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Molecular Weights of Polymers

Prof. Premamoy Ghosh
Polymer Study Centre
"Arghya" 3, Kabi Mohitlal Road
P.P. Haltu, Kolkata- 700078

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Key Words

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Introduction

For many reasons, particularly to know more about polymer molecular systems, it is necessary to characterize them with respect to (i) the chemical identity of their repeat units, (ii) nature of end groups present, (iii) existence of branching with nature of branch units and their frequency, (iv) presence of comonomer units and also copolymer composition and comonomer sequence distribution in copolymer systems, (v) solubility and associated features, (vi) optical properties covering clarity or degree of clarity and refractive index, and (vii) resistance properties with reference to thermal, mechanical and electrical resistances, photoresistance or photostability, chemical and weather resistance, corrosion resistance, and also bioresistance or resistance to biodegradation. But what is more important and fundamental is knowledge about the molecular weight of a given polymer. For molecular weight determination, it is necessary to dissolve the polymer in an appropriate solvent and begin with a dilute solution.

Concept of Average Molecular Weight

A specified polymer material is generally a mixture of molecules of identical or near – identical chemical structure and composition, but differing in degree of polymerization (DP) or molecular weight. The molecules produced by polymerization reaction have chain lengths that are distributed according to a probability function that is governed by the polymerization mechanism and by the condition prevailing during the process. A concept of average molecular weight, therefore, assumes importance and very much relevant. However, assignment of a numerical value to the molecular weight will be dependent on the definition of a particular average. An average molecular weight, $\overline{M}$ may in fact be generally expressed as

$$\overline{M} = f_1 M_1 + f_2 M_2 + f_3 M_3 + \text{------} = \Sigma f_i M_i \qquad (1)$$

Here, M_1 , M_2 , M_3 etc. refer to molecular weights of different sizes of molecules and the coefficients f_1 , f_2 , f_3 etc. are fractions such that their summation Σf_i equals to unity. The average molecular weight $\overline{M}$ may otherwise be expressed as

$$\overline{M} = \frac{\Sigma N_i M_i^{\,a}}{\Sigma N_i M_i^{\,(a-1)}} \qquad (2)$$

where, N_i is the number of molecules, each of which is characterized by the molecular weight M_i and the index 'a' may have any real value. Two very important average molecular weight widely recognized and used are (i) number average molecular weight, $\overline{M}_n$ and (ii) weight average molecular weight, $\overline{M}_w$. Setting $a = 1$ in equation (2), one obtains the expression for the number average molecular weight, $\overline{M}_n$:

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \qquad (3)$$

Equation (3) can, in fact, be expressed as a simple summation series resembling equation (1) where the fractional coefficients are actually the mole fractions of the respective molecular species existing in the polymer system such that total weight $W = \Sigma N_i M_i$ and total number of molecules $N = \Sigma N_i$, Thus,

$$\overline{M}_n = \frac{W}{N} = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{N_1}{N} M_1 + \frac{N_2}{N} M_2 + \frac{N_3}{N} M_3 + \text{------}$$
$$= f_1 M_1 + f_2 M_2 + f_3 M_3 + \text{-------} \qquad (4)$$

On the other hand, however, setting $a = 2$ in equation (2), one finds the expression for weight average molecular weight, $\overline{M}_w$, i.e.,

$$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \qquad (5)$$

Equation (5) can also be rearranged and expressed as a summation series as given by equation (1), but in this case, the fractional coefficients actually correspond to weight fractions of different molecular species present. So, one may write :

$$\overline{M}_w = \frac{\Sigma N_i M_i \,.\, M_i}{\Sigma N_i M_i} = \frac{\Sigma w_i M_i}{\Sigma w_i} = \frac{\Sigma w_i M_i}{W}$$

$$= \frac{w_1}{W} M_1 + \frac{w_2}{W} M_2 + \frac{w_3}{W} M_3 + \text{------}$$

$$= f_1 M_1 + f_2 M_2 + f_3 M_3 + \text{-------} \qquad (6)$$

Here, w_1, w_2, w_3, etc. stand for weight of different molecular species having molecular weight M_1, M_2, M_3 etc. respectively and $\Sigma w_i = W$ gives the total weight of all the molecules present.

The obvious consequences of above definitions imply that $\overline{M}_w \geq \overline{M}_n$, i.e., $\overline{M}_w / \overline{M}_n \geq 1$; the equality, however, relates to a perfectly monodisperse polymer sample where all the polymer molecules are of equal molecular weight, i.e. $M_1 = M_2 = M_3 = \text{-----} = M$. So, for monodisperse systems, $(\overline{M}_w / \overline{M}_n) = 1$. Deviation from unity of the ratio $M_w / \overline{M}_n$, known as the distribution ratio is taken as a measure of polydispersity of the polymer sample. The said ratio is also referred to as polydispersity index; a higher value of the ratio means a greater polydispersity.

Evaluation of number average molecular weight is helpful for having a good understanding of polymerization mechanism and relevant kinetics. $\overline{M}_n$ is useful in the analysis of kinetic data and assessing or ascertaining effects of many side reactions such

as chain transfer, inhibition and retardation and also autoacceleration effects during vinyl and related polymerizations. The number average molecular weight assumes prime importance in the context of studies of solution properties that go by the name of colligative properties viz., vapour pressure lowering, freezing point depression, boiling point evaluation and osmometry. Polymer molecules of lower molecular weight or even low molecular weight soluble impurities contribute equally and enjoy equal status with polymer molecules of higher molecular weights in determining the colligative properties.

On the other hand, weight average molecular weight assumes importance in the context of various bulk properties of polymers, particularly the rheological and resistance properties. Softening/melting and hot deformation, melt – viscosity or melt – flow, tensile and compressive strength, elastic modulus and elongation at break, toughness and impact resistance and some other bulk properties of polymers are better appreciated on the basis of weight average molecular weight, keeping in mind, however, the influence of chemical nature of the repeat units, degree of branching and cross linking, thermal or thermomechanical history of the polymer sample, etc.

Number Average Molecular Weight

Number average molecular weight can be evaluated using dilute solution of a polymer making use of ebulliometric (boiling point elevation), cryoscopic (freezing point depression) and osmometric (membrane osmometry) measurements.Direct measurements of vapour pressure lowering of dilute polymer solution lack precision and mostly produce uncertain results. Vapour – phase osmometry, however, allows indirect exploitation of vapour pressure lowering of polymer solution at equilibrium as can be related through the Clapeyron equation and in this method, one measures a temperature difference that can be related to vapour pressure lowering. This difference in temperature is comparable to or of the same order of magnitude as those observed in cryoscopy and ebulliomtry. These methods require calibration with low molecular weight standards and they may produce reliable results for polymer molecular weights < 30,000. The working equations for ebulliometric, cryoscopic and osmometric measurements are as follows:

$$\lim_{c \to o} \frac{\Delta T_b}{c} = \frac{RT^2}{\rho \Delta H_v} \cdot \frac{1}{M} \qquad (7)$$

$$\lim_{c \to o} \frac{\Delta T_f}{c} = \frac{RT^2}{\rho \Delta H_f} \cdot \frac{1}{M} \qquad (8)$$

$$\lim_{c \to o} \frac{\pi}{c} = \frac{RT}{M} \qquad (9)$$

where, ΔT_b , ΔT_f , and π are boiling point elevation, freezing point depression and osmotic pressure, ρ is the density of the solvent, ΔH_v and ΔH_f are respectively the latent heat of vaporization and of fusion of the solvent per gram, c is the polymer (solute)

concentration in g/cm^3 and M is the solute molecular weight. Very low observed temperature differences (of the order of 10^{-3} ^{0}C) for low finite concentrations of a polymer of the molecular weight range of $\geq$ 20,000 and lack of development of equipments for ebulliometric and cryoscopic measurements have turned them unattractive and less useful. Vapour pressure lowering for low finite concentrations is also very low (of the order of 10^{-3} mm Hg) for such polymers. The osmotic method is in more wide use than other colligative techniques as because the osmotic response is of a magnitude that is easily observable and measurable, even though success of this method is contingent upon availability of prefect osmotic membranes.

Membrane Osmometry

Let us take the case of a dilute polymer solution of a low finite concentration separated from the pure solvent by a semipermeable membrane. The chemical potential of the solvent (μ_s) in solution is lees than that (μ_o) of pure solvent and therefore, to keep the system in equilibrium, the chemical potential of the solvent on the two sides of the membrane requires to be balanced and made equal. This is readily done by applying an excess pressure, π , called the osmotic pressure to the solution side to compensate for the difference in chemical potential. The equilibrium condition can thus be expressed as :

$$\mu_o - \mu_s = \Delta \mu_1 = -\pi \overline{V_1}$$

$$\text{Or,} \qquad RT \ln f_1 x_1 = -\pi \overline{V_1} \tag{10}$$

where, R is the universal gas constant, T, the absolute temperature, $\overline{V_1}$, the partial molar volume, f_1, the activity coefficient of the solvent in solution, and x_1, the solvent mole fraction; for a very dilute solution, $f_1 \rightarrow 1$ and $\overline{V_1}$ may be taken as equal to the molar volume V_1^0 of the pure solvent. Replacing solvent mole fraction x_1 by $(1 - x_2)$, where x_2 is the mole fraction of the (polymer) solute in solution, and expanding the logarithm factor, one obtains

$$\pi V_1^0 = RT \left(x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \text{------} \right) \tag{11}$$

If c is the concentration of the solute in gram per unit volume of the solution, then for a very low value of c and very high value of $\overline{M_n}$, x_2 is given by

$$x_2 = \frac{c / \overline{M}_n}{1/ V_1^0 + c / \overline{M}_n} \simeq \frac{V_1^0 c}{\overline{M}_n} \tag{12}$$

Combining equation (11) and (12), one obtains

$$\pi / c = \frac{RT}{\overline{M}_n} \left\{ 1 + \frac{1}{2} \left(\frac{V_1^0}{\overline{M}_n} \right) c + \frac{1}{3} \left(\frac{V_1^0}{\overline{M}_n} \right)^2 c^2 + \text{-----} \right\} \tag{13}$$

Polymer solutions largely deviate from ideality, thus rendering the value of f_1 less than unity; even at a very low finite concentration at which precision osmometric measurement is possible. The real coefficients of concentration terms in equation (13) are somewhat higher than those shown in the equation. Even then, the π / c term may be expressed as a power series in c using empirical coefficients :

$$\pi / c = RT\ (A_1 + A_2 c + A_3 c^2 + \text{-----}) \tag{14}$$

Or alternatively,

$$\pi / c = \frac{RT}{\overline{M}_n}\ (1 + \Gamma_2 c + \Gamma_3 c^2 + \text{-----}) \tag{15}$$

where, $\Gamma_2 = A_2 / A_1$, $\Gamma_3 = A_3 / A_1$ and so on, and $A_1 = (1 / \overline{M}_n)$

The coefficient A_2, A_3 etc. are referred to as second, third, etc. virial coefficients. For most cases and for all practical purposes, the term in c^2 and those in higher powers of c may be neglected. Thus, π / c is measured as a function of c in unit of g/dl at a given temperature and plotted graphically; extrapolation of the low concentration range linear plot with a positive slope to $c \rightarrow o$ gives an intercept that equals the parameter $(RT / \overline{M}_n)$.

Alternatively, (π/RTc) may be graphically plotted against c, fig. 1, and direct evaluation of the number average molecular weight $\overline{M}_n$, then readily follows from the measure of the intercept. The plots are linear over the low concentration region (very dilute solutions) in each case of (a) and (b) in fig. 1. The slope of each linear portion of the plot may be used to calculate the second virial coefficient. In good solvents and over relatively high concentration range, the plots may turn concave upward, more so, for the plot as in part (a) of fig.1.

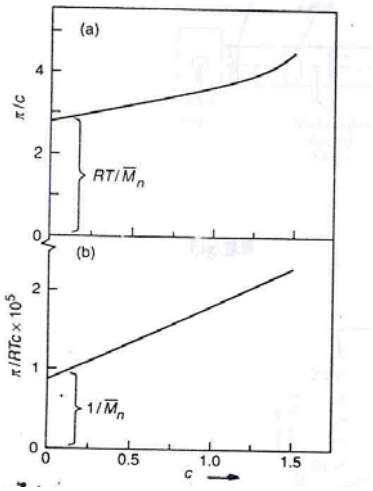


Fig. 1: Plots of π / c vs. c and π /RTc vs. c for Determination of $\overline{M}_n$.
(Courtesy: Tata McGraw –Hill, New Delhi)

The osmotic pressure equation may be modified to the form

$$\frac{\pi}{RTc} = \frac{1}{M_2} + \frac{\rho_1}{M_1 \rho_2^2}\left(\frac{1}{2} - \chi_1\right) c + \text{-----} \qquad (16)$$

where subscripts 1 and 2 stand for solvent and polymer solute respectively, ρ for the density parameter, and χ_1 is the polymer – solvent interaction constant according to the Flory – Huggins theory. Equation (16) permits plot of (π / RTc) vs c where the intercept gives the polymer molecular weight (number overage) and the value of the slope may be used to calculate the value of Flory – Huggins polymer – solvent interaction constant χ_1.

Both slope and curvature are zero at θ temperature. The membrane osmometry is based on the principle described in fig. 2. The membrane used is of critical importance. It should permit the small solvent molecules to permeate through but would be non permeable to even the smallest macromolecules present in the test polymer sample. So, the membrane is better called semipermeable. All measurements in a specific case must necessarily be made at a specified and constant temperature, preferably using the same semipermeable membrane too. The thermodynamic drive to reach equilibrium causes entry of (more) solvent molecules from the solvent chamber to the solution side, thereby causing the liquid level in the solution side to rise till the hydrostatic pressure on the membrane on the solution side balances the osmotic pressure on the same in the solvent side. Use of a narrow capillary over each of the solution and solvent chambers makes it easy to follow the rise in liquid height on the solution side and finally to measure the difference in liquid heights on the two sides on attainment of the equilibrium. The difference in liquid levels at equilibrium is used to calculate the osmotic pressure.

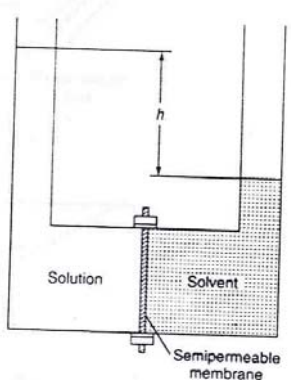


Fig. 2: Operating Principle and Schematic Presentation of a Membrane Osmometer
(Courtesy: Tata McGraw –Hill, New Delhi)

Membranes based on cellulose such as regenerated cellulose (gel cellophane) are most widely used. Other suitable membrane materials are collodion (nitrocellulose, 11 – 13% N_2) and denitrated collodion, poly(vinyl alcohol), poly(vinyl butyral), etc. Osmometer cell and assembly according to Zimm and Meyerson, and shown in fig. 3, is more popular for its simplicity. Time periods required for attainment of equilibrium in classical osmometers using dilute polymer solutions range on the average between 10 – 25 h.

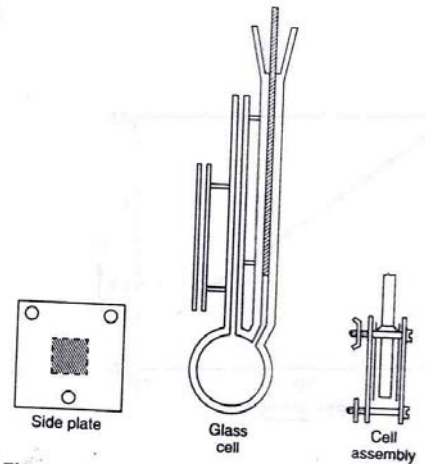


Fig. 3: Sections and Parts of a Zimm – Meyerson Osmometer
(Courtesy: Tata McGraw –Hill, New Delhi)

Different models of high–speed osmometers have been developed. Most of them feature a closed solvent chamber gadgeted with a sensitive pressure-sensing device without the use of a capillary. Such equipments use suitable photoelectric or other devices for sensing pressure or pressure difference employing a servomechanism or else, using a strain gauge. The high-speed equipments permit attainment of equilibrium within 5 min.

Weight Average Molecular Weight: Light Scattering By Polymer Solutions

The subject of scattering of light by gaseous systems (Rayleigh scattering) or by colloidal system suspended in a liquid medium (Tyndal scattering) has been widely studied. The intensity of scattered light depends on the polarizability of the molecules or particles compared with that of the surrounding medium in which they exist, i.e. dissolved, mixed or suspended. It further depends on the molecular or particle size and on their concentration. If the homogeneous mixture, solution or dispersion is sufficiently dilute, the intensity of the scattered light is equal to the sum of the contributions from the individual molecules / particles, each being unaffected by the others in the medium.

Let us now consider a beam of light passing through an optically inhomogeneous medium of path length, l is being scattered in all directions; The intensity of the transmitted beam I decreases exponentially and is related to that I_o of the incident beam and the relationship may be expressed as,

$$I = I_o \, e^{-\tau l} \tag{17}$$

Here, the parameter τ is referred to as turbidity. Let us take the case of a polymer solution. Thermal agitation of the molecules in solution causes instantaneous local fluctuation of density and concentration. For different polarizabilities of solute and solvent, the intensity of light scattered by a tiny volume element also varies with such fluctuations arbitrarily on a continuous basis. The effect arising from density fluctuations can be accounted for by subtracting the intensity of the light scattered by the pure solvent from that scattered by the solution.

The work expended to produce a given concentration fluctuation is related directly to the free energy of dilution, ΔG_1. So, the scattered light intensity can be used to measure the thermodynamic properties. The scattered light intensity from a solution is commonly expressed in terms of its turbidity τ, which is the fraction by which the scattered beam is reduced over 1 cm path length of solution according to equation (17). For polymer molecules of size smaller than the wave length of light used, τ is expressed as :

$$\tau = \frac{32\ \pi^3\ k\,T\,n^2\,c\,(\partial n / \partial c)^2\ \overline{V_1}}{3\,\lambda^4\,(-\ \partial\,\Delta G_1 / \partial c)} \qquad (18)$$

Here, k is Boltzmann's constant, n the refractive index of the medium, $(\partial n / \partial c)$, the change in refractive index with concentration, c, λ, the wave length of the incident beam and ΔG_1 signifies the difference between the molar free energy of the pure solvent and partial molar free energy of the solvent in solution of concentration c. Now, having the relation $\Delta G_1 = -\pi\,\overline{V_1}$ based on equation (10), where π is the osmotic pressure and using the relation between π and molecular weight, one may logically write.

$$-\ (\partial\,\Delta G_1 / \partial c) = \frac{RT\,\overline{V_1}}{M}\ \ (1 + \Gamma_2 c + ...) \qquad (19)$$

Combining equations (18) and (19), one may derive

$$H\,(c / \tau) = (1/M)\ \ (1 + \Gamma_2 c + ...) \qquad (20)$$

where, $H = (32\ \pi^3\ n^2 / 3\,\lambda^4\,N_o)\,(\partial n / \partial c)^2$, is a constant for a given solute – solvent system. and $N_o = R/k$ is the Arogadro's number. If τ is determined as a function of c and $H(c / \tau)$ is plotted against c, then the intercept on the $H(c / \tau)$ axis as obtained on extrapolation of the straight line plot to zero concentration or more appropriately to infinite dilution, fig. 4, permits ready calculation of the molecular weight M, which for a polydisperse polymer solute, can be shown to be the weight average molecular weight M_w.

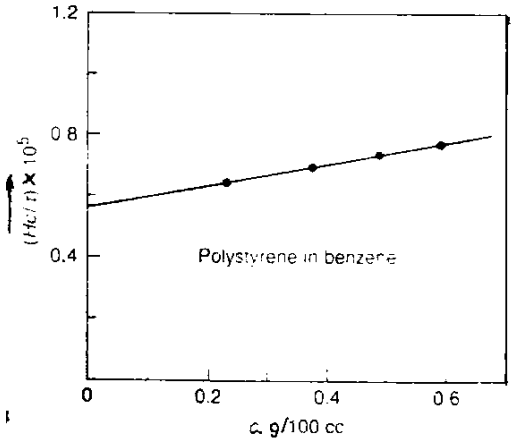


Fig. 4 : A Typical Linear Plot of Hc/τ vs. c for Determination of $\overline{M_w}$
(Courtesy: Tata McGraw –Hill, New Delhi)

Light scattering photometers employ photoelectric technique for measurements of scattering data. The measurement principle and approach is a simple one and is outlined in fig.5. It is absolutely important and necessary that the measuring chamber, and the solvent and solutions are kept dirt or dust free. The specified scattering glass – cell is placed on the fixed center – table and centred on the axis of rotation of the receiver photomultiplier tube assembly; this assembly can be rotated and fixed at desired angular positions for measurements of the scattered light. Besides the measurements of intensities of incident and scattered light, i.e. the turbidity. τ , it is necessary to determine the refractive index n of solvent and the parameter $(\partial n / \partial c)$ using a differential refractometer. The choice of solvent is also important. The difference in the refractive index between the polymer and the solvent should be as large as possible. A solvent of low second virial coefficient makes a more precise evaluation of $\overline{M}_w$ possible by the usual method of extrapolation to infinite dilution condition, i.e. to zero concentration. Molecular weights ranging from 10,000 to 10,000,000 are measurable by this technique.

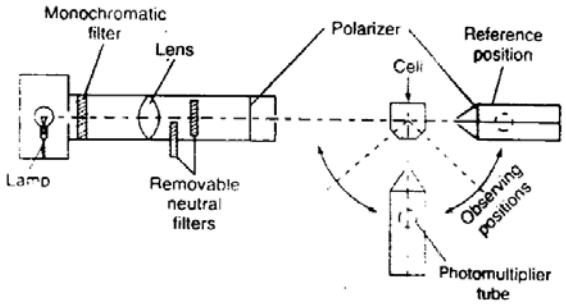


Fig. 5: Operating Line and Principle of Light Scattering Photometer
(Courtesy: Tata McGraw –Hill, New Delhi)

Assessment of Shape of Polymer Molecules

For polymer molecules much smaller than the wave length (λ) of the incident light, the scatterings in the forward and backward directions measured at two angles symmetrical about 90^0 (say 45^0 and 135^0) are not appreciably different. But for particles larger than about a tenth of the wavelength of light, the scattered light intensity follows a lowering trend from front to rear. The intensity ratio $(i_{45^\circ} / i_{135^\circ})$, known as dissymmetry ($Z$) of light scattering is unity for small particles and its value increases with increase in size of homogeneously mixed, dispersed or dissolved particles. Evaluation of the dissymmetry may be advantageously used to estimate particle size, which is the effective expanse of the particle. If the particle weight is also determined or known, then the measure of dissymmetry gives an idea about the shape of the particles as to whether they are characteristically spherical, disc-like, rod-like or random coils. There are, however, some intrinsic limitations to this approach of particle shape determination.

Methods of average molecular weight determination of a given polymer sample by membrane osmometry (giving $\overline{M}_n$) and light scattering (giving $\overline{M}_w$) are viewed as absolute methods, and the ratio M_w / M_n can then be used to get an idea about the distribution ratio or poly dispersity index of the polymer studied.

Viscosity Average Molecular Weight

The viscosity of a polymer solution (η) is higher than that (η_o) of the pure solvent at a specified temperature and the increase in medium viscosity on dissolving the polymer in the solvent is a function of both molecular weight and concentration of the polymer solute. The solution viscosity can be measured easily; it however, falls far short of giving a direct and absolute value of polymer molecular weight.

Despite this shortcoming, viscometry has emerged as a useful and simple technique in the context of having a measure of polymer molecular weight. If the polymer solution is very dilute and as a result, the change in density due to the dissolved polymer is negligible, then the viscosities of the solvent and the solution at a given temperature would be proportional to their flow times in a given capillary viscometer such that the relative viscosity, η_r expressed by the ratio, (η / η_o) would be given by the flow time ratio (t / t_o), where t_o is the flow time of a given volume of the solvent and t is the flow time of the same volume of solution respectively. The parameter called specific viscosity, η_{sp} as defined by $\eta_{sp} = (\eta - \eta_o) / \eta_o = (t - t_o) / t_o$ as well as the relative viscosity (η_r) are dimensionless.

If the solute polymer molecules do not interfere with one another during flow through the fine capillary of the viscometer, then the increase in viscosity due to the presence of the dissolved polymer molecules is proportional to their concentration and the parameter η_{sp} / c, called the reduced viscosity would be theoretically expected to be a constant. In reality, however, for most polymer – solvent systems, η_{sp} / c is generally found to increase with increase in the value of c, as in fig. 6. For dilute polymer solutions, a plot of η_{sp} / c vs. c is usually a straight line with a positive slope. The viscometric parameter called the intrinsic viscosity or the limiting viscosity number, $[\eta]$ for a given polymer – solvent system at a given temperature is given by the intercept of the linear plot of η_{sp} / c vs. c i.e. by extrapolation of the plot (fig. 6) to a condition of zero concentration, or more precisely to infinite dilution condition and the viscosity average molecular weight (M_v) is given by the semi empirical Mark – Houwink equation :

$$Lt\,.\,c \rightarrow o\,, \quad \eta_{sp} / c = [\eta] = K \overline{M}_v^{\,a} \tag{21}$$

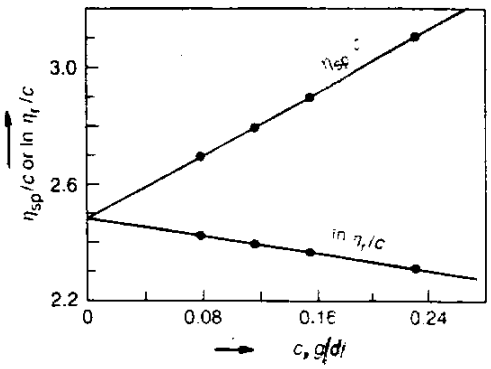


Fig. 6 : Viscometric Plots (η_{sp} / c) vs. c and $(ln\ \eta_r / c)$ vs. c
(Courtesy: Tata McGraw –Hill, New Delhi)

where K and a are known as Mark Houwink constants for a particular polymer – solvent system at the given temperature. η_{sp} / c at finite concentration may be expressed as a function of $[\eta]$ and the relevant expression is known as Huggins' equation.

$$(\eta_{sp} / c) = [\eta] + k_1 [\eta]^2 c \qquad (22)$$

Another useful equation known as Kraemer's equation runs as follows:

$$(\ln \eta_r)/ c = [\eta] + k_2 [\eta]^2 c \qquad (23)$$

The term $(\ln \eta_r)/ c$ is commonly referred to as the inherent viscosity. The reduced viscosity, inherent viscosity and intrinsic viscosity are commonly expressed in the unit of reciprocal concentration, i.e. decilitre per gram (dl / g), c being commonly expressed as g / dl or g/*100* cc. The constants k_1 and k_2 of equations (22) and 23) are known as Huggins' constant and Kraemer's constant respectively. For most cases k_2 is negative and it is the general experience that $k_1 – k_2 = 0.5$. The slope of each plot, left hand side vs. c for each of Huggins' equation and Kraemer's equation is proportional to $[\eta]^2$ and the two plots made using common ordinate and abscissa would extrapolate to a common point on the ordinate. One can thus get a precise $[\eta]$ value based on such duel plots as in fig. 6.

Each of the above two equations provides a basis for determination of polymer molecular weight from viscometric measurements. The value of $\underline{M}_v$ thus obtained is not an absolute value in view of incomplete interpretations of K and a values (equation (21)).

One has to determine the K and a values by measuring the $[\eta]$ values of monodisperse polymer samples whose molecular weights have been obtained from, one of the absolute methods such as osmometry (giving $\overline{M}_n$) and light scattering (giving $\overline{M}_w$) and making use of respective plot of log $[\eta]$ vs. log M, which is a straight line plot. The value of the constant, a (exponent of molecular weight in equation (21)) is obtained from the slope of the plot, fig. 7. The value of the exponent a usually varies between 0.5 and 0.8. It does not fall below 0.5 normally and it may exceed 0.8 in rare cases, particularly for solutions of polyelectrolytes bearing no added salt.

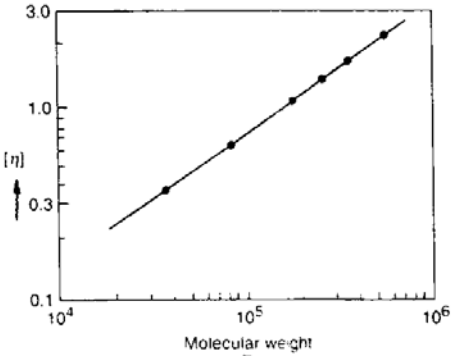


Fig. 7 : Logarithmic Plot of $[\eta]$ vs. M (Schematic).
(Courtesy: Tata McGraw –Hill, New Delhi)

K and a are best understood for nearly all systems if $[\eta]$ is determined at the theta (θ) temperature, when $a = 0.5$; K depends on the measuring temperature while remaining independent of solvent, keeping in mind of course that the solvent fixes the temperature of measurement. At the θ temperature, the change in solvent chemical potential due to interaction with the segments of the polymer solute is zero, and the deviations from ideality just vanish. So, the free energy of interactions of solute segments within a volume element is zero. θ temperature is in fact the lowest temperature for complete miscibility of the solute in the poor solvent used at the theoretical limit of infinite molecular weight. The ideality is attained at $T = \theta$ in view of the position that chain molecular dimensions are unperturbed by intramolecular interactions.

General Expression for Viscosity Average Molecular Weight

At infinite dilution ($c \rightarrow o$), the polymer molecules in solution contribute to viscosity discretely without mutual interference. Solubilization of a polymer sample is preceded by a large amount of swelling if left undisturbed and the swelling degree is higher in a better solvent. Similarly, the intrinsic viscosity is also higher in a good solvent than in a poor solvent. What all these would mean is that in a better solvent, as the polymer chain molecules go into solution, a unit mass of the same expands more to give a higher hydrodynamic volume.

Let there be a heterogeneous (polydisperse) polymer in dilute solution of concentration c considered to behave ideally in that the individual molecules contribute to viscosity enhancement independently of one another. In that event, if $(\eta_{sp})_i$ be the specific viscosity contribution due to the species of size i, then one may express the overall specific viscosity η_{sp} as

$$\eta_{sp} = \Sigma\, (\eta_{sp})_i \tag{24}$$

Considering M_i and c_i as the molecular weight and concentration of the species of size i and in view of the ideal specific viscosity component $(\eta_{sp})_i = K M_i^{\,a} c_i$, it is further possible to write.

$$\eta_{sp} = K \Sigma\, M_i^{\,a} c_i \tag{25}$$

and so,

$$(\eta_{sp}/c) = [\eta] = (K \Sigma\, M_i^{\,a} c_i)/c \tag{26}$$

where, $c = \Sigma\, c_i$ stands for overall concentration taking all polymer species into consideration. Further taking $c = \Sigma\, c_i = \Sigma\, N_i\, M_i$, and considering the (Mark Houwink) equation (21), one may have :

$$[\eta] = K \frac{\Sigma\, N_i\, M_i^{(1+a)}}{\Sigma\, N_i\, M_i} = K \overline{M}_v^{\,a} \tag{27}$$

such that,

$$\overline{M}_v = \left\{ \frac{\Sigma\, N_i\, M_i^{(1+a)}}{\Sigma\, N_i\, M_i} \right\}^{1/a} \tag{28}$$

Clearly, one may see that for the limiting case when $a = 1$, $\overline{M}_v = \overline{M}_w$

The viscometric studies as a means of molecular characterization of polymers are recognized to be very simple in respect of experimental approach and apparatus needed and hence, widely practiced. Dilute solution viscosity is very easily measured using capillary viscometers of the Ostwald type or the Ubbelohde type, fig. 8. The Ubbelohde type is a suspended level dilution viscometer having the advantage that the flow time measured is independent of the volume of liquid (for solvent and solutions) in the viscometer; measurements at a series of concentrations can be conveniently done by successive dilution within the viscometer itself. All flow time measurements for solvent and solutions of different concentration or dilution are carried out in a thermostated bath regulated within $\pm$ 0.1 ^{0}C. The flow time data are then plotted graphically using equation (22) and/or (23) and then extrapolated to infinite dilution ($c \rightarrow o$) to obtain the value of $[\eta]$ or the intrinsic viscosity, as has been described earlier in this chapter. $\overline{M}_v$ is then calculated out using the Mark – Houwink equation and taking help of appropriate K and a values from the literature, if available, or from an independent determination as described earlier.

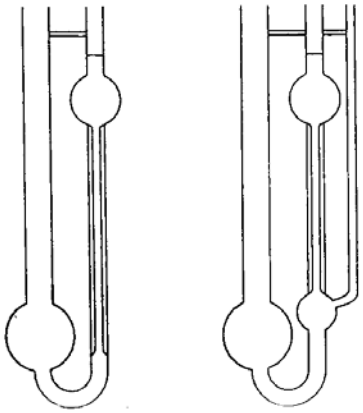


Fig. 8 : (a) Ostwald – type and (b) Ubbelohde – type Capillary Viscometers
(Courtesy: Tata McGraw –Hill, New Delhi)

Z-Average Molecular Weight ($\overline{M}_z$)

The Z – average molecular weight, $\overline{M}_z$ is expressed as :

$$\overline{M}_z = \frac{\Sigma N_i M_i^{\,3}}{\Sigma N_i M_i^{\,2}} \qquad (29)$$

For a given molecular weight distribution, the various average molecular weights come in the order $\overline{M}_n < \overline{M}_v \leq \overline{M}_w < \overline{M}_z$. The Z-average molecular weight is commonly measured by sedimentation equilibrium method using an ultracentrifuge.

The ultra centrifugation techniques are somewhat complicated and much less commonly employed for molecular weight measurements of synthetic polymers, even though, they are more commonly used for characterizing biological polymers such as proteins and enzymes.

Employing a low speed of rotation with the polymer solution in the cell held in position and operating the ultracentrifuge under constant conditions for a long period avoiding convection related disturbances within the cell, a state of equilibrium is reached. Under equilibrium condition, the polymer fractions get distributed in the cell according to size or molecular weight distribution. The force of sedimentation on a molecular species in solution is just balanced by its tendency to diffuse out. For dilute solutions closely approaching ideal behaviour and for a monodisperse polymer, the molecular weight M is expressed as

$$M = \frac{2\,RT\,ln\,(c_2 / c_1)}{(1 - v\,\rho)\,\omega^2\,(r_2^2 - r_1^2)} \qquad (30)$$

where c_1 and c_2 are the concentration at two points corresponding to distances r_1 and r_2 in the cell and ω is the angular velocity of rotation, v, the partial specific volume of the polymer and ρ, the density of the medium. The solvent chosen should be preferably a poor solvent having a density far different from that of the polymer so as to facilitate sedimentation; the solvent and polymer must also differ in refractive index so as to facilitate easy measurement. For a poly disperse polymer, different approaches for measuring the concentration as a function of r yield different molecular weight averages (M_w or M_z). Measurements based on refractive index yield M_z. Preparative ultracentrifugation is utilized in fractionating polymer samples and in separating them from easily sedimented contaminants.

General Requirement for Extrapolation to Infinite Dilution

Solubility and solution features of polymers are quite complicated indeed, much as a consequence of their big sizes and chain – like structures and significant interplay of intrachain and/or interchain entanglements and also complex solute – solvent interactions contributing to retardation of flow behaviours of its molecules not only under melt conditions, but also in dilute solutions. High solution viscosity even for very dilute solutions, compared to the solvent viscosity is a unique feature of polymer material systems.

A simple theory conceives a polymer chain molecule as an assemblage of a large number of tiny spheres or dots (chain repeat units) on a lattice work, which are sequentially joined or tied together by flexible (covalent chemical) bonds of equal lengths. A polymer molecular chain may assume certain specific arrangements on the lattice sites out of many statistically possible arrangements. For ideal solution behaviour, there should be no contact or interaction between segments of different chains, which can be nearly approached and possibly attained only in situations of infinite dilution. But actual measurements of solution properties at such vanishing concentrations with any degree of certainty are simply not practically possible.

This position thus necessitates extrapolation of measured properties at finite concentrations to infinite dilution meaning $c \rightarrow o$. For actual measurements at finite concentrations, howsoever dilute, the interaction between the chain molecules or

intermolecular chain segments can not be altogether ignored due to short range or long range entanglements of the long, flexible molecular chains.

Polymer Fractionation and Molecular Weight Distribution

In a poor solvent or more precisely in a non-solvent, a polymer will have retarded, restricted or poor solubility. On dropwise addition of a non – solvent to a dilute solution of a polymer in a good solvent under stirring conditions, some amount of the polymer will be thrown out of solution with the development of some turbidity and then causing a precipitate to appear at a certain point. It is the common experience that polymer molecules of the highest molecular weight or molecular weight range get separated and precipitated first. On separation of the first fraction of polymer precipitate, further dropwise addition of the non – solvent in a similar manner throws out at a subsequent point a second fraction of polymer having the next higher molecular weight or molecular weight range. In this manner one may obtain and isolate several or a large number of successive fractions of polymer as precipitate coming in decreasing order of molecular weight or molecular weight range.

The separation into fractions may be made narrower or sharper if after adding the requisite volume of the non – solvent for development of turbidity, the mixture is slightly warmed to render the system just homogeneous again and then the system is slowly cooled to the working temperature to allow the precipitate to reappear in the mixture. The process is repeated to isolate successive fractions of decreasing molecular weight or molecular weight range.

Each of the successive fractions is carefully isolated, washed with excess non – solvent, dried and weighed, and its molecular weight determined by one of the techniques discussed in this chapter. It is then possible to draw an integral molecular weight distribution curve as given in fig. 9; the curve exhibits a plot of cumulative weight percent against molecular weight. The integral distribution curve may be differentiated at selected points of molecular weight to obtain a differential molecular weight distribution curve as shown in fig. 10. The relative positions of $\overline{M}_n$, $\overline{M}_v$, $\overline{M}_w$, $\overline{M}_z$ are shown on this curve.

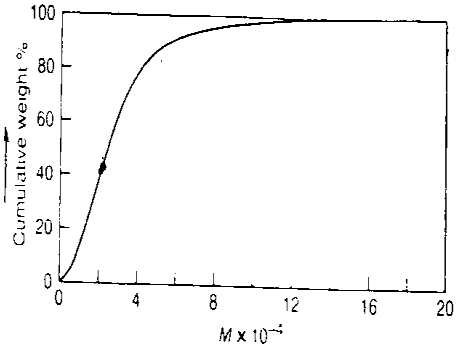


Fig..9: A Typical Integral Molecular Weight (M) Distribution Curve

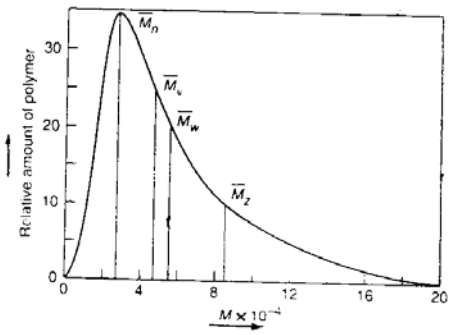


Fig. 10 :A Typical Differential Molecular Weight Distribution Curve.

(Courtesy: Tata McGraw –Hill, New Delhi)

It is important to recognize that the above approach separates the various molecular species primarily on the basis of their solubility characteristics, and not really on the basis of their molecular weight or size. For a given polymer, however, the solubility characteristics are dependent not only on chain length, but also on branching including branch nature and branch frequency or degree of branching, cross linking, end groups present and also on changes in chemical structure on storage and aging.

Gel Permeation Chromatography

In a chromatographic separation process the solute is transferred between two phases – one stationary and the other moving; the transfer is allowed to take place in a long packed column (column chromatography) or on a thin sheet of paper (paper chromatography). In gel permeation chromatography, the same solvent or liquid is allowed to form the two phases in a column packed with a micro-porous gel (cross linked polymer), such that the stationary phase is made up of the part of the solvent that is inside the porous gel particles, while the mobile phase is made up of the flowing solvent part remaining outside the gel particles.

The driving force behind the transfer of solute polymer molecules between the two phases is the diffusional drift that causes a difference in concentration of the solute in the two phases; the transfer process is, however, largely restricted by the solute (polymer) molecules capacity to penetrate or permeate through the pore structure of the gel. The gels commonly used are hard, incompressible polymers based on micro-porous polystyrene (having been cross linked with use of selected dose of divinyl benzene during polymerization of styrene) prepared by suspension polymerization technique. Another gel material in common use is fine micro-porous glass bead. The pores in the gels used are nearly of the size comparable with the size of the polymer molecules.

A known amount of polymer dissolved in a known volume of solvent is injected into a solvent stream flowing down the gel packed column. The solute (polymer) molecules flow past the porous beads of the packed gel mass and at the same time diffuse into their inner pore structures according to the size distribution of the solute polymer molecules and pore–size distribution of the gel mass. A fractionation of the polymer mass is thereby achieved consequently, as the entry of the larger molecules into the pores of the gel is more restricted or may be completely hindered due to relatively low pore sizes. They have the better chance of flowing round the gel beads and finally flowing out of the gel column faster, spending less time inside the gel. The smaller polymer molecules, however, follow just the opposite trend as they find easy entry into the gel pores and spend longer times inside the gel. The largest among the (polymer) solute molecules emerge first while the smallest of them emerge last from the gel column. This technique, commonly known as the "gel permeation chromatography" (GPC), allows fractionation of polymer molecules according to their size. For an appropriately selected gel, the smallest of the solute (polymer) molecules find most of the stationary phase most readily accessible.

The method requires an initial empirical calibration of a column or a set of columns packed with gels of graded pore sizes to yield a calibration curve such as the one shown

in fig. 11, that relates the molecular size parameter *[η] M* (see equation (31)) and the retention volume by means of which a plot of amount of solute versus retention volume of a test polymer known as its chromatogram, fig. 12, can be converted into a molecular size distribution curve from which again a molecular weight distribution curve can be drawn.

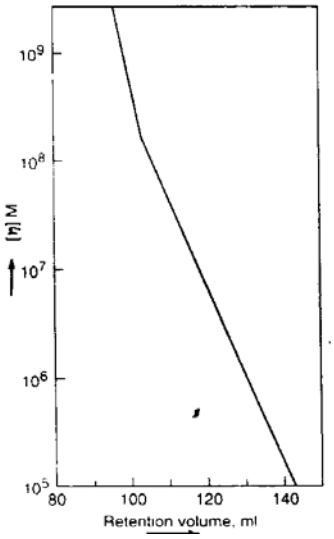


Fig.11:Plot of *[η] M* vs. Retention Volume Giving the Calibration Curve for Gel Permeation Chromatography (*GPC*)

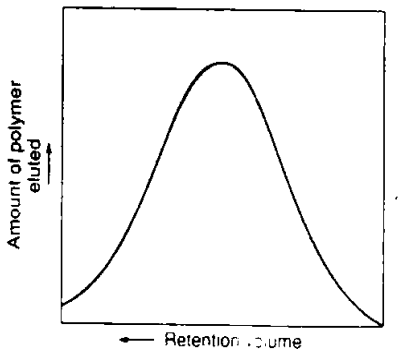


Fig.12:A Typical *GPC* Chromatogram Showing a Plot of Amount of Polymer Eluted vs. Retention Volume

(Courtesy: Tata McGraw –Hill, New Delhi)

The GPC is a fast and neat technique for both preparative and analytical work applicable to a wide variety of linear and branched polymer systems ranging from low to very high molecular weights. The method requires a sample size of only a few milligrams and the analysis is complete in a time scale of 2 – 5 h.

Gel permeation chromatography allows separation of molecules in a given polymer sample according to their molecular sizes or hydrodynamic volumes. Any extraneous physico – chemical factors that measurably perturb the hydrodynamic volumes of the dissolved polymer molecules and also infuse change in their rate of elution would complicate measurements and interpretations and may also lead to erroneous, inconclusive results. Non-polar polymers bearing limited number of charged side groups (e.g. $-COO^-$, $-SO_3^-$, etc.) such as the ionomers or even those having charged end groups, are prone to be absorbed on the surface of the microgels as they pass through the columns, and thereby offer enhanced resistance to the normal elution process and in that case, the size exclusion basis of separation by GPC loses its relevance. Such a phenomenon would lead to larger elution volumes and hence to relatively low molecular weights than actual. Moreover, the ion – containing polymers have a tendency to agglomerate in solvents of low polarity, and in that event, fractionation and molecular weight determination based on separation according to molecular size in solution or hydrodynamic volume are largely affected. Analysis by GPC may be reliable if in such cases the charged groups are turned nonionic or by selecting an eluent solvent that would

prevent adsorptive anchorage of polymers on the surface of gel particles or beads and would prevent macromolecular aggregation. A good knowledge about the history of the test polymer including its method and condition of synthesis and its microstructure, particularly in respect of presence of charged groups would be helpful in planning solvent selection for separation and fractionation employing GPC. Modern microprocessor controlled GPC equipments provide printout data about the polydispersity index or distribution ratio M_w / M_n.

Molecular Size Parameter

The molecular size parameter given by the expression $[\eta] M$ is conveniently used in the GPC calibration plot, fig. 11. The intrinsic viscosity term $[\eta]$ of a polymer solution is known to be proportional to the effective hydrodynamic volume of its molecules in solution, $[(\overline{r}^2)^{1/2}]^3$ divided by the molecular weight, i.e.

$$[\eta] = \Phi \frac{(\overline{r}^2)^{3/2}}{M} \tag{31}$$

where the value of the proportionality constant Φ, commonly referred to as the Flory – Fox constant is reported to vary between 2.0×10^{21} and 2.8×10^{21}. The linear parameter $\overline{r}$ represents the actual end to end distance of the polymer molecule in solution. Equation (31) may be modified simply by replacing $(\overline{r}^2)^{1/2}$ by $\alpha (\overline{r}_o^2)^{1/2}$ where α having a value > 1, is known as the expansion factor and $(\overline{r}_o^2)^{1/2}$ is the unperturbed end – to – end distance (under ideal situation) and $K = \Phi (\overline{r}_o^2 / M)^{3/2}$ is a constant for a given polymer, independent of solvent

$$[\eta] = \Phi \frac{(\overline{r}_o^2)^{3/2} \alpha^3}{M} = \Phi \left(\frac{\overline{r}_o^2}{M} \right)^{3/2} . M^{1/2} . \alpha^3 = K M^{1/2} . \alpha^3 \tag{32}$$

and molecular weight. At θ temperature or under θ condition, $\alpha = 1$, so,

$$[\eta]_\theta = K M^{1/2} \tag{33}$$

This expression allows estimation of or getting to a measure of the unperturbed dimension $(\overline{r}_o^2)^{1/2}$ of the polymer chain. The value of α is dependent on the nature of the solvent used. α has a relatively high value for use of a thermodynamically 'good' solvent and in the limiting case of $T = \theta$, $\alpha = 1$. In any solution form, a polymer molecule generally exists as a randomly coiling mass having conformations that occupy many times the volume of all its segments. However, in a poor solvent characterized by poor solute – solvent interactions, the coils remain relatively contracted, while in good solvents they are relatively expanded or extended through interplay of different degrees of solute – solvent interaction, leading to a relatively large value for the expansion factor α.

Polymer End Groups and End Group Analysis

Molecular characterization of polymers, particularly linear polymers, by end group count assumes importance, particularly for low polymers, and the relevant analytical data may be used for the determination of polymer molecular weight, which would invariably be $\overline{M}_n$.

Use of chemical methods, mostly titrimetric, for selected, suitable linear polymer systems (e.g. polyesters or polyamides bearing – *COOH* and – *OH* or – *COOH* and – NH_2 end group respectively) requires that the polymer is free from traces of impurities and that the structure of the polymer based on prior considerations be such as to bear a known number of chemically determinable specified functional groups per molecule. For a precisely linear polymer, quantitative determination of all end groups present (each polymer molecule having two end groups, one at each end) would give a direct measure of the number of polymer molecules in a given mass of the polymer, and hence, a measure of the average molecular weight ($\overline{M}_n$) then obviously follows. Chemical methods of end group determination are generally reliable for molecular weight $\leq$ 25,000, and they are therefore more suited to characterize thermoplastic condensation (step – growth) polymers, where $\overline{M}_n$ is seldom >25,000.

Selected / suitable chemical methods may be applicable for molecular characterization and end group estimation of vinyl polymers, if formed in the presence of a calculated dose of a strong chain transfer agent, such as a mercaptan, carbon tetrachloride or hydrogen sulfide[1], etc. If the polymer chain length is overwhelmingly determined by chain transfer, the number of polymer molecules may be related to the fragments of the chain transfer agent incorporated in the polymer chain end as determined, taking recourse to chemical analysis. Often, such incidence of a chain transfer reaction would create two chain ends (one consequent to the interception of the propagation process by the chain transfer reaction and the other consequent to reinitiation that follows).

Alternatively, molecular weight of a vinyl polymer may at times be calculated from a count of the initiator fragments occurring in the polymer, provided the initiation and termination mechanisms are known with good degree of certainty and that chain transfer is unimportant.

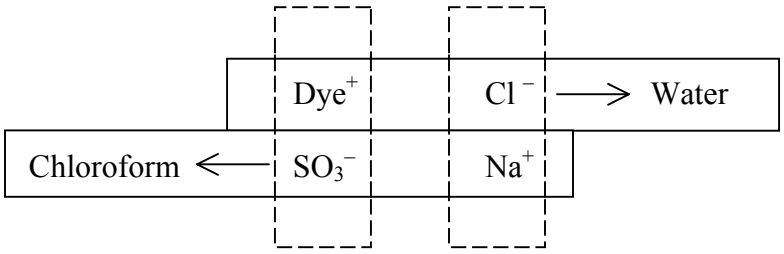
Chemical methods as tools of molecular weight determination are only selectively applicable in systems where end groups are easily characterizable chemically, and they become insufficiently sensitive when the molecular weight is large. Spurious sources of end groups admitted into the system inadvartently and not taken into account in the assumed reaction mechanism become more and more consequential as the molecular weight increases; with increase in molecular weight the number of actual end groups ultimately comes down to a point where their quantitative determination turns very difficult if not impractical and uncertain.

Some worthy and relevant physical methods of end group detection and estimation are : tracer technique, infra red absorption spectroscopy and ultra violet absorption

spectroscopy. Even though the suitability of physical methods has been widely advocated, some uncertainty about these methods can not be ruled out, especially in respect of their quantitative aspects because of the end group content of polymers being very low and because of odd difficulties in removing adsorbed impurities from them. Another difficulty with the physical methods arises when more than one type of end groups exist and when imperfections are given rise to in the polymer chain structure during polymerization due to branching, chain transfer and uncontrolled thermal chain degradation. Sensitive colorimetric methods for end group analysis appear to be of some importanec.

Palit, Ghosh and Coworkers developed two sensitive dye techniques viz., (i) the biphasic dye partition technique and (ii) the monophasic dye interaction technique; they found wide applicability for simple and rapid detection of polymer end groups and their quantitative estimation in favourable cases.

(i) The Dye Partition Technique: When chloroform or benzene solution of a specified amount of a polymer containing an ionizable end group (basic or acidic) is shaken with aqueous solution of a suitable ionic dye (acidic or basic) taken in equal volume proportion, the dye gets partitioned into the organic layer (say, chloroform layer) thereby rendering the organic layer coloured with an intensity proportional to the concentration of the appropriate ionic end group present; with corresponding polymer having no specified ionizable end group or with the simple organic solvent containing no dissolved polymer, i.e. for the control experiment, the non-aqueous phase remains colourless, indicating that adsorption of the water soluble dye by the polymer or the organic solvent is practically negligible and that when only a polymer with appropriate concentration of specified ionic end groups is present, the dye is proportionately partitioned to the organic layer. End groups that have been studied and analyzed by the dye techniques are : – *COOH,* – *OH* (transformed to – *COOH* by phthalation in the presence of phthalic anhydride in pyridine medium or to – OSO_3H group by chlorosulfonation using $ClSO_3H$ in pyridine medium and then on purification in each case by several reprecipitations and drying before testing), – NH_2 and halogen atom, end groups (– *Cl,* – *Br,* transformed to quaternary (pyridinium) halide end groups by thermally treating them with pyridine at 95^0C for 24 h and subsequently purifying the treated polymer by repeated precipitations and drying), and – OSO_3^- , – SO_3^- and related anionic sulfoxy end groups. The principle of dye partition may be schematically shown[1] as follows :



(34)

(ii) The Dye Interaction Technique : This technique is employed in homogeneous benzene solution. Some basic (rhodamines, crystal violet etc.) and acid (eosin, crythrosin, etc.) dyes when extracted with benzene from their aqueous solutions (at pH 10 – 12 and pH 4 – 5 respectively) yield highly sensitive coloured benzene extracts which change colour when treated with dilute benzene solution of polymers containing ionic (acidic or basic) (end) groups.

Colorimetic / spectrophotometric analysis of the colour changes or colour developments in the organic (polymer containing) layer enables quantitative analysis of end groups by the dye techniques; appropriate calibration curves obtained by use of such simple compounds as sodium lauryl sulfate, a strong organic acid or a fatty amine or quaternary ammonium / pyridinium compounds are used for quantitative estimation.

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