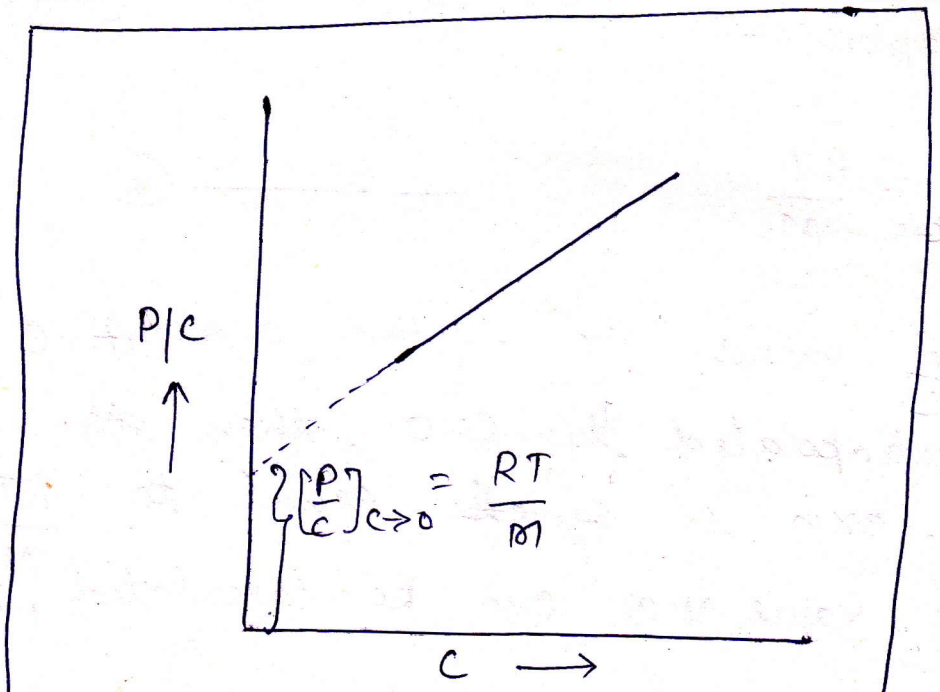


Fig. 1 Variation of reduced osmotic pressure with concentration

→

Plot of polymethyl acrylate

Gel Permeation chromatography (GPC)

An elegant method used for the fractionation of polymers is gel permeation chromatography. The technique when applied by biologists for the separation of proteins from a mixture is called gel filtration chromatography and by colloid chemists to separate colloidal dispersions according to size is called size exclusion chromatography.

⇒ It is liquid solid elution chromatography that separates the polydispersed polymer into several fractions by means of the sieving action of a cross-linked polystyrene gel. The gel material act as stationary phase and is commercially available with a wide distribution of pore size (1 – 10^6 nm). This is an expensive technique but provides a very quick information on fractionation and MWD. A single run can yield the value of all the averages together with the distribution of relative molecular weights.

⇒ The GPC column is packed with above mentioned insoluble polystyrene or polystyrene-polydivinyl-benzene gels. The solvent is forced continuously through the sets of columns at a controlled rate of about 1 ml/min by a high pressure pump. The polymer sample is injected at a position upstream of the column. The detector is located downstream of the column and responds sensitively to the presence of the polymer in a small volume of eluent. A variety of detector techniques are used. The common ones measure differences in refractive index, UV absorption or light scattering.

Principle:- The basic principle underlaying the separation of different fractions of a polydispersed sample is based on the size of individual polymer molecules but explore the pore system of the column material. Large molecules are excluded from small pores and can only diffuse into a restricted part of the pore system within the beads while smaller ones would enter into the pores of the bead. Thus large molecules would have less residence time and would emerge first. Following figure ① schematically illustrates the principle of GPC.

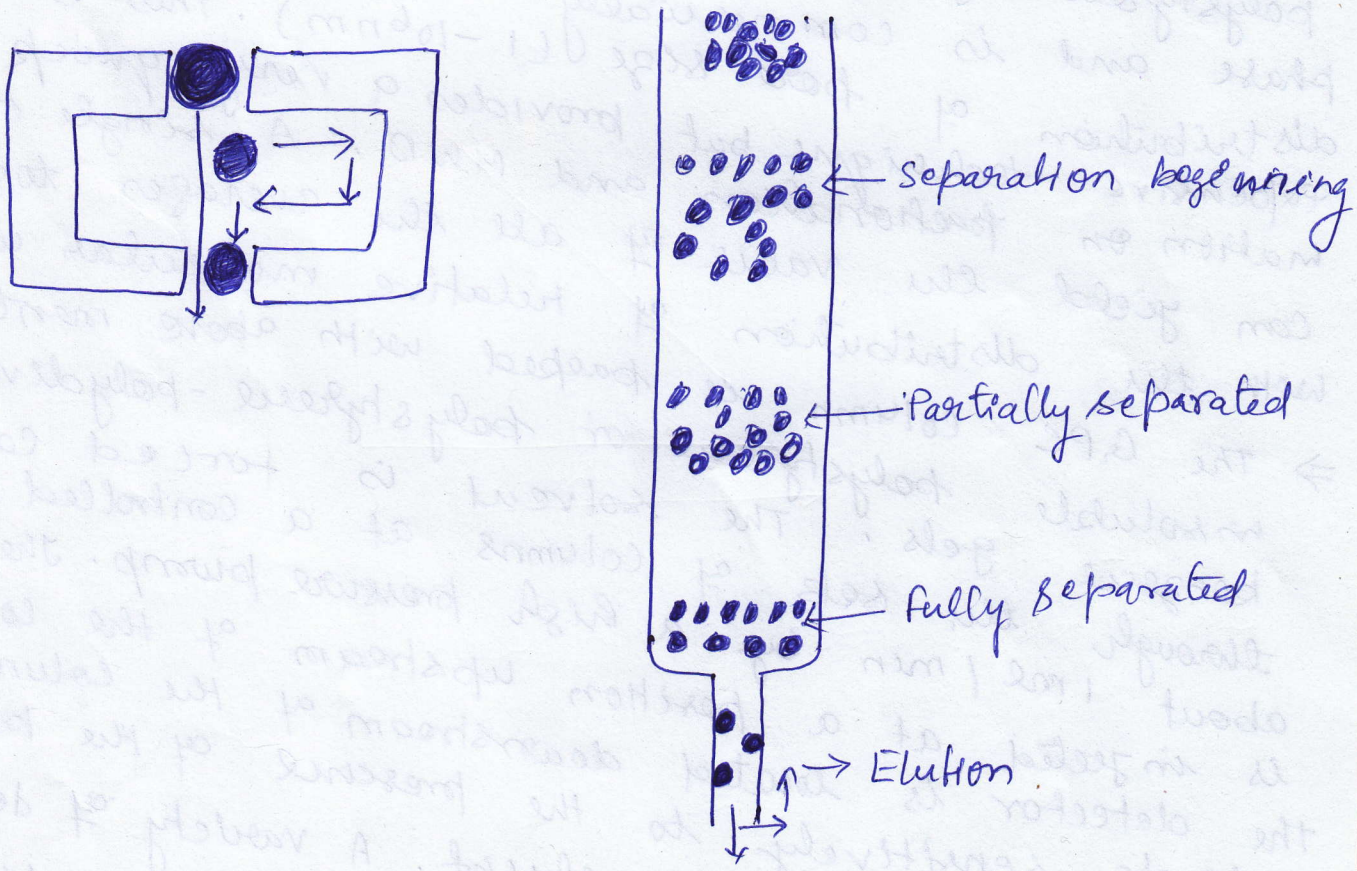


Fig. 1 Schematic presentation of the basic principle involved in GPC

A calibration curve is necessary to obtain information from GPC. Several samples of narrow dispersed polymers like polystyrene, polyethylene oxide etc of varying mol. wt. (these are available commercially) are first eluted separately from the column and the retention time (or volume) for each sample is determined. This procedure provides a calibration plot, which can be used to obtain the mol. wt. of an unknown polymer fraction. A GPC run of the sample provides a plot between record output versus elution volume. Another plot between log mol. wt. versus elution vol. is then constructed which is linear as shown in Fig. 2

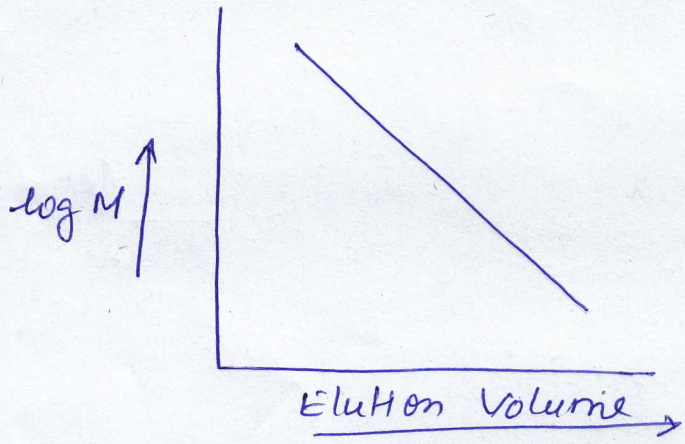


Fig. 2 Calibration plot of log molecular weight versus elution volume for a narrow dispersed polymer of known molecular weight