POLYMER CHEMISTRY

13.1 INTRODUCTION

Polymers are macromolecules which are composed of billions of repeating units. Their vast range of applications has significantly enhanced the attention of scientists towards study of their synthesis and structural analysis.

The structural unit of polymer is its repeating unit. Repeating unit repeats itself in structure thousands of times and fabricates a polymer. Monomers are assembled in a repeating unit. Sometimes repeating unit is made up of a single monomer as in homopolymer, sometimes it is made up of two monomers as in copolymer and sometimes it is made up of three monomers as in terpolymer. Thus number of monomers in a repeating unit may vary. In this way control on monomers, controls repeating unit which in turn control polymer. This is how structure of polymer is managed by proper control at such small level.

There is a vast range of polymers, so many classification schemes are possible. Origin, nature, structure, polarity, homogeneity, functioning, thermosensitivity and many more are used as basis in this chapter for classification of polymers. Polymerization is a complex process which has its own kinetics. Addition and condensation polymers are used nowadays in material science, electronics, plastic industry, textiles, aerospace technology and many more. Thus their yield is monitored by study of their kinetics. Kinetics provides information about ratios of monomers incorporating into the polymer and left in reaction mixture at any time. It helps to estimate reaction completion time without any experimental work. Moreover 100% conversion is also estimated under various sets of reaction conditions. Copolymers are also significantly used nowadays. Study about their classification, models, kinetics and reactivity ratios are also included in this chapter.

All polymeric chains synthesized at same time are not of same mass. Polydispersity exists among them. Number, z, mass and viscosity average molecular weights are normally used to describe molar mass of a polydisperse system of polymer. Many methods like viscometry, osmometry, light scattering, sedimentation and many other methods are explained over here by which different average molar masses of polymers can be measured with accuracy. Analytical method like gel permeation chromatography is also discussed in this chapter by which every molar mass fraction of polymer can be separated and analyzed.

13.2 CLASSIFICATION OF POLYMERS

Different trends of classification of polymers are reported due to vastness of polymers according to their structure, property, origin, sensitivity, physical state, mode of formation and polarity. Thus aforementioned characteristics are used as basis for classification of polymers as shown in Fig. 13.1.
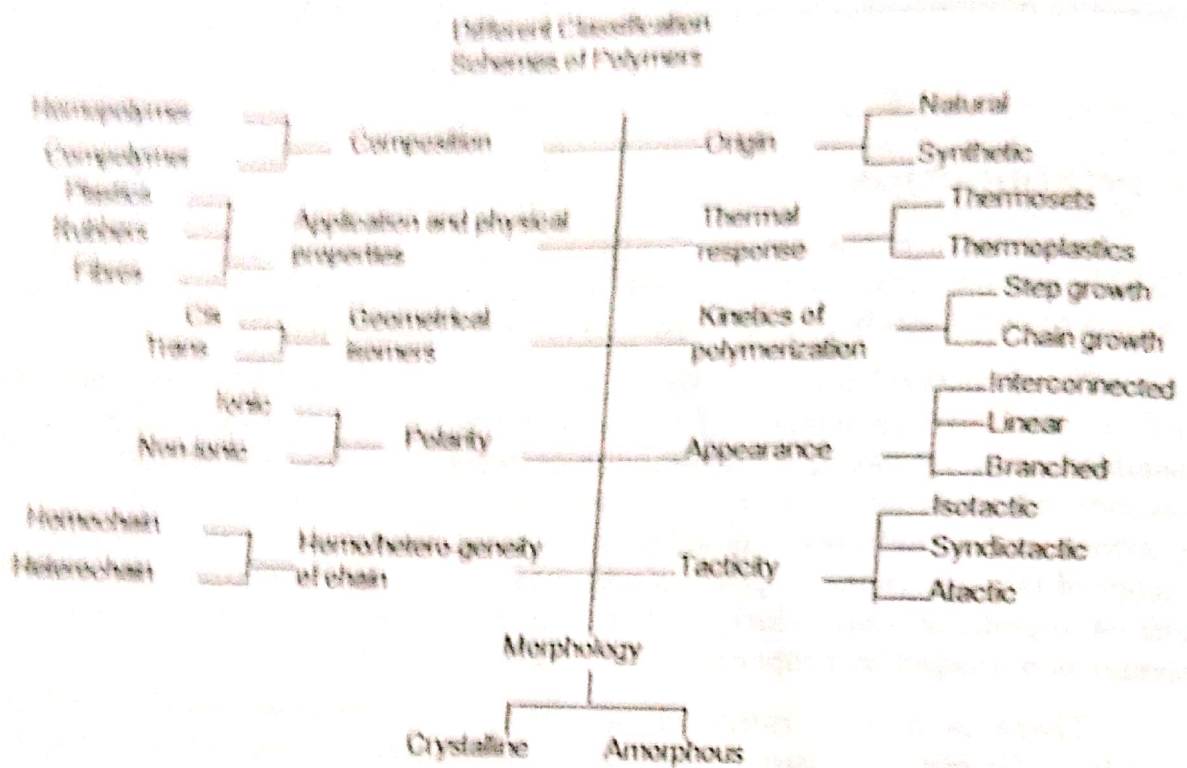

Fig. 13.1 Different classification schemes of polymers

(1) On the Basis of Origin/Occurrence

Natural, synthetic and semi-synthetic are three major divisions of polymers on the basis of their occurrence or origin.

(a)   **Natural Polymers:** As name indicates, origin of natural polymers is nature i.e.; animals, plants or rocks. Examples of such polymers are: natural rubber (1, 4-cis-polyisoprene), starch, quartz, proteins, cellulose etc.

(b)   **Synthetic Polymers:** Such polymers which are synthesized by man are known as synthetic polymers, e.g.; polystyrene, polyvinyl chloride (PVC), polyester etc.

(c)   **Semi-synthetic Polymers:**   These are chemically modified natural polymers by man for commercial purposes. Semi-synthetic polymers either have backbone of natural polymers and pendent group of synthetic polymers or their one block is made up of natural polymers and other component is made up of synthetic polymers. Hydrogenated rubber, cellulose nitrate and cellulose acetate are some examples of semi-synthetic polymers.

(2) On the Basis of Kinetics of Polymerization

Addition and condensation polymerization are two basic kinetic mechanisms for formation of polymers.

(a) **Chain Growth Polymerization:** Self addition of monomers occurs in addition polymerization (chain growth polymerization). No foreign molecule incorporated in chain during growth of polymer. No side product is formed. Molecular weight of polymer is exactly multiple of molecular weight of monomer. Mostly olefins follow addition polymerization as butadiene gives polybutadiene, styrene gives polystyrene and vinyl chloride gives polyvinylchloride.

(b) **Step Growth Polymerization:** Monomers have functional groups like carboxyl (-COOH) and amino (-NH₂). Two or more than two monomers react in step-wise manner and produced a polymer along with elimination of small molecules. This sort of polymerization is called step growth (condensation) polymerization. Nylon, polyurethane and polyester are some examples of step growth polymers.

(3) On the Basis of Polarity

Main chain of polymers or their pendent groups often contain charges. Thus ionic and non-ionic are two categories on the basis of polarity of polymers.

(a) **Non-Ionic Polymers:** Non-ionic polymers have no charge containing moiety in polymer. Polyethylene and polypropylene are two examples of non-ionic polymers.

(b) **Ionic Polymers:** Ionic polymers have charge on pendent groups, as in polymer (sulfonated polyethylene) of ethylene sulfite. These are also known as polyelectrolytes.

Polyethylene　　　　　　**Sulfonated polyethylene**
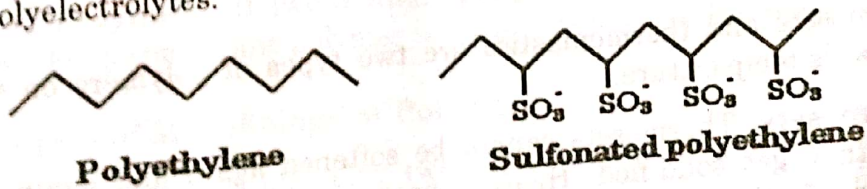
(4) On the Basis of Structure of Polymers

Polymers can be branched or inter-linked, but versatile pattern of branching and interlinking gives a wide range of different polymers.

(a) **Linear Polymers:** A non-branched and straight chain of bonded monomers which has only two ends is called linear polymer. They are mostly synthesized by condensation polymerization. Nylon and polystyrene are linear polymers.

(b) **Branched Polymers:** Sometimes small branches of finite length are attached to main chains of polymers, termed as branched polymers. These branches can be of made up of molecules similar or dissimilar to main chain. Thus branched polymers are further sub-divided into graft copolymer, star polymer, comb-like polymer, dendrimer.

(i)   **Graft Copolymers:** One type of molecules form main chain and other type of molecules form branches on these main chains.

(ii)   **Star Polymers:** Sometimes terminals of many linear polymers join at common point and form star polymers.

(iii)   **Dendrimers:** Dendrimers are tree-like in structure. They have no backbone. Extensive branching perpetuates in such a way which give an unusual structure called dendrimer.

(iv)   **Comb Polymers:** These branched polymers have a backbone over which branches are hanging just like comb.

(c)   **Crosslinked or Network Polymers:** Different chains of polymers get interconnected by covalent bonds and form crosslinked polymers. Point of interconnection is called crosslinking point. Density of crosslinked polymers determine by density of crosslinking points or junctions per unit volume. Crosslinking pattern in network polymers can be two or three dimensional. Thus on the dimensions of crosslinking, network polymers are further subdivided into two categories.

(i)   **Planar Network Polymer Structures:** Two dimensional crosslinking containing polymers are called planar network polymer structures. Graphite is their common example. Ladder polymers are also planar polymers. They have two main chains which are crosslinked just like ladder.

(ii)   **Space Network Polymer Structures:** Three dimensional crosslinked polymers are called space network polymer structures. Diamond is their well known example.

(5) On the Basis of Thermal Behavior

Thermosets and thermoplastics are two types of polymers on the basis of response towards temperature.

(a)   **Thermosets:** Thermosets cannot be softened again and again on heating, once they get solidified. Heating produces chemical reactions which lead towards further growth or crosslinking. Thus these polymers cannot be recycled. Epoxy resins, diene rubbers and unsaturated polyesters are some examples of thermosets.

(b)   **Thermoplastics:** Thermoplastics like polyvinyl chloride, polyethers etc can be softened and solidified again and again on heating and cooling respectively. Heating or cooling does not produce chemical changes in them, so they can be recycled many times.

(6) On the Basis of Tacticity

Polymers having different spatial arrangements of atoms around asymmetric carbon have different properties. This difference in spatial arrangements (configuration) is called tacticity. Tacticity make polymers optically active. Tacticity produces optical isomerism in polymers. Optically active monomers can be R (rectus) or S (sinister) rotatory. Here isomeric polymers differ only in head to tail linkages of

optically active monomers. Thus isotactic, syndiotactic and atactic are three different categories of polymers on the basis of pattern of head to tail linkages of repeating units.

(a) **Isotactic:** Isotactic polymers like erythrodiisotactic and threodiisotactic, have same configuration of every chiral carbon. Thus isotactic sequence can be represented as R-R-R-R-R-R or S-S-S-S-S-S. Isotacticity highly favors closest packing of molecules and crystallinity among isotactic, syndiotactic and atactic polymers.

(b) **Syndiotactic:** If dextro and levo rotatory repeating units attach alternatively, then syndiotactic polymer is formed. It is represented as R-S-R-S-R-S-R. Erythrodisyndiotactic and threodisyndiotactic are examples of this kind of polymers. These polymers are less crystalline and packed than isotactic polymers.

(c) **Atactic or Heterotactic:** There is no pattern of linkage of two optically active monomers in atactic polymers. Monomers can be linked head to head, tail to tail and head to head for some portion of chain, thus represented as R-R-R-R-S-R-S-R-S-S-S-R. Atacticity hinders crystallinity and packing. Thus they are least crystalline and packed among all three listed types.

(7) On the Basis of Geometrical Isomerism in Polymers

Arrangement of atoms or groups around double bond produces geometrical isomerism in molecules. C is and trans are two basic categories of geometrical isomers.

(a) **Cis Polymers:** If two similar groups are positioned on same side of double bond then cis polymer is formed as cis-1,3-butadiene (synthetic rubber).

(b) **Trans Polymers:** If two similar groups are positioned on opposite side of double bond then trans polymer is formed as trans-1,3-butadiene.

(8) On the Basis of Morphology of Polymers

Amorphous and crystalline are two different kinds of polymers on the basis of their morphology.

(a) **Crystalline Polymers:** Polymers are not completely crystalline rather they are semi-crystalline which have regions of crystalline as well as amorphous polymers. This sort of polymers is characterized by melting point (T_m) at which crystalline phase transform into solid amorphous phase. Thermosets are crystalline polymers while thermoplastics decompose on heating to high temperatures.

(b) **Amorphous Polymers:** Amorphous polymers are characterized by glass transition temperature (T_g) at which hard glass state converted into soft rubbery state.

(9) On the Basis of Application and Physical Properties of Polymers

Rubbers, plastics and fibers are three principle types of polymers on the basis of their physical properties and applications.

(a) **Rubbers:** Rubbers are commonly called elastomers. They are mechanically weak, dimensionally unstable and highly elastic polymers. Their tensile strength lies in range of 300 to 3,000 psi. They have low molecular cohesion. Thus their molecular cohesion is less than 2 Kcal/gmol per 0.5 nm chain length. Rubbers are not highly crosslinked. If they become crosslinked upto desired limit then they become more useful for better applications. Crosslinking of rubber is termed as vulcanization.

(b) **Plastics:** Plastics are dimensionally stable and highly elastic substances. 4,000 to 15,000 psi is range of their tensile strength. They are stronger than rubbers. Plastics exhibit molecular cohesion in range of 2-5 Kcal/gmol per 0.5 nm chain length. They can be soft and flexible or hard and rigid. Phenol-formaldehyde resins, nylon, polyamides, polyvinyl chloride are some examples of common plastics.

(c) **Fibres:** Fibres are strongest among rubbers, plastics and fibres. Their tensile strength lies in range of 20,000 to 150,000 psi. Molecular cohesion of fibres is 4-10 Kcal/gmol per 0.5 nm chain length. Natural and synthetic fibres are largely used in textile, because of their high mechanical strength, thermal insulation, flexibility and softness. Cotton cellulose and silk are natural fibres while polyamides and polyesters are synthetic fibres.

(10) On the Basis of Homo/Heterogeneity of Polymers

Homochain and heterochain polymers are two different types of polymers on the basis of homo/heterogeneity.

(a) **Homochain Polymers:** Such polymers which made up of only one kind of atoms are called homochain polymers, like diamond, graphite, and linear polymers of sulfur and selenium.

(b) **Heterochain Polymers:** Heterochain polymers are made up of more than one kind of atoms. This kind of polymers is more extensively found in list of polymers. Silicones, polyethylene, polyesters, nylon and polyphosphoric acid are some examples of heterochain polymers.

(11) On the Basis of Composition of Polymers

Type of monomer units involved in formation of polymers is the base of classification here. Homopolymer and copolymer are two general kinds on this basis.

(a) **Homopolymers:** Homopolymers are made up of only one kind of monomers e.g.; polystyrene, polyvinylchloride etc. Interestingly, all homochain polymers are homopolymers but all homopolymers are not homochain polymers.

(b) **Copolymers:** Copolymers are made up of two kinds of monomer units. Nylon and polyesters are copolymers.

Example 13.1

Identify which polymers are formed by addition and which formed by condensation polymerization.

(a) $-(CH_2-CH_2)_n-$

(b) $-(OC-CH_2-CO-NH-CH_2-NH)_n-$

(c) $-(CH-CH(C_6H_5))_n-$

(d) $-(O-CH=CH-O-N-CH=CH-N)_n-$
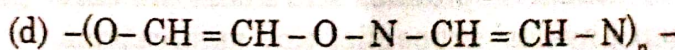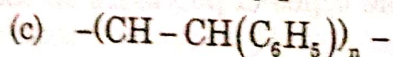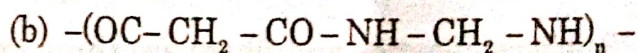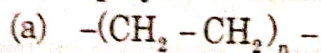
Solution

(a) and (c) are synthesized by addition polymerization while (b) and (d) are formed by condensation polymerization.
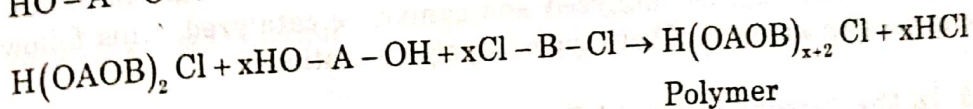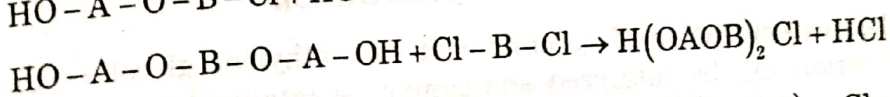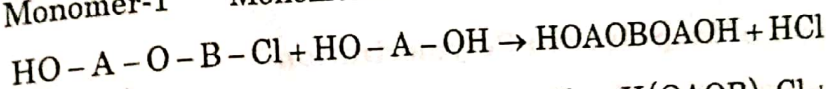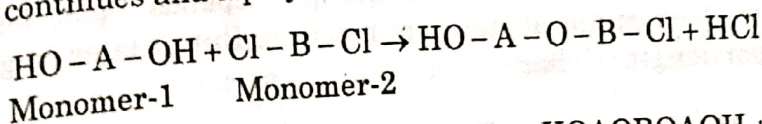
13.3 POLYMERIZATION

Polymerization is a process by which a polymer is synthesized. Route or mechanism of polymerization of different monomers is different. Thus step growth and chain growth are two kinds of kinetic mechanisms of polymerization.

13.4 STEP GROWTH POLYMERIZATION

Polyfunctional monomers polymerize to form step growth polymers. Polyfunctional monomers give a branched polymer as they have more than two reacting sites, while bifunctional monomers give a linear polymer.

Bifunctional monomer-1 HO-A-OH and bifunctional monomer-2 Cl-B-Cl react and initially form HO-A-O-B-Cl along with elimination of hydrochloric acid (HCl). Later HO-A-O-B-Cl reacts with HO-A-OH and yields HO-A-O-B-O-A-OH and HCl. Thus a small molecule of HCl eliminates at every step growth of chain. In this way, polymerization continues and a polymer is formed. General scheme is

$$HO-A-OH+Cl-B-Cl \rightarrow HO-A-O-B-Cl+HCl$$
Monomer-1 Monomer-2

$$HO-A-O-B-Cl+HO-A-OH \rightarrow HOAOBOAOH+HCl$$

$$HO-A-O-B-O-A-OH+Cl-B-Cl \rightarrow H(OAOB)_2\,Cl+HCl$$

$$H(OAOB)_2\,Cl+xHO-A-OH+xCl-B-Cl \rightarrow H(OAOB)_{x+2}\,Cl+xHCl$$
Polymer

Following are some examples of condensation polymerization of some bifunctional monomers.

1. Polyester

$$HO(CH_2)_2\,OH+HOOC(CH_2)_2\,COOH \xrightarrow{-H_2O} HO(CH_2)_2\,OOC(CH_2)_2\,COOH$$
1,4-Butanediol Succinic acid

$$HO(CH_2)_2\,OOC(CH_2)_2\,COOH+nHO(CH_2)_2\,OH+nHOOC(CH_2)_2\,COOH$$
$$\xrightarrow{-nH_2O} HO\left[(CH_2)_2\,OOC(CH_2)_2\,COO\right]_{n+1}H$$
Polyester

2. Polyamide

$$H_2N(CH_2)_6\,NH_2+HOOC(CH_2)_4\,COOH \xrightarrow{-H_2O} H_2N(CH_2)_6\,HNOC(CH_2)_4\,COOH$$
Hexamethylene Adipic acid

diamine

$$H_2N(CH_2)_6 \, HNOC(CH_2)_4 \, COOH + nH_2N(CH_2)_6 \, NH_2 + nHOOC(CH_2)_4 \, COOH$$

$$\xrightarrow{-nH_2O} H_2N\left[(CH_2)_6 \, HNOC(CH_2)_4 \, CON\right]_{n+1} H$$
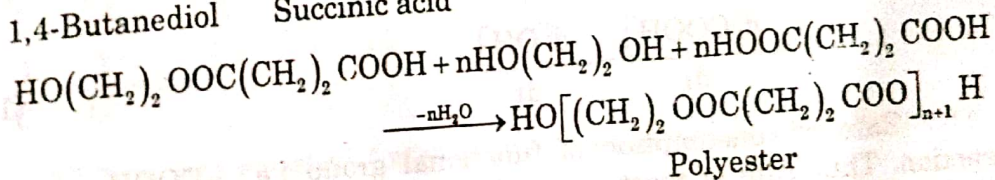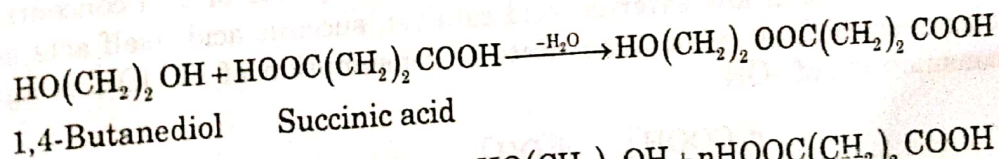
Nylon 6,6 (polyamide)
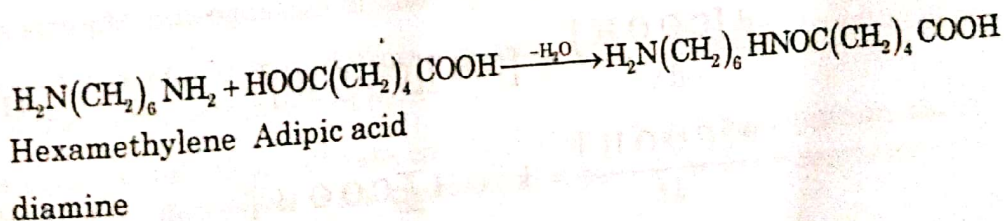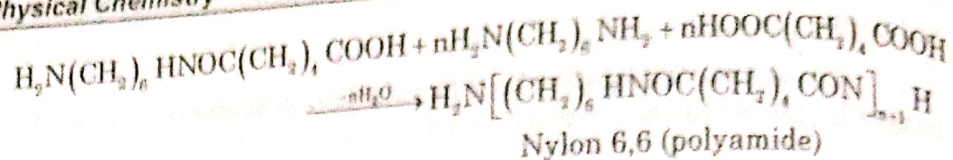
13.4.1 Characteristics of Step Growth Polymerization

Following are some basic characteristics of step growth polymerization.

(i)   This polymer is formed in steps, so small molecules are eliminated during polymerization.

(ii) Equimolecular proportions of both monomers should be used, so that they equally incorporated in polymer, otherwise polymer have that functional group in excess whose monomer was used in greater quantity.

(iii) Non-equimolecular proportions of monomers yield low molecular weight polymer.

(iv) Pure monomers should be used otherwise side reactions may occur and polymer yield decreases.

(v)   Reaction between two functional groups depends upon length of chain attached to them in initial stages of reaction. But at later stages, it does not depend upon length of chain.

13.4.2 Kinetics of Step Growth Polymerization

Let esterification of succinic acid with ethylene glycol as an example. This polymerization can be catalyzed and cannot be catalyzed, thus following discussion comprises on kinetics of both types of polymerizations.

(a) In the Absence of Acid Catalyst

Rate of reaction between carboxylic acid and alcohol in the absence of any external catalyst is a third order reaction. Rate of reaction is directly proportional to first power of alcohol concentration and second power of acid concentration, because in the absence of any external acid catalyst, succinic acid itself acts as catalyst and monomer, both at same time. Rate of consumption of –COOH is equal to rate of consumption of –OH.

$$-\frac{d[COOH]}{dt} = -\frac{d[OH]}{dt} \tag{13.1}$$

Rate of consumption of functional group i.e.; –COOH or –OH, is rate of reaction. Thus rate of reaction can be written in terms of rate of consumption of –COOH.

$$-\frac{d[COOH]}{dt} \propto [OH][COOH]^2 \tag{13.2}$$

$$-\frac{d[COOH]}{dt} = k[OH][COOH]^2 \tag{13.3}$$

k is rate constant of reaction. The molar concentration of $-OH$ and $-COOH$ group is equal and can be represented as C.

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$$-\frac{dC}{dt} = kC^3$$

So, by separating variables, we get

$$-\frac{dC}{C^3} = kdt$$

(13.4)

By integrating above equation, we get

$$-\int\frac{dC}{C^3} = k\int dt$$

$$-\left[\frac{C^{-3+1}}{-3+1}\right] = kt + c$$

$$\left[\frac{1}{2C^2}\right] = kt + c$$

(13.5)

C is concentration of succinic acid and ethylene glycol at any time while their initial concentration is C_0. Thus on application of boundary conditions, we get

$$\left[\frac{1}{2C_0^2}\right] = c$$

(13.6)

Putting value of c from equation (13.6) into (13.5), we get

$$\frac{1}{2C^2} = kt + \frac{1}{2C_0^2}$$

$$\frac{1}{2C^2} - \frac{1}{2C_0^2} = kt$$

$$\frac{1}{C^2} - \frac{1}{C_0^2} = 2kt$$

$$\frac{1}{C^2} = \frac{1}{C_0^2} + 2kt$$

(13.7)

Equation (13.7) is rate equation for step growth polyesterification. Following are results predicted on the basis of this equation.

(i)   This is a straight line equation in intercept form.

(ii) *   Intercept of the plot obtained from equation (13.7) is equal to inverse of square of initial concentration of monomers.

(iii)   Slope is equal to two times of rate constant (Fig. 13.2). This equation shows that value of C decreases with passage of time. It means reactants are consumed during polymerization.
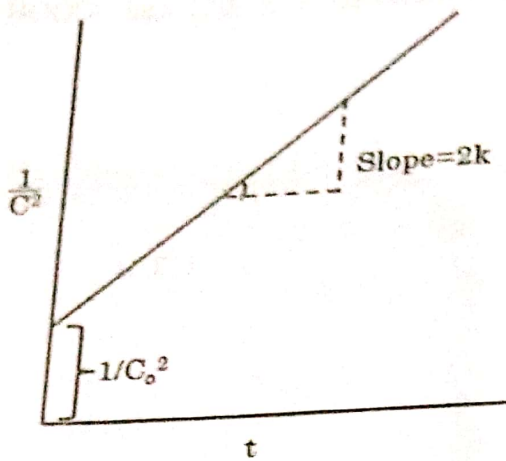
Fig. 13.2 Plot of $1/C^2$ versus time
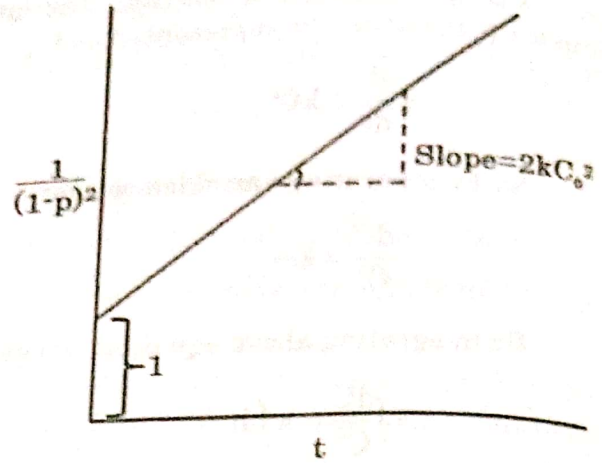
Fig. 13.3 Plot of $1/(1-p)^2$ versus time

It was assumed that concentration of water is negligible.

Extent of reaction (p) is stated as the fraction of functional groups that have consumed at time t. It is ratio of –COOH groups reacted to initial concentration of – COOH [equation (13.8)]. As it is more convenient to express rate equation in terms of extent of reaction, thus relationship for extent of reaction and concentration is

$$p = \frac{C_o - C}{C_o} \tag{13.8}$$

$$pC_o = C_o - C$$

$$C = C_o - pC_o$$

$$C = C_o(1-p) \tag{13.9}$$

Putting value of C from equation (13.9) into (13.7), we get

$$\frac{1}{(C_o(1-p))^2} = \frac{1}{C_o^2} + 2kt$$

$$\frac{1}{C_o^2(1-p)^2} - \frac{1}{C_o^2} = 2kt$$

$$\frac{1}{C_o^2}\left(\frac{1}{(1-p)^2} - 1\right) = 2kt$$

$$\frac{1}{(1-p)^2} - 1 = 2C_o^2kt$$

$$\frac{1}{(1-p)^2} = 2C_o^2kt + 1 \tag{13.10}$$

Equation (13.10) is required rate expression in terms of extent of reaction. Following are results which can be obtained from this equation.

(i) Order of reaction is equal to three in self catalyzed step growth polymerization.

(ii) Units of rate constant are $dm^6 mol^{-2}s^{-1}$.

(iii) Half life period for the reaction is inversely proportional to the square of initial concentration of reactant i.e,

From equation (13.7), we get

$$\frac{2}{C_o^2} = \frac{1}{C_o^2} + kt_{1/2}$$

$$\frac{1}{C_o^2} = kt_{1/2}$$

$$t_{1/2} \propto \frac{1}{C_o^2}$$

(iv) Fig. 13.3 is obtained from equation (13.10) which is a straight line equation in intercept form.

(v) Intercept of graph in Fig. 13.3 is 1 while its slope is $2kC_o^2$. As C_o is known mostly, thus value of slope helps to find value of rate constant of reaction.

(vi) Maximum and ideal value of extent of reaction is 1. This equation helps to find time when extent of reaction becomes 1. As $p \to 1$, then $(1-p)^2 \sim 0$, applying these conditions to equation (13.10)

$$\frac{1}{(1-p)^2} = 2C_o^2 kt + 1$$

$$\infty = 2C_o^2 kt + 1$$

Ignoring value of intercept as it is very much small as compared to infinity.

Thus

(13.11)

$$\infty = 2C_o^2 kt$$

This equation shows that product of 2, k, t and C_o^2 is infinity. 2, k and C_o^2 are constants. Thus time is only variable. It means infinite time is required in step growth polymerization to achieve 100 % conversion of reactants into products.

(b) In the Presence of Acid Catalyst

Rate of consumption of –COOH is also equal to rate of consumption of –OH here and represents rate of reaction in the presence of acid catalyst.

$$\text{Rate of reaction} = -\frac{d[COOH]}{dt} = -\frac{d[OH]}{dt}$$

Rate of reaction between carboxylic acid and alcohol in the presence of any external acid catalyst is a second order reaction. Rate of reaction is directly proportional to first power of concentrations of alcohol, acid and catalyst. But concentration of catalyst remains constant during the progress of reaction. So,

$$\text{Rate of reaction} \propto [OH][COOH][H^+] \tag{13.12}$$

Thus rate of reaction can be written in terms of rate of consumption of $-OOH$.

$$-\frac{d[COOH]}{dt} \propto [OH][COOH][H^+]$$

$$-\frac{d[COOH]}{dt} = k[OH][COOH][H^+] \tag{13.13}$$

k is rate constant of acid catalyzed reaction.

Catalyst is that specie which does not consume during reaction and boosts up rate of reaction only. Thus concentration of H^+ remains constant throughout polymerization. So

$$k' = k[H^+] \tag{13.14}$$

k' is another constant which is can be substituted instead of $k[H^+]$ in equation (13.13).

$$-\frac{d[COOH]}{dt} = k'[OH][COOH] \tag{13.15}$$

Concentration of each of the monomers at any time is C. So

$$-\frac{dC}{dt} = k'C^2$$

$$-\frac{dC}{C^2} = k'dt \tag{13.16}$$

Integrating above equation, we get

$$-\int \frac{dC}{C^2} = k' \int dt$$

$$-\left[\frac{C^{-2+1}}{-2+1} \right] = k't + c$$

$$\frac{1}{C} = k't + c \tag{13.17}$$

C_0 is initial concentration of acid, it means C_0 is concentration of acid at time=0. Thus on application of boundary conditions, we get

$$c = \frac{1}{C_0}$$

Putting value of c from above equation into equation (13.17), we get

$$\frac{1}{C} = k't + \frac{1}{C_0}$$

(13.18)

Equation (13.18) is rate equation for acid catalyzed step growth polyesterification. Following results are deduced from this equation.

(i)   This is a straight line equation in intercept form.

(ii) Intercept of graph manipulated from equation (13.18) is equal to inverse of initial concentration of one of the monomers as sketched in Fig. 13.4.

(iii) Slope of plot of Fig. 13.3 is equal to constant k' (Fig. 13.4).

On comparison of equation (13.18) and (13.13), we deduced that intercept is greater in the presence of external acid catalyst as compared to absence of external catalyst. We also inferred that slope is greater in case of acid catalyzed polymerization as compared to that of no external catalyst, because slope is ratio of $1/C^2$ to time in the absence of catalyst while it is ratio of $1/C$ to time in the absence of catalyst. Square of concentration in the absence of catalyst more rapidly decreases value of slope and hence value of rate constant of polymerization. Thus comparison of equations (13.13) and (13.18) verifies that rate of reaction is faster in the presence of catalyst rather in the absence of catalyst.
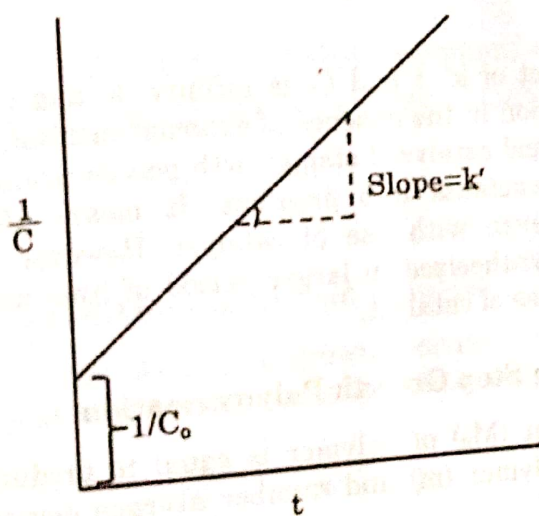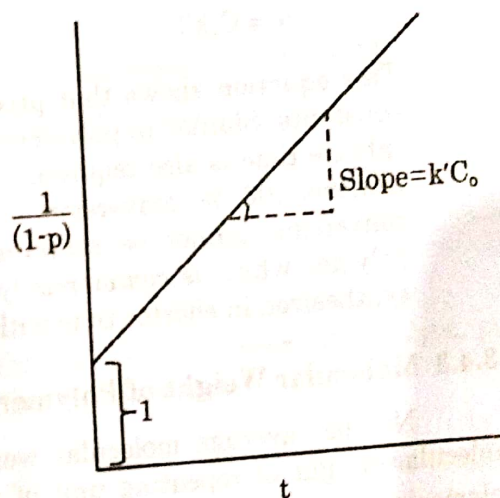

Fig. 13.4 Plot of 1/C versus time

Fig. 13.5 Plot of 1/(1-p) versus time

It was assumed that concentration of water is negligible.

From equation (13.9), available concentration of reactant in terms of extent of reaction can be written as

$$C = C_0 (1 - p)$$

Putting value of C from above equation into (13.18), we get

$$\frac{1}{C_0 (1 - p)} = \frac{1}{C_0} + k't$$

$$\frac{1}{C}\left(\frac{1}{(1-p)} - 1\right) = k't$$

$$\frac{1}{(1-p)} - 1 = Ck't$$ (13.19)

$$\frac{1}{(1-p)} = Ck't + 1$$

Equation (13.19) is required rate expression in terms of extent of reaction. Following are results which can be obtained from this equation.

(iv) Fig. 13.5 is obtained from equation (13.19) which is a straight line equation in intercept form.

(v) Intercept of graph in Fig. 13.5 is 1 while its slope is $k'C_0$. As C_0 is known mostly, thus value of slope helps to find value of rate constant of reaction.

(vi) This equation also helps to find time when extent of reaction becomes 1. As $p \to 1$, then $(1-p) \sim 0$, applying these conditions to equation (13.19)

$$\infty = C_o k't + 1$$

Ignoring value of intercept as it is very much small as compared to infinity. Thus

$$\infty = C_o k't$$

This equation shows that product of k', t and C_0 is infinity. k' and C_0 are constants. Similar to polymerization in the absence of external catalyst, here infinite time is also required in acid catalyzed step growth polymerization to achieve. 100 % conversion of reactants into products. It means 100 % conversion cannot be achieved even with use of catalyst. However, that polymer which is commercially synthesized in larger period of time will be synthesized in shorter time with use of catalyst.

13.4.3 Molecular Weight of Polymer in Step Growth Polymerization

Number average molecular weight (M_n) of polymer is equal to product of molecular weight of repeating unit of polymer (m) and number average degree of polymerization ($\overline{x_n}$). So

$$M_n = m \times \overline{x_n}$$ (13.20)

$\overline{x_n}$ is equal to ratio of total number of molecules of succinic acid initially (N_0) to number of molecules of acid present in reaction at time t, so

$$\overline{x_n} = \frac{N_o}{N}$$ (13.21)

$$p = \frac{N_o - N}{N_o}$$

$$pN_o = N_o - N$$

$$N = N_o - pN_o$$

$$N = N_o(1-p)$$

$$\frac{N_o}{N} = \frac{1}{(1-p)}$$

(13.22)

By equating equations (13.22) and (13.21), we get Carother's equation (13.23).

$$\overline{x}_n = \frac{1}{(1-p)}$$

(13.23)

When p→1 then $\overline{x}_n \to \infty$, it shows that high $\overline{x}_n$ can be obtained at high degree of conversion.

Comparing equation (13.20) and (13.23)

$$M_n = m \times \frac{1}{(1-p)}$$

With the help of above equation, we deduced when p→1 then $M_n \to \infty$. It shows that high M_n can be obtained at high degree of conversion.

$$(1-p) = \frac{m}{M_n}$$

(13.24)

(c) In the Absence of Acid Catalyst

For M_n of step growth polymer synthesized in the absence of catalyst, put value of (1-p) from equation (13.24) into equation (13.10) to get

$$\left(\frac{M_n}{m}\right)^2 = 2kC_o^2 t + 1$$

(13.25)

Equation 13.25 says that $\left(\frac{M_n}{m}\right)^2$ is a linear function of time. It means M_n increases with passage of time. For infinite value of times, M_n will be very high.

(d) In the Presence of Acid Catalyst

For M_n of step growth polymer synthesized in the presence of catalyst, put value of (1-p) from equation (13.24) into equation (13.19)

$$\frac{M_n}{m} = Ck't + 1$$

(13.26)

It is inferred from equation (13.26) that M_n is almost directly proportional to t. It means M_n increases with passage of time.

Example 13.2

Tetramethylenediamine and succinic acid with 1:1 mole ratio react with each other to form a polymer. Calculate the number average degree of polymerization for 3% conversion of each reactant into polymer.

Solution

Number of unreacted specie=N=3

Total amount of species participate in reaction=N_o=97

Degree of polymerization=$\bar{x}_n$=?

As we know that

$$P = \frac{N_0 - N}{N_0}$$

By putting values, we get

$$P = \frac{100 - 3}{100}$$

$$P = 0.97$$

By using Carothers's equation

$$\bar{x}_n = \frac{1}{(1-p)}$$

By putting value of P in above equation we get

$$\bar{x}_n = \frac{1}{(1-0.97)}$$

$$\bar{x}_n = 16.92$$

Example 13.3

Calculate the number average degree of polymerization for a monomer conversion of 98% and 99% using Carothers's equation for the reaction of one mole of adipic acid with one mole of hexamethylenediamine to produce Nylon-6, 6.

Solution

(i) $N_0 = 100$

$N = 2$

As we know that

$$P = \frac{N_0 - N}{N_0}$$

By putting values in above equation, we get

$$P = \frac{100 - 2}{100}$$

$$P = 0.98$$

By using Carothers's equation

$$\bar{X}_n = \frac{1}{(1-p)}$$

By putting value of P in above equation, we get

$$\bar{X}_n = \frac{1}{(1-0.98)}$$

$$\bar{X}_n = 50$$

(ii) $N_0 = 100$

$N = 1$

As we know that

$$P = \frac{N_0 - N}{N_0}$$

$$P = \frac{100 - 1}{100}$$

$$P = 0.99$$

By using Carothers's equation

$$\bar{X}_n = \frac{1}{(1-p)}$$

By putting value of P in above equation, we get

$$\bar{X}_n = \frac{1}{(1-0.99)}$$

$$\bar{X}_n = 100$$

13.5 CHAIN GROWTH POLYMERIZATION

Chain growth polymerization occurs through a reactive centre or carrier specie. Carrier specie grows by combining with monomers and polymerization occurs.

13.5.1 Types of Chain Growth Polymerization

There are four basic types of chain growth polymerization on the basis of nature of chain carrier specie. Free radical, cation, anion and co-ordination polymerizations are these four types, if chain carrier species are free radical, cation, anion and specie having properties of charge as well as free radical respectively.

13.5.2 Steps of Chain Growth Polymerization

Initiation, propagation and termination are three basic steps of all types of chain polymerization.

(i) Initiation

In initiation, initiator is added to generate a carrier specie which can be a radical or ion or have characteristics of radical along with that of ion. Sometimes initiator is not added, light rays or heat is used to break bonds in initiator and generates reactive centers. Bonds in initiator are weak, they easily break away and reactive centers are formed. These reactive centers react with monomer and transfer reactive center to monomer.

(ii) Propagation

During this process, low molecular weight species formed in initiation rapidly combine with more monomers and a high molecular weight polymer is synthesized. Thus this step can be called a growth step.

(iii) Termination

All reactive centers become inactive during this step. Combination (coupling) and chain transfer (disproportionation) are two routes of termination. During coupling two active polymer chains combine with each other and form a single polymer. Thus molecular weight of resulting polymer will be sum of two growing chains. On other side, disproportionation is little different from combination. Two growing polymer chains are also involved here but some atoms transfer from one chain to other. So that one chain develops double bond at one end and other chain only satisfies its active center. Suppose we have free radical polymerization, then termination by combination and chain transfer will be

$$
\text{Termination}
\begin{cases}
\text{Combination } 2\sim\text{CH-}\overset{\cdot}{\text{C}}\text{H} \rightarrow \sim\text{CH-CH-CH-CH}\sim \\
\qquad\qquad\qquad\;\; \underset{X}{|} \qquad\qquad\quad \underset{X}{|}\;\underset{X}{|} \\
\text{Chain} \\
\text{transfer } 2\sim\text{CH-}\overset{\cdot}{\text{C}}\text{H} \rightarrow \sim\text{CH-CH}_2 + \sim\text{CH=CH} \\
\qquad\qquad\qquad \underset{X}{|} \qquad\qquad \underset{X}{|} \qquad\quad \underset{X}{|}
\end{cases}
$$

13.5.3 Free Radical Chain Growth Polymerization

That type of chain growth polymerization in which carrier specie is a free radical called as free radical chain growth polymerization. This polymerization also has three steps: initiation, propagation and termination.
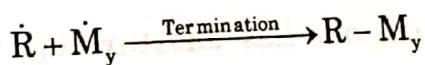
(i) Initiation

During initiation, initiator (I) dissociates and produces two primary free radicals represented by $\dot{R}$. Rate constant of initiator dissociation is k_d. Then $\dot{R}$ reacts with monomer M and produces $\dot{M}_1$. Rate constant of this reaction is k_i. Specie $\dot{M}_1$ is basically $R - \dot{M}$, so $\dot{M}_1$ has R as neutral end group on one side and M as free radical end group on other side. Thus R itself becomes neutral by developing bond with M and converts M to a free radical. $\dot{M}_1$ is birth mark of polymer chain.

$$I \xrightarrow{k_d} 2\dot{R} \tag{13.27}$$

$$\dot{R} + M \xrightarrow{k_i} \dot{M}_1 \tag{13.28}$$

Among these two reactions of initiation, reaction represented in equation (13.27) is slow while other reaction is fast. This is solely due to the high reactivity of free radicals. Thus dissociation of initiator is rate determining step of initiation.

Initiator forms free radicals ($\dot{R}$) in pairs, so there are chances that these free radicals neutralize each other due to cage effect of solvent. As free radicals are present in cage of solvent molecules which does not let free radicals to move apart easily. So there are chances to recombination of $\dot{R}$. Thus fraction of generated free radicals gets wasted. Chances of recombination of $\dot{R}$ are much high under usage of high concentration of I.

Moreover $\dot{R}$ can also react with oxygen, thus presence of oxygen is also a cause behind wastage of primary radicals. Primary radicals also consumed during termination. Some radicals join with growing chain ($\dot{M}_y$) and produces dead polymer ($R - M_y$).

$$\dot{R} + \dot{M}_y \xrightarrow{Termination} R - M_y$$

Thus a number of routes are possible by which initiator efficiency (f) gets reduced, as ratio of number of polymerization initiating radicals to total number of generated primary radicals is initiator efficiency.

(ii) Propagation

Propagation is second and fast step in which monomers are rapidly added to a growing chain and high molecular weight chain is formed. $\dot{M}_1$ reacts with M and forms $\dot{M}_2$. Similarly $\dot{M}_2$ reacts and form a long polymer chain. It is assumed that rate of propagation does not depends upon length of polymer chain, so almost all monomers have consumed during propagation, thus rate of propagation is considered equal to rate of polymerization.

$$\dot{M}_1 + M \xrightarrow{k_r} \dot{M}_2$$

$$\dot{M}_2 + M \xrightarrow{k_r} \dot{M}_3 \qquad (13.29)$$

$$\dot{M}_n + M \xrightarrow{k_r} \dot{M}_{n+1}$$
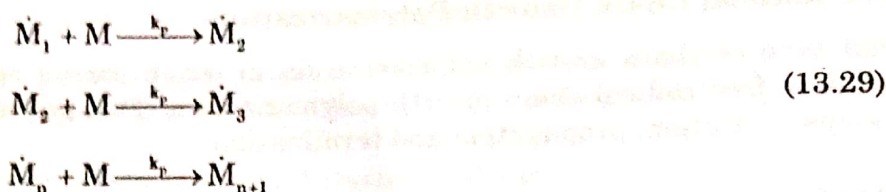
(iii) Termination

Growth of chains stops in this step. Growing polymer chains also stabilize them in this step by disproportionation and combination processes.

Following are some characteristics of combination process.

(a)   It is a bimolecular process as two growing chains are involved in it.

(b)   Combination results in a polymer of greater molecular weight as compared to weight of individual growing chains.

(c)   Total number of dead polymer chains produced by combination is half as compared to that of growing chains which combined to form dead polymer.

(d)   Polymers formed by combination have two initiator primary radicals per molecule of polymer, as initiator radicals are present at both ends of chain as end group. By determining number of end groups in a chain we can manipulate that this polymer is terminated by combination or not.

(e) $\dot{M}_n$ and $\dot{M}_m$ are two growing chains, they combine and form a dead polymer M_{n+m}. Bond between $\dot{M}_n$ and $\dot{M}_m$ in M_{n+m} just like this $M_n - M_m$. In this high molecular weight polymer is formed by combination as compared to that by disproportionation.

$$\dot{M}_n + \dot{M}_m \xrightarrow{k_{tc}} M_{n+m} \qquad (13.30)$$

Following are some characteristics of disproportionation process.

(a)   Disproportionation is also a bimolecular process.

(b)   Number of dead polymers formed by disproportionation is equal to number of reactant growing chains.

(c)   Out of two terminated dead polymers, one has unsaturation and other has not.

(d)   Dead polymers produced by disproportionation have one primary free radical per dead polymer. Primary radical is present only at one end of dead polymer as end group while monomer is present at other end of polymer.

(e) M'_n and M'_m are two dead polymers formed from $\dot{M}_n$ and $\dot{M}_m$ terminated by disproportionation process. Some atoms are transferred from $\dot{M}_m$ to $\dot{M}_n$ and saturated M'_n and unsaturated M'_m produced. Thus by determination of unsaturation similar to monomer in end group of polymer, it can be deduced that the polymer is terminated by disproportionation.

$$\dot{M}_n + \dot{M}_m \xrightarrow{k_{td}} M'_n + M'_m$$

$$(13.31)$$
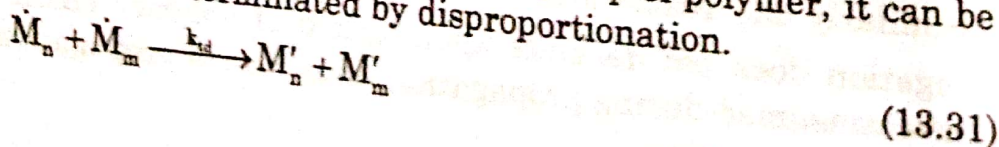
13.5.3.1 Kinetics of Free Radical Chain Growth Polymerization

Kinetic study of chain growth polymerization is manipulated from kinetic study of all three steps: initiation, propagation and termination, of chain polymerization.

(a) Initiation

As rate determining step is dissociation of initiator because $k_d <<< k_i$, so we have to consider equation (13.27) for determination of rate of initiation (R_i). R_i is equal to rate of formation of $\dot{M}_1$.

$$R_i = \frac{d[\dot{M}_1]}{dt} \qquad (13.32)$$

Rate of decomposition of initiator is equal to half of rate of formation of $\dot{M}_1$, because one molecule of initiator produces two molecules of primary radicals and two $\dot{R}$ can produce two molecules of $\dot{M}_1$. So

$$-\frac{d[I]}{dt} = \frac{1}{2}\frac{d[\dot{M}_1]}{dt} \qquad (13.33)$$

From equation (13.27), we get

$$-\frac{d[I]}{dt} = k_d[I] \qquad (13.34)$$

Equating equation (13.33) and (13.34)

$$\frac{1}{2}\frac{d[\dot{M}_1]}{dt} = k_d[I]$$

$$\frac{d[\dot{M}_1]}{dt} = 2k_d[I] \qquad (13.35)$$

Thus R_i is

$$R_i = 2k_d[I]$$

As previously explained that all generated initiator molecules do not involved in initiation of polymerization. A number of molecules get wasted by oxygen gas, solvent cage effect and due to many other reasons. Therefore only a fraction (f) is involved in initiation of polymerization, so above equation will be

$$R_i = \frac{d[\dot{M}]}{dt} = 2fk_d[I] \qquad (13.36)$$

(b) Propagation

Rate of propagation is equal to rate of consumption of monomer M. Thus using reactions of equation (13.29), rate of propagation is generally written as

$$R_p = -\frac{d[M]}{dt} = k_p[M][\dot{M}]$$
(13.37)

(c) Termination

Equations (13.30) and (13.31), both shows chain termination is a bimolecular process whether occurs by combination or chain transfer. So rate of termination is deduced as

$$R_{tc} = k_{tc}[\dot{M}][\dot{M}] \quad \text{(termination by combination)} \quad (13.38)$$

$$R_{td} = k_{td}[\dot{M}][\dot{M}] \quad \text{(termination by disproportionation)} \quad (13.39)$$

Adding equation (13.39) and (13.38) as termination occurs by both routes

$$R_t = R_{tc} + R_{td}$$

$$R_t = k_{tc}[\dot{M}][\dot{M}] + k_{td}[\dot{M}][\dot{M}]$$

$$R_t = (k_{tc} + k_{td})[\dot{M}]^2$$

$$R_t = k_t[\dot{M}]^2$$
(13.39a)

And rate of consumption of $\dot{M}$ during termination is

$$R_t = -\frac{1}{2}\frac{d[\dot{M}]}{dt} = k_t[\dot{M}]^2$$

$$-\frac{d[\dot{M}]}{dt} = 2k_t[\dot{M}]^2$$
(13.40)

Practically quantity of $\dot{M}$ is negligible, it means rate of formation of $\dot{M}$ during initiation is equal to rate of consumption of M during termination. So on application of steady state condition

$$-\frac{d[\dot{M}]}{dt} = 0$$

$$+\frac{d[\dot{M}]}{dt} = -\frac{d[\dot{M}]}{dt}$$
(13.41)

Putting values from equations (13.36) and (13.40) respectively into equation (13.41)

$$2fk_d[I] = 2k_t[\dot{M}]^2$$
(13.41a)

$$[\dot{M}]^2 = \frac{fk_d[I]}{k_t}$$
(13.41b)

Taking square root of above equation

$$\sqrt{[M]^2} = \sqrt{\frac{fk_d[I]}{k_t}}$$

$$[M] = \sqrt{\frac{fk_d[I]}{k_t}} \qquad (13.42)$$

Substituting value of $[M]$ from equation (13.42) into equation (13.37)

$$R_p = k_p[M]\sqrt{\frac{fk_d[I]}{k_t}}$$

$$R_p = k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}} \qquad (13.43)$$

Following are results drawn from equation (13.43)

(i) Equation (13.43) is a straight line equation passing through origin.

(ii) k_p, k_d, k_t and f are constants. If we kept $[M]$ constant, then rate of polymerization directly depends upon square root of concentration of initiator as shown in Fig. 13.6.

$$R_p \propto [I]^{\frac{1}{2}} \qquad \text{(when [M] is constant)}$$

(iii) Similarly if we kept $[I]^{1/2}$ constant, then rate of polymerization is directly proportional to concentration of monomer as shown in Fig. 13.7.

$$R_p \propto [M] \qquad \text{(when } [I]^{1/2} \text{ is constant)}$$

(iv) Comparison of points (ii) and (iii) shows that R_p more significantly depends upon concentration of monomer, as R_p is proportional to square root of $[I]$ and first power of $[M]$.

(v) If efficiency of utilization of primary free radical does not depend upon concentration of monomer, then f will be considered constant and

$$\frac{R_p}{[M][I]^{\frac{1}{2}}} = k_p\left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}} = \text{constant}$$

Under this condition, by increasing concentration of monomer or initiator, rate of polymerization increases as ratio $R_p/[M][I]^{1/2}$ is a constant quantity.
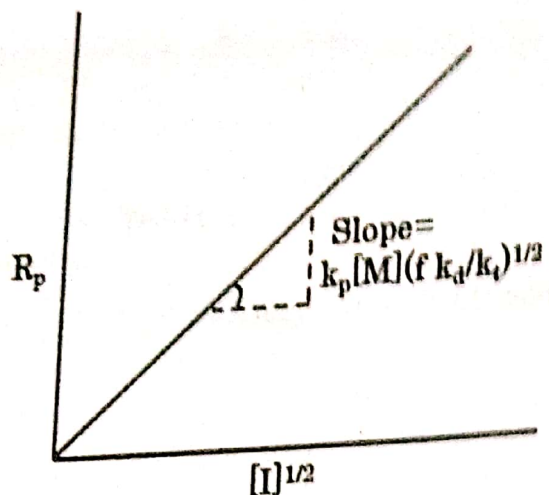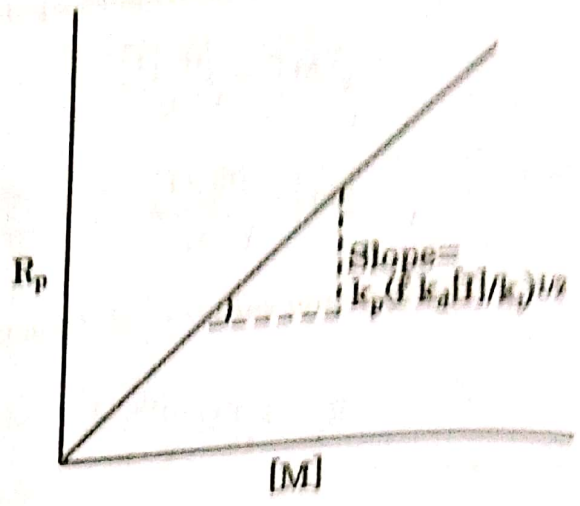
Fig. 13.6 Plot of R_p versus $[I]^{1/2}$.

Fig. 13.7 Plot of R_p versus $[M]$.

Putting value of $\left[\dot{M}\right]$ into equation (13.39), expression for rate of termination can be deduced as

$$R_t = k_t \left(\frac{2fk_d[I]}{k_t} \right)$$

$$R_t = 2fk_d[I] \qquad (13.44)$$

Results drawn from equation (13.44) are

(i)   Equation (13.44) is a straight line equation passing through origin.

(ii)   It is deduced from this equation that R_t is linearly and positively dependent upon concentration of initiator as shown in Fig. 13.8. It means by increasing concentration of monomer, rate of termination increases.
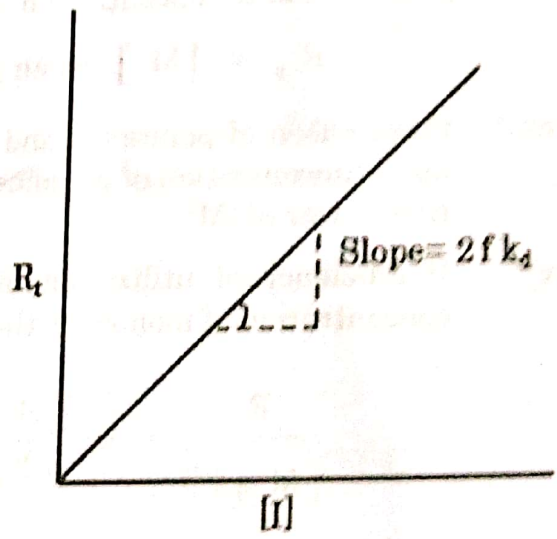
$$R_t \propto [I]$$

(iii)   Slope of this plot is equal to $2fk_d$. So by calculating slope, we can calculate rate of dissociation of initiator and can manipulate speed of initiation step.

Fig. 13.8 Plot of R_t versus $[I]$

In this way, expressions for rate of propagation (13.43) and rate of termination (13.44) are derived which help to calculate rates along with concentration of initiator.

13.5.3.2 Degree of Polymerization

Number average degree of polymerization ($\bar{x}_n$) is ratio of rate of propagation and rate of termination. So

$$\bar{x}_n = \frac{\text{Rate of propagation}}{\text{Rate of termination}}$$

$$\bar{x}_n = \frac{R_p}{R_t} \tag{13.45}$$

Putting values of R_p and R_t from equations (13.43) and (13.44)

$$\bar{x}_n = \frac{k_p[M]\left(\dfrac{fk_d[I]}{k_t}\right)^{\frac{1}{2}}}{2fk_d[I]}$$

$$\bar{x}_n = \frac{k_p\left(\dfrac{fk_d}{k_t}\right)^{\frac{1}{2}}[M][I]^{\frac{1}{2}}}{2fk_d[I]}$$

$$\bar{x}_n = \frac{k_p\left(\dfrac{1}{k_t}\right)^{\frac{1}{2}}[M]}{2(fk_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}}$$

$$\bar{x}_n = \frac{k_p[M]}{2(fk_t k_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}} \tag{13.46}$$

Equation (13.46) helps to conclude following results

(i) Equation (13.46) is a straight line equation passing through origin.

(ii) $\bar{x}_n$ is directly proportional to concentration of monomer, means high concentration of monomer helps to build polymer of long length.

(iii) $\bar{x}_n$ is inversely proportional to square root of concentration of initiator which is contrary to equation (13.43), where rate of polymerization is directly proportional to square root of concentration of initiator. It means if we increase concentration of initiator, then rate of polymerization increases but chain length decreases. Rate of polymerization increases, because larger number of initiator molecules can generate large quantity of primary free radicals, which have ability to react with a greater quantity of monomers and speeds up polymerization rate. On the other hand, by employing high concentration of initiator, there are greater chances of growing polymer chains to combine with primary free radicals of initiator and terminates polymerization, thus chain length decreases. In this way, concentration of

initiator has dual effect. If we gain in speed of polymerization, then we lose chain length at the same time.

13.5.3.4 Kinetic Chain Length

Number of monomer molecules that consumed by a single primary free radical which can initiates polymerization of a chain is called kinetic chain length. Kinetic chain length is directly proportional to x_n.

$$x_n \propto v \qquad (13.47)$$

$$x_n = (\text{constant}) \, v$$

Value of constant of above equation depends upon route of termination: combination or disproportionation, adopted by growing polymer chain.

(i) Combination

Value of constant is 2 for termination by combination, because in combination two polymer chains combine and x_n becomes double of kinetic chain length. Thus equation (13.47) will be

$$x_n = 2v \qquad (13.48)$$

$$v = \frac{x_n}{2}$$

Putting value of x_n from equation (13.46) into equation (13.48)

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

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

$$v = \frac{k_p [M]}{4 \left(f k_t k_d \right)^{\frac{1}{2}} [I]^{\frac{1}{2}}} \qquad (13.49)$$

Equation (13.49) shows similar results to equation (13.46). It also shows inverse relation with $[I]^{1/2}$ and direct with $[M]$. In addition to x_n, kinetic chain length is another parameter to study length of polymer chains. So, similar results are drawn.

(ii) Disproprtionation

Value of constant is 1 for termination by disproportionation. It is because two polymer chains do not combine, some atoms are transferred from one chain to other only. Thus x_n becomes equal to kinetic chain length. Thus equation (13.47) will be

$$\bar{x}_s = v \qquad (13.50)$$

Putting value of $\bar{x}_s$ from equation (13.46) into equation (13.50)

$$v = \frac{k_p[M]}{2(fk_2 k_t)^{\frac{1}{2}}[I]^{\frac{1}{2}}} \qquad (13.51)$$

Equation (13.51) shows similar results to equation (13.49) as equation (13.51) is similar to equation (13.49).

13.5.3.5 Instantaneous Kinetic Chain Length

Instantaneous kinetic chain length is ratio of rate of formation of growing polymer chains and rate of formation of dead polymers. Instantaneous kinetic chain length provides picture in terms of termination processes rather effective fraction off initiator primary radicals. So

$$v_i = \frac{\text{Rate of formation of growing polymer chains}}{\text{Rate of formation of dead polymer chains}} \qquad (13.52)$$
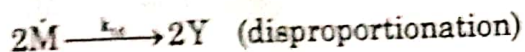
If all dead polymer chains are represented by Y, then

$$2\dot{M} \xrightarrow{k_{tc}} Y \quad \text{(combination)}$$

Rate of termination by combination (R_{tc}) is given as

$$R_{tc} = +\frac{d[Y]}{dt} = k_{tc}[\dot{M}]^2 \qquad (13.53)$$

and

$$2\dot{M} \xrightarrow{k_{td}} 2Y \quad \text{(disproportionation)}$$

Rate of termination by disproportionation (R_{td}) is given as

$$R_{td} = +\frac{1}{2}\frac{d[Y]}{dt} = k_{td}[\dot{M}]^2$$

$$+\frac{d[Y]}{dt} = 2k_{td}[\dot{M}]^2 \qquad (13.54)$$

Overall rate of formation of dead chains during termination is obtained by adding equation (13.53) and (13.54)

$$+\frac{d[Y]}{dt} = k_{tc}[\dot{M}]^2 + 2k_{td}[\dot{M}]^2$$

$$\frac{d[Y]}{dt} = (k_{tc} + 2k_{td})[\dot{M}]^2 \qquad (13.55)$$

Putting values of rate of formation of growing radicals and rate of formation of dead chains from equation (13.37) and (13.55) respectively into equation (13.52)

$$v_i = \frac{k_p[M][\dot{M}]}{(k_{tc} + 2k_{td})[\dot{M}]^2}$$

$$v_i = \frac{k_p[M]}{(k_{tc} + 2k_{td})[\dot{M}]} \tag{13.56}$$

For more detailed and comprehensive view, a new parameter ξ introduced. ξ is used to express rate of formation of dead polymer chains per termination. So that it can be manipulated that whether combination or disproportionation, process of termination is contributing more in termination. So

$$\xi = \frac{\text{Rate of formation of dead chains}}{\text{Rate of termination}}$$

Putting value from equation (13.55) into above equation

$$\xi = \frac{(k_{tc} + 2k_{td})[\dot{M}]^2}{k_t[\dot{M}]^2}$$

$$\xi = \frac{k_{tc} + 2k_{td}}{k_t} \tag{13.57}$$

Thus v_i and ξ provides a better study. Equation (13.57) shows that it is a constant factor which is independent of concentration of monomer and initiator, while equation (13.56) shows that v_i positively depends upon concentration of monomer.

13.5.3.6 Chain Transfer

When a growing polymer chain becomes dead polymer and a new one is initiated, this is termed as chain transfer. Transfer agent in chain transfer is not monomer only, but it can occur with solvent, initiator, polymer and modifier. Let we have a growing polymer chain ($\dot{M}_n$) and transfer agent XY, both reacts and form stable $M_n - X$ and free radical $\dot{Y}$.

$$\dot{M}_n + XY \rightarrow M_n - X + \dot{Y}$$
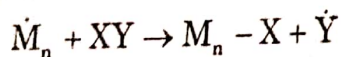
(i) Monomer Transfer

When a growing polymer chain ($\dot{M}_n$) converts a monomer into a free radical and itself become stable, then monomer transfer occurs.
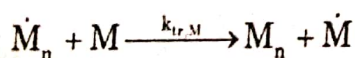
$$\dot{M}_n + M \xrightarrow{k_{tr,M}} M_n + \dot{M}$$

Rate of monomer transfer can be written by using above reaction

$$R_{tr,M} = k_{tr,M}[\dot{M}_n][M] \tag{13.58}$$

Where $k_{tr,M}$ is rate constant of monomer transfer reaction. Transfer constant of monomer transfer is

$$C_{tr,M} = \frac{k_{tr,M}}{k_p} \qquad (13.59)$$

(ii) Solvent Transfer

Solvent transfer occurs when growing polymer chain ($\dot{M}_n$) is involved with solvent molecules (S). As result of chain transfer, solvent molecules convert into free radicals and polymer chain becomes stable.

$$\dot{M}_n + S \xrightarrow{k_{tr,s}} M_n + \dot{S}$$

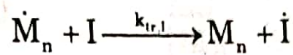Rate of solvent transfer can be written by using above reaction

$$R_{tr,S} = k_{tr,S}\left[\dot{M}_n\right]\left[S\right] \qquad (13.60)$$

Where $k_{tr,S}$ is rate constant of solvent transfer reaction. Solvent transfer constant is

$$C_{tr,S} = \frac{k_{tr,S}}{k_p} \qquad (13.61)$$

(ii) Initiator Transfer

Chain transfer agent is initiator in initiator transfer. Here is its chain transfer reaction

$$\dot{M}_n + I \xrightarrow{k_{tr,I}} M_n + \dot{I}$$

Rate of initiator transfer is

$$R_{tr,I} = k_{tr,I}\left[\dot{M}_n\right]\left[I\right] \qquad (13.62)$$

Where $k_{tr,I}$ is rate constant of initiator transfer reaction. Initiator transfer constant can be written as

$$C_{tr,I} = \frac{k_{tr,I}}{k_p} \qquad (13.63)$$

As we know number average degree of polymerization ($\bar{x}_n$) is ratio of propagation rate and termination rate. But here many chain transfer reactions are possible, so $\bar{x}_n$ is ratio of propagation rate to sum of termination rates by all processes.

$$\bar{x}_n = \frac{\text{Rate of chain growth}}{\text{Sum of rate of formation of dead polymers by all processes}}$$

In addition to monomer transfer, solvent transfer and initiator transfer, termination is also included in dead polymer formation. Thus above equation will be

$$\bar{x}_n = \frac{R_p}{R_{tr,M} + R_{tr,S} + R_{tr,I} + R_t}$$

$$\frac{1}{\bar{x}_n} = \frac{R_{tr,M} + R_{tr,S} + R_{tr,I} + R_t}{R_p} \tag{13.64}$$

Putting value of R_t from equation (13.39a) into (13.41a)

$$2fk_d[I] = 2R_t$$

$$R_t = fk_d[I] \tag{13.65}$$

Putting values of $R_{tr,M}$, $R_{tr,S}$, $R_{tr,I}$, R_p and R_t from equations (13.58), (13.60), (13.62), (13.37) and (13.65) into (13.64)

$$\frac{1}{\bar{x}_n} = \frac{k_{tr,M}\left[\dot{M}_n\right][M] + k_{tr,S}\left[\dot{M}_n\right][S] + k_{tr,I}\left[\dot{M}_n\right][I] + \left(\dfrac{2fk_d[I]}{2}\right)}{k_p\left[\dot{M}_n\right][M]}$$

$$\frac{1}{\bar{x}_n} = \frac{k_{tr,M}\left[\dot{M}_n\right][M] + k_{tr,S}\left[\dot{M}_n\right][S] + k_{tr,I}\left[\dot{M}_n\right][I] + fk_d[I]}{k_p\left[\dot{M}_n\right][M]}$$

$$\frac{1}{\bar{x}_n} = \frac{k_{tr,M}\left[\dot{M}_n\right][M]}{k_p\left[\dot{M}_n\right][M]} + \frac{k_{tr,S}\left[\dot{M}_n\right][S]}{k_p\left[\dot{M}_n\right][M]} + \frac{k_{tr,I}\left[\dot{M}_n\right][I]}{k_p\left[\dot{M}_n\right][M]} + \frac{fk_d[I]}{k_p\left[\dot{M}_n\right][M]}$$

$$\frac{1}{\bar{x}_n} = \frac{k_{tr,M}}{k_p} + \frac{k_{tr,S}[S]}{k_p[M]} + \frac{k_{tr,I}[I]}{k_p[M]} + \frac{fk_d[I]}{k_p\left[\dot{M}_n\right][M]} \tag{13.66}$$

Substituting $C_{tr,M}$, $C_{tr,S}$ and $C_{tr,I}$ into equation (13.66) by using equations (13.59), (13.61) and (13.63) respectively

$$\frac{1}{\bar{x}_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{[I]}{[M]} + \frac{fk_d[I]}{k_p\left[\dot{M}_n\right][M]} \tag{13.67}$$

Using equation (13.41a), concentration of initiator is determined as

$$[I] = \frac{k_t\left[\dot{M}_n\right]^2}{fk_d} \tag{13.68}$$

Putting value of [I] from equation (13.68) into equation (13.67)

$$\frac{1}{\bar{x}_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{1}{[M]}\left(\frac{k_t\left[\dot{M}_n\right]^2}{fk_d}\right) + \frac{fk_d}{k_p\left[\dot{M}_n\right][M]}\left(\frac{k_t\left[\dot{M}_n\right]^2}{fk_d}\right)$$

$$\frac{1}{x_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{k_t[M_n]^2}{fk_d[M]} + \frac{k_t[M_n]}{k_p[M]} \tag{13.69}$$

From equation (13.37), we get

$$[M_n] = \frac{R_p}{k_p[M]}$$

Substituting value of $[M_n]$ from above equation into equation (13.69)

$$\frac{1}{x_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{k_t\left(\dfrac{R_p}{k_p[M]}\right)^2}{fk_d[M]} + \frac{k_t\left(\dfrac{R_p}{k_p[M]}\right)}{k_p[M]}$$

$$\frac{1}{x_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{k_t R_p^2}{fk_d k_p^2[M][M]^2} + \frac{k_t R_p}{k_p k_p[M][M]}$$

$$\frac{1}{x_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{k_t R_p^2}{fk_d k_p^2[M]^3} + \frac{k_t R_p}{k_p^2[M]^2}$$

or

$$\frac{1}{x_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\left(\frac{k_t}{fk_d k_p^2}\right)\frac{R_p^2}{[M]^3} + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2} \tag{13.70}$$

Equation (13.70) gives average degree of polymerization in terms of chain transfer constants.

(iii) Chain Transfer to Solvent

If initiator of low $C_{tr,I}$ value is used and $R_p/[M]^2$ kept constant by adjusting the concentration of initiator, then equation (13.70) will be

$$\frac{1}{x_n} = \frac{1}{(x_n)_o} + C_{tr,S}\frac{[S]}{[M]} \tag{13.71}$$

Following results are drawn from equation (13.71)

(i)   Equation (13.71) is a straight line equation in intercept form as shown in Fig. 13.9.

(ii)   Slope of graph is equal to $C_{tr,S}$.

(iii) Intercept of the graph provides value of inverse of number average degree of polymerization in the absence of solvent transfer agent.

If $[S] \rightarrow 0$, then

$$\frac{1}{x_n} = \frac{1}{(x_n)_o}$$

Thus this graph provides values of constants, that is why it is excessively used to study free radical polymerization of styrene.
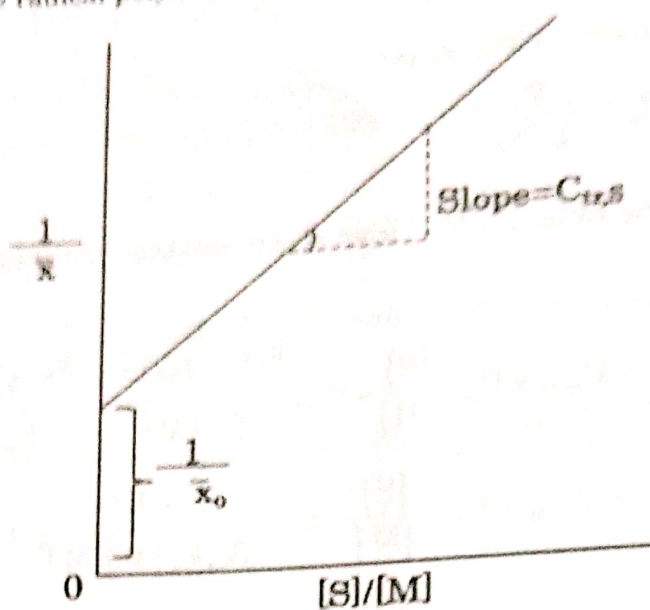

Fig. 13.9 Plot of [S]/[M] versus $\dfrac{1}{\bar{X}_n}$

(iv) Chain Transfer to Monomer and Initiator

If chain transfer to solvent is absent, then equation (13.70) will be

$$\frac{1}{\bar{X}_n} = C_{tr,M} + C_{tr,I}\left(\frac{k_t}{fk_d k_p^2}\right)\frac{R_p^2}{[M]^3} + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2}$$

Previous discussion shows that initial form of above equation is

$$\frac{1}{\bar{X}_n} = C_{tr,M} + C_{tr,I}\frac{[I]}{[M]} + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2} \qquad (13.72)$$

Following results are drawn from equation (13.72)

(i)   Equation (13.72) is a straight line equation in intercept form.

(ii)   If R_p is plotted against $\dfrac{1}{\bar{X}_n}$, then for small values of [I], [I]$\rightarrow$0, equation (13.72) will be

$$\frac{1}{\bar{X}_n} = C_{tr,M} + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2}$$

As $C_{tr,M}$, k_t and k_p^2 are constants, so a linear plot obtained. Similar plot also obtained if $\dfrac{1}{\bar{X}_n}$ is plotted versus $1/[M]^2$.

(iii) For large values of [I], if R_p is plotted against $\dfrac{1}{\overline{X}_n}$ by using equation (13.72), then a non-linear graph results because role of chain transfer to initiator becomes prominent.

Thus this graph provides information about role of initiator on relation of R_p and $\dfrac{1}{\overline{X}_n}$ and, of $[M]^2$ and $\dfrac{1}{\overline{X}_n}$.

Example 13.4

If $\overline{M}_n$ of polymer of glycol and 1,2-ethandiamine is 25,000 g/mol, then calculate its degree of polymerization.
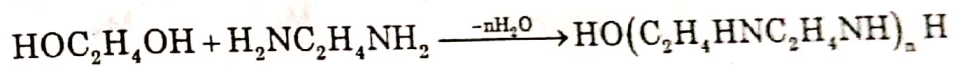
Solution

Number average molecular weight $= \overline{M}_n = 25,000$ g/mol

Molecular mass of water $= M_w = 18$ g/mol

Molecular mass of repeating unit $= M_r = 86$ g/mol

Degree of polymerization $= n = ?$

Polymerization reaction is

$$HOC_2H_4OH + H_2NC_2H_4NH_2 \xrightarrow{-nH_2O} HO(C_2H_4HNC_2H_4NH)_n H$$

Molecular weight of polymer $= (86 \times n) + 18$

$$25000 = (86 \times n) + 18$$
$$86 \times n = 24982$$
$$n = 290.48$$

13.6 COPOLYMERIZATION

That type of polymer which is made up of two monomers is called copolymer. The process by which copolymer is synthesize known as copolymerization.

13.6.1 Classification of Copolymers

On the basis of arrangement of monomeric units in copolymer, copolymers are divided five different classes. Structure of all classes is different from each other. Classification scheme and structure of each class is shown in Fig. 13.10 while their detail is as follows

(i) Statistical Copolymer: If arrangement of monomeric units in copolymer is completely according to statistical laws, then that copolymer is termed as statistical copolymer.

(ii) Alternate Copolymer: If two monomeric units successively alternate each other in polymer, then it is alternate copolymer.

(iii) Random Copolymer: These copolymers have no specific pattern of arrangement of monomeric units.

(iv) Graft Copolymer: That branched copolymer in which one monomeric unit forms backbone and other forms branches attached to this backbone is known as graft copolymer.

(v) Block Copolymer: Many monomeric units of one type combine and form block. Later these blocks of both monomeric units get arranged linearly and form block copolymer.
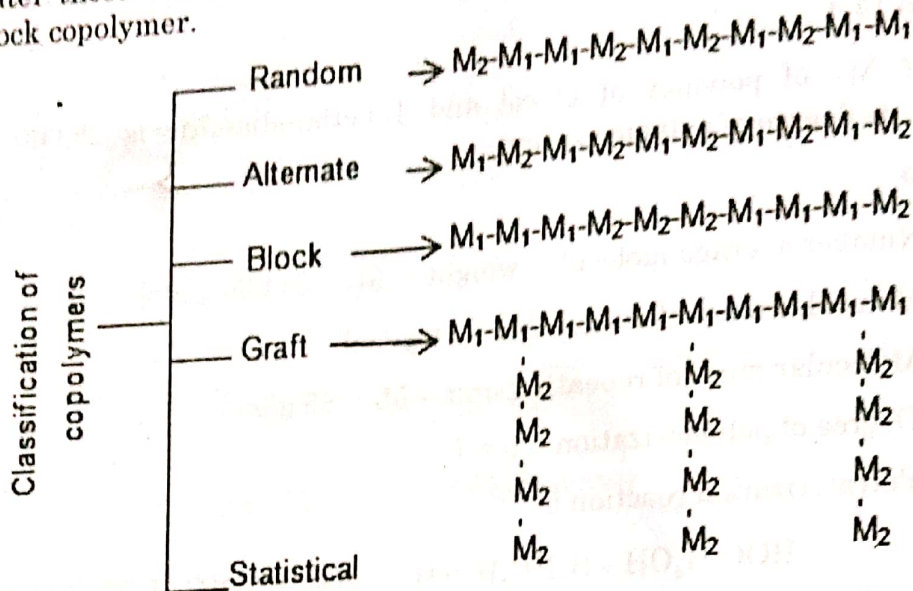

Fig. 13.10 Classification of copolymers along with sketch of structure of each class of copolymer

13.6.2 Kinetics of Copolymerization

Copolymerization can occur through step as well as chain growth polymerization. It depends upon monomers whether they prefer step growth or chain growth. Here we use free radical chain growth polymerization to explain kinetics of copolymerization. Initiation and termination are same as discussed before while propagation is different in copolymerization.

Let M_1 and M_2 are two commoners involved in copolymerization and $\dot{M}_1$ and $\dot{M}_2$ are their growing radicals respectively. Growing radicals may has $\dot{M}_1$ or $\dot{M}_2$ as growing end group in binary mixture. So there are four possible propagation reactions because there are equal chances for $\dot{M}_1$ to bind with M_1 or M_2 and vice versa for $\dot{M}_2$ radicals.

Reaction I: $\dot{M}_1$ binds with M_1, so terminal reactive end group and penultimate specie is of M_1. k_{11} is rate constant of self addition of $\dot{M}_1$ to M_1.

Reaction II: $\dot{M}_1$ binds with M_2 and product has terminal reactive end group and penultimate specie of M_2 and M_1 respectively. k_{12} is rate constant of $\dot{M}_1$ addition to M_2.

Reaction III: Here $\dot{M}_2$ binds with M_2, and product has terminal reactive group and penultimate specie of M_2. k_{22} is rate constant of self addition of $\dot{M}_2$ to M_2.

Reaction IV: $\dot{M}_2$ binds with M_1, product has reactive end group of M_1 and penultimate specie of M_2. k_{21} is rate constant of $\dot{M}_2$ addition to M_1.

$$\text{Reaction-I} \quad \sim\sim\dot{M}_1 + M_1 \xrightarrow{k_{11}} \sim\sim M_1 - \dot{M}_1 \quad \text{or} \quad \sim\sim \dot{M}_1$$

$$\text{Reaction-II} \quad \sim\sim\dot{M}_1 + M_2 \xrightarrow{k_{12}} \sim\sim M_1 - \dot{M}_2 \quad \text{or} \quad \sim\sim \dot{M}_2$$

$$\text{Reaction-III} \quad \sim\sim\dot{M}_2 + M_2 \xrightarrow{k_{22}} \sim\sim M_2 - \dot{M}_2 \quad \text{or} \quad \sim\sim \dot{M}_2$$

$$\text{Reaction-IV} \quad \sim\sim\dot{M}_2 + M_1 \xrightarrow{k_{21}} \sim\sim M_2 - \dot{M}_1 \quad \text{or} \quad \sim\sim \dot{M}_1$$
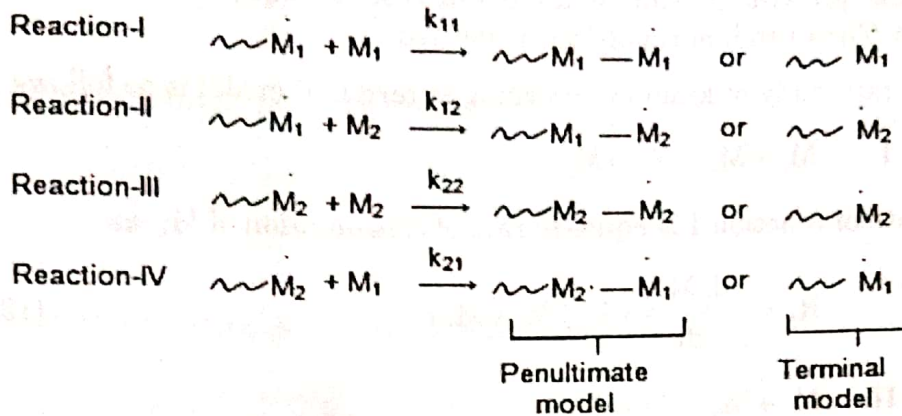
Penultimate model   Terminal model

Fig. 13.11 Brief sketches of products according to penultimate and terminal models

Terminal and penultimate models are such propositions which describe reactivity of growing free radicals in copolymerization. Fig. 13.11 exhibits brief sketches of products considered according to penultimate and terminal models. Following is detail of these models

(i) **Penultimate Model:** This model suggests that reactivity of growing polymer chain depends upon last two units of chain. It means reactivity of products of reaction-I and reaction-IV are not equally reactive for further propagation of chain and vice versa for products of reaction-II and reaction III.

(ii) **Terminal Model:** This model proposed that reactivity of growing polymer chain only depends upon last unit of chain. It means reactivity of product of reaction-I and reaction-IV, and products of reaction-II and reaction III have equal reactivity for further propagation of chain.

We discuss kinetics of copolymerization within perspective of terminal model as

(a) It is not so complicated to describe.

(b) It gives general principle by which most of the copolymerizations have been explained successfully.

By accepting general propositions of terminal model, following fruitful conclusions from some suitable limitations can be successfully drawn

Case I $k_{11} \gg k_{12}$ and $k_{22} \gg k_{21}$

If case-I is applicable, then terminal reactive group prefers self addition of monomers and block copolymer polymerized. If $k_{11} \ggg k_{12}$ and $k_{22} \ggg k_{21}$, then homopolymer may formed because there is much greater tendency of self addition of monomers which may not give a single chance to bind with monomer of other kind.

Case II $k_{12} \gg k_{11}$ and $k_{21} \gg k_{22}$

Under these conditions, growing polymer chain of one type prefers to bind with monomer of other type, thus alternate copolymer is formed.

Case II   I $k_{12} = k_{11}$ and $k_{21} = k_{22}$

Now, growing polymer chain of one type has equal tendency to bind with both monomers. Thus random copolymer is formed.

Detail study of kinetics according to terminal model is as follows

Reaction I $\dot{M}_1 + M_1 \xrightarrow{k_{11}} \dot{M}_1$

Rate of reaction-I is equal to rate of consumption of M_1, as

$$R_I = -\frac{d[M_1]}{dt} = k_{11}[\dot{M}_1][M_1] \qquad (13.73)$$

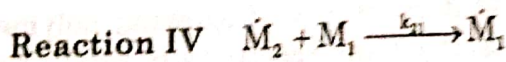**Reaction II** $\dot{M}_1 + M_2 \xrightarrow{k_{12}} \dot{M}_2$

Rate of reaction-II is equal to rate of consumption of M_2, as

$$R_{II} = -\frac{d[M_2]}{dt} = k_{12}[\dot{M}_1][M_2] \qquad (13.74)$$

Reaction III $\dot{M}_2 + M_2 \xrightarrow{k_{22}} \dot{M}_2$

Rate of reaction-III is equal to rate of consumption of M_2, as

$$R_{III} = -\frac{d[M_2]}{dt} = k_{22}[\dot{M}_2][M_2] \qquad (13.75)$$

Reaction IV $\dot{M}_2 + M_1 \xrightarrow{k_{21}} \dot{M}_1$

Rate of reaction-IV is equal to rate of consumption of M_1, as

$$R_{IV} = -\frac{d[M_1]}{dt} = k_{21}[\dot{M}_2][M_1] \qquad (13.76)$$

Monomer M_1 is consumed during reaction-I and IV, so

$$-\frac{d[M_1]}{dt} = R_I + R_{IV}$$

Thus, equations (13.73) and (13.76) are used to write equation for rate total of consumption of M_1

$$-\frac{d[M_1]}{dt} = k_{11}[\dot{M}_1][M_1] + k_{21}[\dot{M}_2][M_1] \qquad (13.77)$$

Monomer M_2 is consumed during reactions II and III, so

$$-\frac{d[M_1]}{dt} = R_{II} + R_{III}$$

Thus, equations (13.74) and (13.75) are used to write equation for rate total of consumption of M_1

$$-\frac{d[M_2]}{dt} = k_{22}[\dot{M}_2][M_2] + k_{12}[\dot{M}_1][M_2] \qquad (13.78)$$

Dividing equation (13.77) by (13.78)

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[\dot{M}_1][M_1] + k_{21}[\dot{M}_2][M_1]}{k_{22}[\dot{M}_2][M_2] + k_{12}[\dot{M}_1][M_2]}$$

Divide and multiply above equation by $[\dot{M}_2]$

$$\frac{d[M_1]}{d[M_2]} = \frac{[\dot{M}_2]}{[\dot{M}_2]}\left(\frac{k_{11}[\dot{M}_1][M_1] + k_{21}[\dot{M}_2][M_1]}{k_{22}[\dot{M}_2][M_2] + k_{12}[\dot{M}_1][M_2]}\right)$$

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1]\dfrac{[\dot{M}_1]}{[\dot{M}_2]} + k_{21}[M_1]\dfrac{[\dot{M}_2]}{[\dot{M}_2]}}{k_{22}[M_2]\dfrac{[\dot{M}_2]}{[\dot{M}_2]} + k_{12}[M_2]\dfrac{[\dot{M}_1]}{[\dot{M}_2]}}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1]\dfrac{[\dot{M}_1]}{[\dot{M}_2]} + k_{21}[M_1]}{k_{22}[M_2] + k_{12}[M_2]\dfrac{[\dot{M}_1]}{[\dot{M}_2]}} \qquad (13.79)$$

$\dot{M}_2$ and $\dot{M}_1$ are two principal radicals present in reaction mixture. As polymerization is a fast process, so steady state condition tells that net concentration of $\dot{M}_1$ and $\dot{M}_2$ is zero in reaction. It means rate of formation of $\dot{M}_1$ is equal to rate of consumption of $\dot{M}_1$ and vice versa for $\dot{M}_2$. Thus rates of reaction-II and IV are equal, and rates of reactions I and III are equal. Self addition reactions of $\dot{M}_2$ and $\dot{M}_1$ are not considered here as product and reactant are same species. So

$$R_{IV} = R_{II}$$

$$k_{21}[\dot{M}_2][M_1] = k_{12}[\dot{M}_1][M_2]$$

$$\frac{[\dot{M}_1]}{[\dot{M}_2]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \qquad (13.80)$$

Substituting equation (13.80) into equation (13.79)

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1]\dfrac{k_{21}[M_1]}{k_{12}[M_2]} + k_{21}[M_1]}{k_{22}[M_2] + k_{12}[M_2]\dfrac{k_{11}[M_1]}{k_{12}[M_2]}}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{21}\dfrac{k_{11}[M_1]^2}{k_{12}[M_2]} + k_{21}[M_1]}{k_{22}[M_2] + k_{21}[M_1]}$$

Dividing nominator as well as denominator of above equation with $k_{21}[M_1]$

$$\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{k_{21}}{k_{21}}\dfrac{k_{11}[M_1]^2}{k_{12}[M_2][M_1]} + \dfrac{k_{21}[M_1]}{k_{21}[M_1]}}{\dfrac{k_{22}[M_2]}{k_{21}[M_1]} + \dfrac{k_{21}[M_1]}{k_{21}[M_1]}}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{k_{11}[M_1]}{k_{12}[M_2]} + 1}{\dfrac{k_{22}[M_2]}{k_{21}[M_1]} + 1} \tag{13.81}$$

Reactivity ratios r_1 and r_2 are

$$r_1 = \frac{k_{11}}{k_{12}}$$

and $$r_2 = \frac{k_{22}}{k_{21}}$$

Substituting reactivity ratios r_1 and r_2 from previous both equations into (13.81)

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1\dfrac{[M_1]}{[M_2]} + 1}{r_2\dfrac{[M_2]}{[M_1]} + 1} \tag{13.82}$$

Equation (13.82) is a copolymer composition equation which gives concentration of monomer M_1 polymerized with respect to concentration of monomer M_2 in time dt. Using this equation we can determine feed ratio of monomers ($[M_1]/[M_2]$) into polymer, as it is generally assumed that feed ratio of mixture is equal to feed ratio of polymer.

It is always not necessary to mention data in terms of feed ratio, term of mole fraction is also used. Monomers are continuously depleting from reaction and

incorporated into polymer, so F_1 and F_2 are mole fractions of monomer M_1 and M_2 into polymer, while their mole fractions left in reaction mixture are f_1 and f_2. So

$$F_2 + F_1 = 1 \tag{13.82a}$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \tag{13.82b}$$

$$F_2 = 1 - F_1 = \frac{d[M_2]}{d[M_1] + d[M_2]} \tag{13.82c}$$

and $\quad f_2 + f_1 = 1 \tag{13.82d}$

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \tag{13.82e}$$

$$f_2 = 1 - f_1 = \frac{[M_2]}{[M_1] + [M_2]} \tag{13.82f}$$

To correlate mole fractions of monomers incorporating into polymer and left in mixture, we modify equation (13.82) as

Multiply nominator and denominator of equation (13.82) with $[M_1][M_2]$

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1][M_2]\dfrac{[M_1]}{[M_2]} + [M_1][M_2]}{r_2[M_1][M_2]\dfrac{[M_2]}{[M_1]} + [M_1][M_2]}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]^2 + [M_1][M_2]}{r_2[M_2]^2 + [M_1][M_2]}$$

Rearranging above equation

$$\frac{d[M_2]}{d[M_1]} = \frac{r_2[M_2]^2 + [M_1][M_2]}{r_1[M_1]^2 + [M_1][M_2]}$$

Add 1 on both sides of above equation

$$\frac{d[M_2]}{d[M_1]} + 1 = \frac{r_2[M_2]^2 + [M_1][M_2]}{r_1[M_1]^2 + [M_1][M_2]} + 1$$

$$\frac{d[M_1] + d[M_2]}{d[M_1]} = \frac{r_2[M_2]^2 + [M_1][M_2] + r_1[M_1]^2 + [M_1][M_2]}{r_1[M_1]^2 + [M_1][M_2]}$$

Now substituting F_1 from equation (13.82b) into above equation

$$\frac{1}{F_1} = \frac{r_2[M_2]^2 + 2[M_1][M_2] + r_1[M_1]^2}{r_1[M_1]^2 + [M_1][M_2]}$$

Divide nominator and denominator of above equation with $([M_1]+[M_2])^2$

$$\frac{1}{F_1} = \frac{r_2\dfrac{[M_2]^2}{([M_1]+[M_2])^2} + 2\dfrac{[M_1][M_2]}{([M_1]+[M_2])^2} + r_1\dfrac{[M_1]^2}{([M_1]+[M_2])^2}}{r_1\dfrac{[M_2]^2}{([M_1]+[M_2])^2} + \dfrac{[M_1][M_2]}{([M_1]+[M_2])^2}}$$

Substituting f_1 and f_2 from equation (13.82e) and (13.82f) into above equation

$$\frac{1}{F_1} = \frac{r_2 f_2^2 + 2f_1^2 f_2^2 + r_1 f_1^2}{r_1 f_2^2 + f_1 f_2}$$

or
$$F_1 = \frac{r_1 f_2^2 + f_1 f_2}{r_2 f_2^2 + 2f_1^2 f_2^2 + r_1 f_1^2} \qquad (13.83)$$

and
$$1 - F_2 = \frac{r_1 f_2^2 + f_1 f_2}{r_2 f_2^2 + 2f_1^2 f_2^2 + r_1 f_1^2}$$

$$F_2 = 1 - \frac{r_1 f_2^2 + f_1 f_2}{r_2 f_2^2 + 2f_1^2 f_2^2 + r_1 f_1^2} \qquad (13.84)$$

Equations (13.83) and (13.84) give amounts of monomers into reaction mixture and polymer at different mole fractions.

13.6.3 Reactivity Ratios and Composition of Polymer

Reactivity ratios r_1 and r_2 are useful to predict nature of copolymer formed. Following are some special cases and their immediate predictions

Special Case I: $r_1 = r_2 = 0$

This is possible when k_{11} and k_{22} are zero and k_{12} and k_{21} are not zero, it means tendency for self addition of monomers is negligible while tendency to add monomer of other type is significant. So both monomers are alternatively add into polymer and a perfect alternate copolymer is fabricated.

Special Case II: $r_1 = r_2 = \infty$

This is possible when k_{12} and k_{22} are zero, accordingly there is large tendency for self addition of monomers as compared to addition of monomer of other kind. So homopolymers are formed.

Special Case III: $r_1 = r_2 = 1$

Now k_{11}, k_{22}, k_{12} and k_{21} are equal, so a competition develops between self addition and non-self addition of monomers. Under such conditions, random copolymer is synthesized.

Special Case IV: $r_1 r_2 = 1$

This is case of ideal copolymerization, under this condition copolymer is truly random but this condition does not prevail mostly due to side reactions and non-ideal reaction conditions.

Example 13.5

If feed ratio of styrene and maleic anhydride is 3:1 and reactivity ratios of styrene and maleic anhydride are 2 and 0.25 respectively, then calculate composition of copolymer.

Solution

Concentration of styrene = $[M_1]$ = 3 $[M_2]$

Concentration of maleic anhydride = $[M_2]$

Reactivity ratio of styrene = r_1 = 2

Reactivity ratio of styrene = r_2 = 0.25

Composition of copolymer= $d[M_1]/d[M_2]$ = ?

Using copolymer composition equation, we have

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1\dfrac{[M_1]}{[M_2]}+1}{r_2\dfrac{[M_2]}{[M_1]}+1} = \frac{2\times\dfrac{3[M_2]}{[M_2]}+1}{0.25\times\dfrac{[M_2]}{3[M_2]}+1} = \frac{2\times3+1}{\dfrac{0.25}{3}+1} = \frac{7}{0.083+1} = 6.46$$

13.7 MOLECULAR WEIGHT AVERAGES

Molecular weight of a polymer cannot have a single value as all chains of polymer synthesized at one time are not equal in length. Thus for this kind of polydisperse system average molecular weight is quoted. Viscosity average, z-average, number average and weight average molecular weights are different molecular weights which can be determined different methods. A single method of characterization cannot measure all kinds of weight averages.

(i) Number Average Molecular Weight

Number average molecular weight ($\overline{M}_n$) is summation of all fractions of polymers multiplied by their molecular masses. Let f_1 is fraction of molecules of mass M_1, f_2 is fraction of molecules of mass M_2 and so on.

$$\overline{M}_n = f_1 M_1 + f_2 M_2 + f_2 M_2 + \dots + f_i M_i$$

Generally it can be written as   (13.85)

$$\overline{M}_n = \Sigma_i \, f_i M_i$$

If N_i is number of molecules of fraction of molecules f_i, and N_{Total} is total number of molecules, then   (13.86)

$$f_i = \frac{N_i}{N_{Total}}$$

where $N_{Total} = \Sigma_i N_i$

Putting value from equation (13.86) into (13.85) as

                                          (13.87)

$$\overline{M}_n = \frac{\Sigma_i N_i M_i}{N_{Total}}$$

Equation (13.87) gives formula for calculation of $\overline{M}_n$.

(ii) Mass Average Molecular Weight

Mass average molecular weight ($\overline{M}_m$) is calculated by summation of all mass fractions multiplied by their respective molecular masses. Let w_1 is mass fraction of molecules of molar mass M_1, w_2 is fraction of molecules of molar mass M_2 and so on.

$$\overline{M}_m = w_1 M_1 + w_2 M_2 + w_2 M_2 + \dots + w_i M_i$$

Generally it can be written as

                                          (13.88)

$$\overline{M}_m = \Sigma_i \, w_i M_i$$

If m_i is mass of molecules having molar mass M_i, and m_{Total} is total mass of sample of polymer, then

                                          (13.89)

$$w_i = \frac{m_i}{m_{Total}}$$

Where, $m_{Total} = \Sigma_i m_i$

Substituting value from equation (13.89) into (13.88) as

$$\overline{M}_n = \frac{\Sigma_i m_i M_i}{m_{Total}}$$

$$\overline{M}_m = \frac{\Sigma_i m_i M_i}{\Sigma_i m_i}$$

We know that

$$m_i = \frac{\Sigma_i N_i M_i}{N_A}, \text{ hence above equation will be}$$

$$\overline{M}_m = \frac{\sum_i \dfrac{N_i M_i}{N_A} M_i}{\sum_i \dfrac{N_i M_i}{N_A}}$$

$$\overline{M}_m = \frac{\sum_i N_i M_i M_i}{\sum_i N_i M_i}$$

$$\overline{M}_m = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \tag{13.90}$$

Equation (13.90) gives formula for calculation of $\overline{M}_m$. $\overline{M}_m > \overline{M}_n$ is applicable for polydisperse system, since longer chain has greater mass, so it can greatly enhance $\overline{M}_m$, while it is very rare that a large number of chains of single fraction is present.

(iii) z-Average Molecular Weight

z-average molecular weight ($\overline{M}_z$) is

$$\overline{M}_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \tag{13.91}$$

Equation (13.91) gives formula for calculation of $\overline{M}_z$. $\overline{M}_z > \overline{M}_m > \overline{M}_n$, this trend exists because weighing factor is $N_i M_i^2$ in $\overline{M}_z$.

Example 13.6

Sample A of polymer is polydisperse. 4, 8, 1 and 3 chains have weight 10,000, 2,000, 5,000 and 15,000 lb/mol respectively. Calculate $\overline{M}_n$, $\overline{M}_m$ and $\overline{M}_z$ and compare their values.

Solution

Number of chains having weight 10,000 lb/mol=4

Number of chains having weight 2,000 lb/mol=8

Number of chains having weight 5,000 lb/mol=1

Number of chains having weight 15,000 lb/mol=3

Using equation (13.87), (13.90) and (13.91), we calculate $\overline{M}_n$, $\overline{M}_m$ and $\overline{M}_z$ as

(i)
$$\overline{M}_n = \frac{\sum_i N_i M_i}{N_{Total}} = \frac{(4 \times 10000) + (8 \times 2000) + (1 \times 5000) + (3 \times 15000)}{(4 + 8 + 1 + 3)}$$

$$\overline{M}_n = \frac{40000 + 16000 + 5000 + 45000}{16} = \frac{106000}{16} = 6.625 \times 10^3 \text{ lb / mol}$$

(ii)

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

$$\overline{M}_w = \frac{\left(4 \times (10000)^2\right) + \left(8 \times (2000)^2\right) + \left(1 \times (5000)^2\right) + \left(3 \times (15000)^2\right)}{\left(4 \times 10000\right) + \left(8 \times 2000\right) + \left(1 \times 5000\right) + \left(3 \times 15000\right)}$$

$$\overline{M}_w = \frac{\left(4 \times 10^8\right) + \left(32 \times 10^6\right) + \left(25 \times 10^6\right) + \left(675 \times 10^6\right)}{108000} = \frac{1.132 \times 10^9}{108000}$$

$$\overline{M}_w = 10.6 \times 10^3 \ lb/mol$$

(iii)

$$\overline{M}_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}$$

$$\overline{M}_z = \frac{\left(4 \times (10000)^3\right) + \left(8 \times (2000)^3\right) + \left(1 \times (5000)^3\right) + \left(3 \times (15000)^3\right)}{\left(4 \times (10000)^2\right) + \left(8 \times (2000)^2\right) + \left(1 \times (5000)^2\right) + \left(3 \times (15000)^2\right)}$$

$$\overline{M}_z = \frac{\left(4 \times 10^{12}\right) + \left(64 \times 10^9\right) + \left(125 \times 10^9\right) + \left(10125 \times 10^9\right)}{\left(4 \times 10^8\right) + \left(32 \times 10^6\right) + \left(25 \times 10^6\right) + \left(675 \times 10^6\right)} = \frac{1.4314 \times 10^{13}}{1.132 \times 10^9}$$

$$\overline{M}_z = 12.64 \times 10^3 \ lb/mol$$

Calculates values shows that

$$\overline{M}_z \left(12.64 \times 10^3 \ lb/mol\right) > \overline{M}_w \left(10.6 \times 10^3 \ lb/mol\right) > \overline{M}_n \left(4 \times 10^3 \ lb/mol\right)$$

13.8 MOLECULAR MASS DETERMINATION METHODS

Osmometry, viscometry, light scattering and sedimentation methods are commonly used methods for determination of molar mass of a polymer. Some methods are given here in detail.

13.8.1 Viscosity Method

Viscosity of a fluid is a fundamental property which has been described in section 11.11. Viscosity measurements can be used for determination of molar mass of a polymer. Ostwald viscometer is the simplest apparatus which is used for measurement of viscosity of a solution. Ostwald viscometer consists of a bulb B with markings x_1 and x_2 attached to a capillary tube C and a reservoir D as shown in Fig. 13.12. A liquid is introduced from C and sucked from B side. Then time of flow of liquid

Fig. 13.12 Ostwald viscometer

from x_1 to x_2 is recorded. The value of relative viscosity can be measured using following formula.
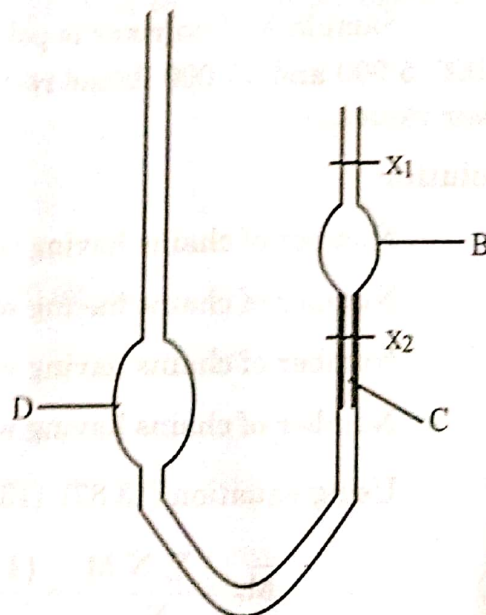
$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{\rho}{\rho_0} \cdot \frac{t}{t_0}$$

Where,

η = viscosity of solution

η_0 = viscosity of solvent

t = time of flow of solution

t_0 = time of flow of solvent

ρ = density of solution

ρ_0 = density of solvent

Time flow can be measured by Ostwald viscometer while densities can be determined by filling gravity bottle. Specific viscosity is obtained from relative viscosity using the following relation.

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

The specific viscosity is converted into reduced viscosity by the relation

$$\eta_{red} = \frac{\eta_{sp}}{C}$$

Where, C is the concentration in gmL^{-1}.

$\dfrac{\eta_{sp}}{C}$ is plotted as a function of concentration of polymer as shown in Fig. 13.13. The intercept of the plot is viscosity of the solution at infinite dilution and it is called intrinsic viscosity i.e.

Intrinsic viscosity $= [\eta] = Lim_{c \to 0} \dfrac{\eta_{sp}}{C}$

The relation between $[\eta]$ and molar mass of a polymer is given by the equation

$$[\eta] = KM^{a}$$

Where, a and K are empirical constants and M is

Fig. 13.13 Plot of η_{sp}/c as a function of concentration.

the molar mass of polymer. The above equation can be used for determination of molar mass of polymer for which K and a are known.
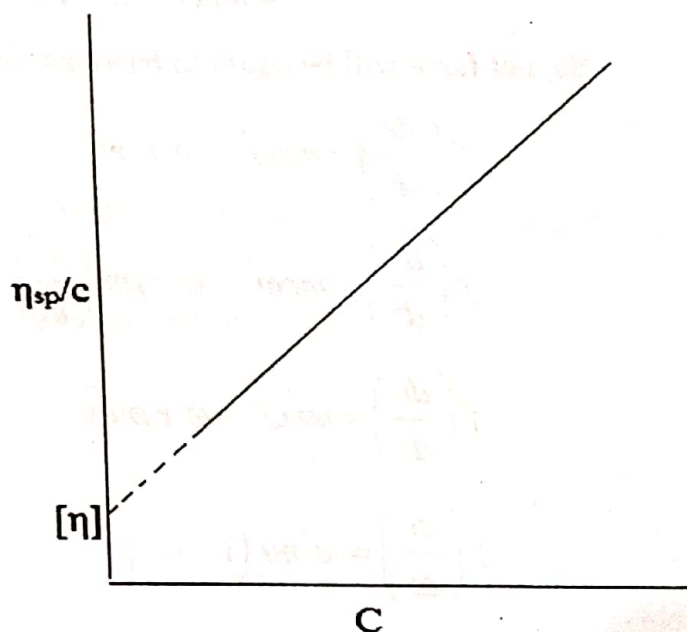
13.8.2 Sedimentation

Let us consider a particle of polymer in solution which moves under the influence of gravitational field. The falling particle having mass m_s experiences a centrifugal force which is equal to $\omega^2 rm$ and buoyancy force. The net force acting on the particle can be written as

$$\text{Net force} = \text{centrifugal force} - \text{buoyancy force}$$

$$= \frac{mv^2}{r} - \omega^2 rm_s$$

$$= \frac{m(r\omega)^2}{r} - \omega^2 rm_s$$

$$= \frac{mr^2\omega^2}{r} - \omega^2 rm_s$$

$$= mr\omega^2 - \omega^2 rm_s \qquad (13.92)$$

Where, ω is the angular velocity of the rotor in radius per second, r is the distance from centre of rotation of particle.

As we know that $m_s = \rho v$, by putting this value in equation (13.92),

$$= mr\omega^2 - \omega^2 r\rho v$$

So, net force will be equal to frictional force

$$f\left(\frac{dr}{dt}\right) = mr\omega^2 - \omega^2 r\rho v$$

$$f\left(\frac{dr}{dt}\right) = mr\omega^2 - \omega^2 r\rho m\left(\frac{v}{m}\right)$$

$$f\left(\frac{dr}{dt}\right) = mr\omega^2 - \omega^2 r\rho m\bar{v}$$

$$f\left(\frac{dr}{dt}\right) = \omega^2 mr\left(1 - \rho\bar{v}\right)$$

$$\left(\frac{dr}{dt}\right) = \frac{\omega^2 mr\left(1 - \rho\bar{v}\right)}{f}$$

$$\frac{dr/dt}{\omega^2 r} = \frac{N_A m\left(1 - \rho\bar{v}\right)}{N_A f}$$

Where, $\bar{v}$ is the partial specific volume, $\frac{dr}{dt}$ is the sedimentation velocity.

Left hand side is replaced by S because the term $\frac{dr/dt}{\omega^2 r}$ is the sedimentation coefficient (S). N_A is Avogadro's number.

$$S = \frac{M\left(1 - \rho\bar{v}\right)}{N_A f}$$

$$M = \frac{SN_A f}{1 - \rho\bar{v}} \qquad (13.93)$$

According to Stoke's law frictional coefficient of a spherical particle is

$$f = 6\pi\eta r_s$$

By putting value of f in equation (13.93), we get

$$M = \frac{SN_A \left(6\pi\eta r_s\right)}{1 - \rho\bar{v}} \qquad (13.94)$$

According to Stoke's Einstein equation, we know

$$D = \frac{k_B T}{6\pi\eta r_s}$$

$$6\pi\eta r_s = \frac{k_B T}{D}$$

Where, k_B is the Boltzmann constant, D is the diffusion coefficient and T is the absolute temperature.

By putting value of $6\pi\eta r_s$ in equation (13.94), we get

$$M = \frac{SN_A k_B T}{D\left(1 - \rho\bar{v}\right)}$$

$$M = \frac{SRT}{D\left(1 - \rho\bar{v}\right)}$$

In the above equation, unknown quantities are $\bar{v}$, D and S. $\bar{v}$ and D can be measured by some separate experiments. The sedimentation coefficient can be determined by the following ways.

$$S = \frac{dr/dt}{\omega^2 r}$$

$$S\partial t = \frac{1}{\omega^2} \frac{dr}{r}$$

By integrating above equation within limits

$$S \int_0^t dt = \frac{1}{\omega^2} \int_{r_0}^{r} \frac{1}{r} dr$$

$$S(t-0) = \frac{1}{\omega^2} |\ln r|_{r_0}^{r}$$

$$St = \frac{1}{\omega^2} (\ln r - \ln r_0)$$
<div align="right">(13.95)</div>

$$St = \frac{\ln\left(\frac{r}{r_0}\right)}{\omega^2}$$

$$S = \frac{1}{t\omega^2} \ln\left(\frac{r}{r_0}\right)$$

By rearranging equation (13.95), we get

$$St\omega^2 = \ln r - \ln r_0$$

$$\ln r = St\omega^2 + \ln r_0$$
<div align="right">(13.96)</div>

Equation (13.96) is an equation of straight line in intercept form as shown in Fig. 13.14 with slope $S\omega^2$. From the slope we can determined the value of sedimentation coefficient.
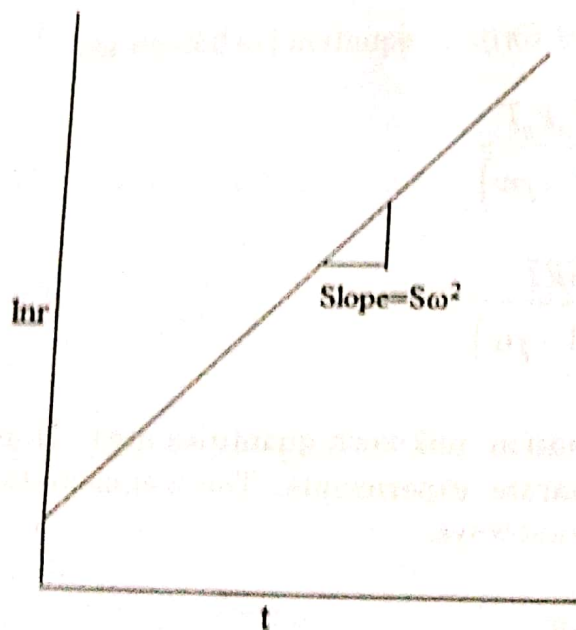
Fig. 13.14 Plot of lnr versus t

13.8.3 Osmometry

Vapour phase and membrane osmometry are two principal types of osmometry used so far to measure number average molecular weight.

(i) Vapour Phase Osmometry

Principle: Addition of solute molecules decreases the vapour pressure of a liquid. Decrease in vapour pressure depends upon number of solute molecules.

Construction and Working: Vapour phase osmometer is shown in Fig. 13.15. Two thermistors are connected to a Wheatstone bridge. Solvent drops were placed in vicinity of both thermistors by using syringes. As both wires are in proximity of same medium as rate of evaporation is same at both wires, so no temperature difference is sensed between both wires and a balance point is established. Now place drop of solution at one thermistor and drop of solvent at the other. Now thermistors detect a temperature difference as rate of evaporation at both ends is unequal. This temperature difference is recorded in terms of potential difference by Wheatstone bridge.

Calculation of Molecular Weight: Output voltage ΔV is related to molecular weight M by following equation

$$\frac{\Delta V}{C} = \frac{K}{\overline{M}_n} + KBC \qquad (13.97)$$

K is a calibration constant. Firstly value of K is determined by using polymer of low and known molecular mass having less polydispersity. Then that value of K is used to determine molecular mass. Voltage difference is measured for solutions of different concentrations, then $\Delta V/C$ is plotted against concentration as shown in Fig. 13.16. Value of slope is equal to KB, while value of intercept is equal to $K/\overline{M}_n$. K is known already by calibration, thus $\overline{M}_n$ is determined.

Advantages: Quick determination of molecular mass along with use of small amount of polymer is two advantages of this method.

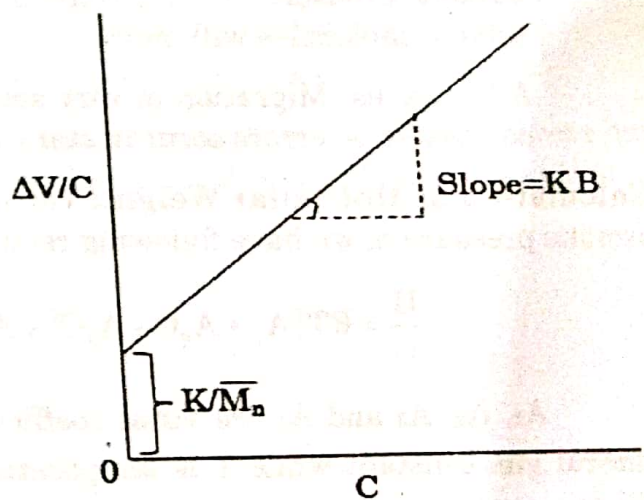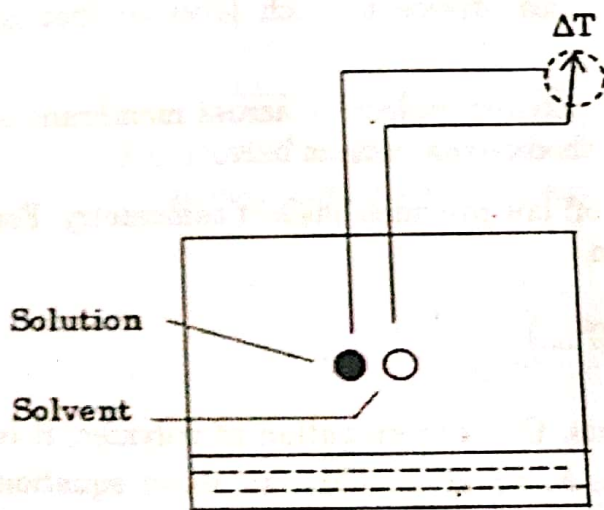**Disadvantages:** Only low molecular weight possessing polymers (~30,000) can be successfully measured by it.

Fig. 13.15 Working of vapour phase osmometry   Fig. 13.16 Plot of $\Delta V/C$ versus C

(ii) Membrane Osmometry

Principle: Osmotic pressure of solvent decreases by addition of solute molecules. Decrease in osmotic pressure depends upon number of solute molecules and related to molar mass of polymer.

Types: Static, dynamic and high speed membrane osmometers are three kinds of membrane osmometers which are normally use.

(I) **Static Membrane Osmometer:** In this osmometer, both chambers are separated by a membrane and they are individually connected to small capillaries as shown in Fig. 13.17. Initially both chambers contain solvent, thus there is no net movement of molecules from one chamber to other. So level of liquid in both capillaries is same as shown in Fig. 13.17 (a). Later solution is placed in one chamber while other contains solvent. Now chemical and osmotic potential of both chambers becomes unequal as shown in Fig. 13.17 (b). Now, solvent molecules move from chamber of low osmotic potential towards chamber of higher osmotic potential via semipermeable membrane until equilibrium gets establish. As a result level of liquid in capillary attached to chamber containing solvent becomes low and vice versa for other chamber. Difference in height of liquid in capillary helps to determine osmotic pressure, in return molecular weight also.

Disadvantages: Time consuming and no membrane is perfectly ideal to completely prevent flow of solute molecules and permit flow of solvent molecules.

(II) **Dynamic Membrane Osmometer:** Here motion of solvent molecules towards chamber of solution is stopped by applying equal and opposite pressure on solution. Thus osmotic pressure is measured in terms that how much pressure has applied to stop flow of solvent molecules.

Advantages: Equilibrium is established soon between both chambers, so it is time saving.

(III) **High Speed Membrane Osmometers:** Here an optical system is used to monitor flow of solvent molecules through membrane. As soon as solvent molecules starts penetrate into membrane, optical system automatically adjusts pressure by a electro-mechanical device to such level so that no solvent molecules will move.

Advantages: Migration of very small polymer molecules across membrane is perverted, so errors occur in static method do not happen here.

Calculation of Molecular Weight: Van't Hoff law provides basis of osmometry. For osmotic pressure Π, we have following relation

$$\frac{\Pi}{C} = RT\left(A_1 + A_2 C + A_3 C^2 + A_4 C^3 ....\right)$$

A_1, A_2, A_3 and A_4 are virial coefficients, C is concentration of polymer, R is general gas constant while T is temperature. A_1 equal to $1/\overline{M}_n$, so above equation will be

$$\frac{\Pi}{C} = RT\left(\frac{1}{\overline{M}_n} + A_2 C + A_3 C^2 + A_4 C^3 \ldots\right)$$

For very dilute solutions, above equation will be

$$\frac{\Pi}{C} = RT\left(\frac{1}{\overline{M}_n} + A_2 C\right)$$

$$\frac{\Pi}{RTC} = \frac{1}{\overline{M}_n} + A_2 C \qquad\qquad (13.98)$$

Following results are drawn from equation (13.98)

(i) Equation (13.98) is a linear equation.

(ii) Plot of π/RTC versus C gives an intercept equal to $1/\overline{M}_n$ and slope equal to A_2 (Fig. 13.18). Thus inverse of intercept gives value of $\overline{M}_n$.

(iii) Value of A_2 is measure of polymer-solvent interactions. High value of slope indicates good polymer-solvent interactions, so that solvent is considered of good quality.

(iv) Low value of slope gives an indication of poor solvent-polymer interactions.

(v) If value of slope is zero, then graph will be parallel to x-axis, and that solvent is considered very poor and called theta solvent.

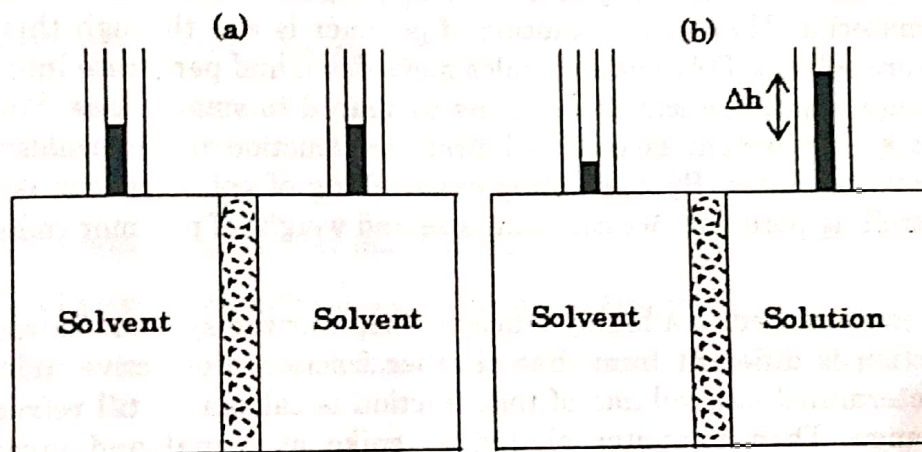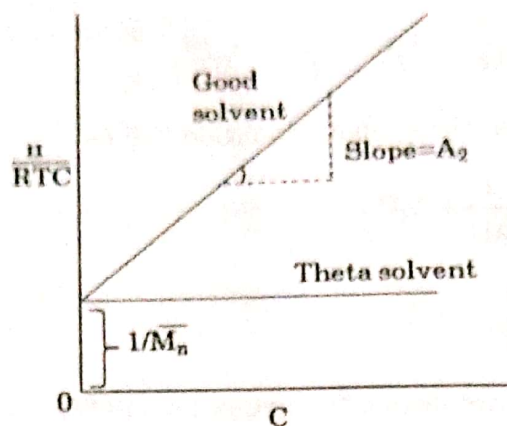This is how molecular weight is determined by osmometry.

Fig. 13.17 Functioning of membrane osmometers (a) when both chambers have solvent, and (b) when one chamber has solvent while other has solution.

Fig. 13.18 Plot of n/RTC versus C

13.9 ANALYTICAL METHODS

Molecular weight distribution determination method is analytical method. Centrifugation, turbidimetry, gradient elution and gel permeation chromatography (GPC) are analytical methods. Among analytical methods, GPC is most reliable and gives detailed and accurate analysis.

13.9.1 Gel Permeation Chromatography

Relative movement of polydisperse polymer solution is studied through chromatographic tank and analysis is done in GPC.

GPC is done with the help of a chromatographic tank filled with beads or gel as packing material. Then dilute solution of polymer is run through this tank with the help of pure solvent. Polymer molecules move down and penetrate into gel spaces. Large molecules cannot penetrate easily as compared to smaller one. So fraction of molecules of higher weight is collected first and fraction of molecules of smaller weights is collected later. By controlling crosslinking of gel, pore size is controlled. Thus by controlling pore size, we can limit size and weight of polymer collected in the end by GPC.

GPC is connected to a highly efficient computerized system. Refractive index of every fraction is different from that of other fraction. Refractive index of every fraction is determined and volume of that fraction is calculated till refractive index does not change. Then computer plotted as spike as signal and gives value of molecular weight. In this way, molecular weight of every fraction and number of fractions are determined.