

## Polymer characterization: Polymer molecular weight determination

(1)

Polymers like simple molecules can dissolve in common solvents. They are composed of functional groups that are chemically reactive, they exhibit colligative properties and at specific wavelength can absorb energy. However, unlike simple they are made up of smaller monomer units of different sizes. These changes in the degree of polymerization give rise to molecules with different molecular weight and different molecular weight distributions.

Polymers can be characterized with respect to

- (a) chemical identity of the repeat unit
- (b) nature of the end group
- (c) nature and extent of cross linking
- (d) solubility
- (e) colligative properties

→ Absolute methods allow the direct computation of polymer molecular weight from measured quantities without assumptions about the chemical and/or physical properties of the tested polymer molecule.

⇒ The equivalent techniques, although direct calculation of polymer molecular weight can be made from measured data requires knowledge of the chemical structure of the polymer molecule.

⇒ the relative methods, ~~or~~ on the other hand measured properties that depend on the chemical and physical structure of the polymer structure, regarding molecular weight curves of polymer standards of the same chemical and physical structure as that of the characterized polymer to be established.

However, all synthetic polymers contain polymer chain of uneven lengths; i.e. they are polydispersed and as such, molecular weight is not a single value but often described as average molecular weight.

The average molecular weight can be expressed in different ways such as number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), viscosity average molecular weight ( $M_v$ ), and higher average molecular weight ( $M_z, M_{z+1}$ ).

The choice of method for polymer molecular weight determination is influenced by factors such as (i) information required (ii) operative region (iii) cost effectiveness (iv) experimental conditions and requirements.

Basic information regarding methods (3)  
For polymer molecular weight determination

S.No	Method	Type	
(1)	End group Analysis	Equivalent  <math>10^5</math> (Operative Region)	$M_n \Rightarrow$ It is cost effective $\Rightarrow$ It requires known concentration $\Rightarrow$ Molecularly specific effectiveness is required.
(2)	Ebullioscopy (boiling pt elevation) and Cryoscopy (freezing point depression)	Absolute  <math>10^4</math> (Operative Region)	$M_n \Rightarrow$ They are cost effective $\Rightarrow$ Require known concentration and large volume $\Rightarrow$ have low resolution.
(3)	Ostometry	Absolute  $10^4 - 10^6$	$M_n \Rightarrow$ It is cost effective $\Rightarrow$ Require known concentration $\Rightarrow$ Is less efficient for high molecular wt determination
(4)	Gel Permeation Chromatography (GPC)	Relative  $10^2 - 10^7$	Different values $\Rightarrow$ It measures wide range of molecular weight $\Rightarrow$ It is sensitive and <del>light</del> has high resolution $\Rightarrow$ It can measure polydispersity
(5)	Light Scattering	Absolute  $10^2 - 10^8$	$M_w \Rightarrow$ It can measure Polydispersity $\Rightarrow$ It requires known concentration $\Rightarrow$ Sample preparation is difficult



(6) Sedimentation equilibrium	Absolute $< 10^6$	$M_w, M_z \Rightarrow$ It can measure Polydispersity $\Rightarrow$ It requires known concentration $\Rightarrow$ Sample preparation is tedious
(7) Viscometry	Relative $10^2 - 10^8$	$M_n \Rightarrow$ It is cost effective $\Rightarrow$ It measures wide range of molecular weight $\Rightarrow$ It requires known concentration $\Rightarrow$ It shows low accuracy for low molecular weight

# Methods of Molecular Weight Determination

(5)

## (I) → Number average molecular weight determination

### (1) Osmometry Techniques —

The two common osmometry techniques used for number average molecular weight determination are the membrane and vapour pressure osmometry. Vapour pressure osmometry is best suited for analyzing polymer samples with  $M_n < 20,000$  g/mol. The limiting factor in membrane osmometry is the diffusion problem of low molecular weight molecules through the membrane.

Membrane osmometry depends to a large extent on the colligative properties of the polymer solution. These properties include osmotic pressure, boiling point elevation, vapour pressure reduction, and the freezing point depression. In this technique, polymer solution and solvent (pure) are separated by a membrane which is semi-permeable only to solvent molecules, and not to the polymer (solute). Because the chemical potential of the pure solvent is higher than that of the solvent in polymer solution, the solvent moves from the pure solvent side to the polymer solution side. If there is an applied pressure, this movement can be hindered such that there is no net flow across the membrane. In this condition, the applied pressure is equal to the osmotic pressure.

However, osmotic pressure of a solution is a function of molecular weight and concentration. So equation is usually used given below

$$\frac{\pi}{c} = RT \left( \frac{1}{M_n} + A_2 c + A_3 c^2 + \dots \right) \quad \text{--- (1)}$$

$$\text{OR } \frac{\pi}{c} = RT \left( \frac{1}{M_n} + T_2 c + T_3 c^2 + \dots \right) \quad \text{--- (2)}$$

where  $c$  is the concentration of the polymer in gram per unit volume of the solution,

PTO



R is the universal gas constant

T is the absolute temperature

A<sub>2</sub> & A<sub>3</sub> are virial coefficient expressed in mL mol/g<sup>2</sup> and measures the polymer solvent interaction.

$\Gamma_2 = A_2/A_1$  &  $\Gamma_3 = A_3/A_1$

The derivation of ① found in BOOK of P. Ghosh. In practice, the term in  $c^2$  and those in higher power of  $c$  are always neglected as such  $\Pi/c$  is measured as a function of  $c$  at a particular temperature. A plot of  $\Pi/c$  against  $c$  results in a graph with the virial coefficient as the slope and an intercept of  $RT/M_n$  from which the number average molecular weight can be derived.

The vapour pressure osmometry requires the use of thermoelectric method in the measurement of lowering vapour pressure since extreme sensitivity is needed for direct measurement. In thermoelectric method, two sensitive thermistors are placed in a chamber saturated with solvent vapour under a controlled temperature. single drop of pure solvent is placed in each of the thermistors such that both the drops and the solvent have the same temp. The drop in one of the thermistor is replaced with polymer solution, this creates temperature imbalance. Since the vapour pressure of the polymer solution is lower than that of the pure solvent, solvent molecules from the saturated phase condense on the polymer solution ~~is lower than that~~ thermistor. As an effect the temp imbalance is small, it changes the resistance of the thermistors. A bridge circuit is used to measure the difference in resistance ( $\Delta R$ ) of the two thermistors for a small value of change in temp ( $\Delta T$ )  $\propto \Delta T \propto \Delta R$ . The working eq of v.p osmometry and the same treatment given to the higher power of  $c$  is

membrane osmometry is also applicable

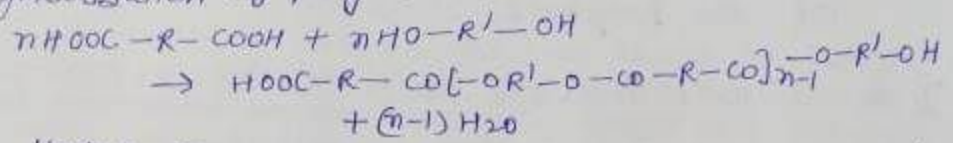
$$\frac{\Delta R}{C} = \left( \frac{\Delta R}{C} \right)_{C \rightarrow 0} (1 + r_2 C + r_3 C^2 + \dots) \quad (3)$$

$$\left( \frac{\Delta R}{C} \right)_{C \rightarrow 0} = \frac{k}{M_n} \quad (4)$$

k is the calibration constant.

### (2) END GROUP ANALYSIS -

This method has importance particularly in the determination of average molecular weight of step growth polymer. Consider the stepwise condensation polymerization of polyesters:



Under the assumption that each polymer chain contains one -OH and one -COOH group, direct measurement of the concentration of the groups can be done using chemical (titrimetric or pH measurement) or spectroscopic (infrared or nuclear magnetic) techniques. This is also applicable to other step growth polymer. However this method requires that the polymer be free of impurities and other groups present in the chain should not interfere in the determination of end group of interest.

For chain addition polymers in which the polymerization proceeds without measurable chain transfer, the use of End Group Analysis requires that the polymer is formed in the presence of a calculated dose of a strong chain transfer agent, such as a mercaptan, carbon tetrachloride or hydrogen sulfide. If the polymer chain length is obtained by chain transfer, the number of polymer molecules may be related to the fragments of the chain transfer agent present in the polymer chain end. Actually, such chain transfer reaction would produce two chain ends, one due to the interception of the propagation process by the chain transfer reaction



and the other resulting from re-initiation that follows the process.  $\bar{M}_n$  may alternatively be calculated for chain addition polymer from a count of the initiator fragments occurring in the polymer, provided the mode of initiation and termination (i.e. combination or disproportionation) are known.

However, the major set back of this technique is the decrease in sensitivity with increasing polymer chain length. This method is restricted to polymer with molecular weight  $< 20,000$  amu. Aside this, it requires the high concentration of the polymer.

II  $\Rightarrow$  WEIGHT AVERAGE MOLECULAR WEIGHT DETERMINATION

(1) Light Scattering Technique -

This method is presumed most popular for the determination of weight average molecular weight ( $\bar{M}_w$ ). It allows polymer molecular weight and structure to be assessed. Fundamentally, if light ~~scattered at an angle to~~ passes through a medium, it scatters at different angles. This technique thus relies on the measurement of light scattered at an angle to the incident ray as it passes through the target. The intensity of scattered light incident on polymer sample is dependant of the polarity, chain size and conc., consequent upon this, light technique measures polymer molecular weight by quantifying the Rayleigh scattering (elastic light scattering) from each polymer molecule. The measurement approach is simple as illustrated by the photomultiplier assembly. (Fig 1). The scattering glass cell is placed on a fixed center tube and positioned at the the centre of an axis of rotation of a receiver photomultiplier tube ~~intensity~~ assembly. The assembly is such that it can be rotated and



fixed at a desired angular position during scattered light measurement. The famousness of this method stems from the fact that wide range of molecular weight (typically  $10^4$  to  $5 \times 10^6$  g/mol) can be determined.

The scattered light and the average molecular weight is related by

$$\Delta R_{\theta} = K_c \overline{M_w} \overline{P(\theta)_z}$$

where  $\Delta R_{\theta}$  is the change in Rayleigh scattering at a specified angle,  $\theta$ ,  $K_c$  is the optical constant  $c$  is the polymer concentration and  $\overline{P(\theta)_z}$  is the average particle scattering factor which accounts for the effects of measuring scattering from large molecules with relatively small wavelengths.

It could be deduced from eq change in Rayleigh scattering is proportional to the sample concentration and molecular weight, hence this method requires high sample concentration to produce a detectable signal. This process is time consuming because it requires that the sample solution is completely free of dust and other impurities as these are capable of influencing the light scattering pattern.

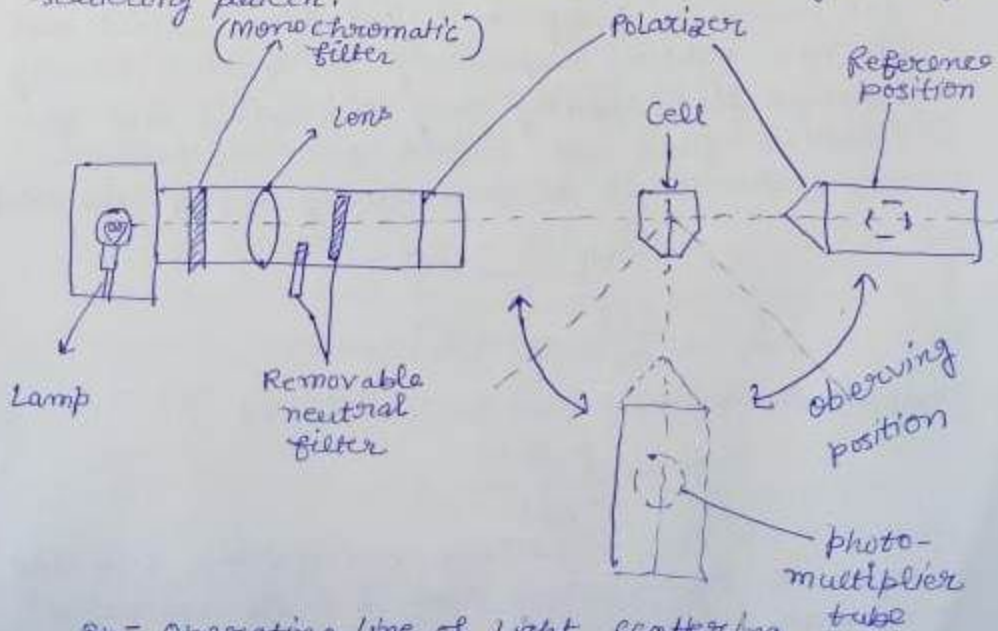


Fig - Operating line of light scattering photometer

### III $\Rightarrow$ Viscosity Average Molecular Weight ( $M_v$ ) (19)

#### Determination

#### 4) viscometry -

Polymers in general dissolve with difficulty in solvents than their corresponding monomers probably due to increased number of methylene group. When a polymer dissolves in a solvent, the viscosity of the solvent increases and polymer chain has direct influence. In 1930, Hermann Staudinger reported a relationship existing between polymer molecular weight and the relative magnitude of increase in viscosity. The measurement of the viscosity of a solution is simple and inexpensive, although somewhat time consuming. The Ubbelohde capillary viscometer is commonly used for polymer solution viscosity determination. The polymer solution is introduced into the reservoir of the viscometer and aspirated to the upper bulb. Air is then admitted which causes the solution to flow down the capillary by gravity. For  $M_v$  determination via this technique the process is performed for pure solvent and polymer solution respectively. The solution flowing through the capillary obey Poiseuille's law for laminar flow and implies that the pressure drop ( $\Delta P$ ) varies as the viscosity ( $\eta$ ) of the soln

$$\Delta P = K\eta \quad \text{--- (1)}$$

$$K = \frac{8RL}{\pi r^4} \quad \text{--- (2)}$$

eg (1), the viscosity can be written as

$$\eta = \frac{\pi \Delta P r^4}{8LR}$$

where  $r$  is the capillary radius (cm),  $L$  is the length of the capillary (cm),  $R$  is the volumetric flow rate through the capillary (cm<sup>3</sup>/s)



The flow rate ( $R$ ) will be inversely proportional to the solution flow time ( $t$ ) if the bulk volume in the viscometer is fixed. However,  $\Delta P$  is a function of solution density ( $\rho$ ), hence

$$\eta = At\rho \quad \text{--- 3}$$

where  $A$  is a constant.

Eq 3 is valid only if  $\Delta P$  is completely used up in overcoming viscous forces (i.e. a dilute solution). If  $t$  and  $t_0$  are the flow rates and  $\eta$  and  $\eta_0$  are the viscosities of polymer solution and pure solvent respectively, the ratio  $t/t_0 = \eta/\eta_0$ . Since the lower limit of the relative viscosity ( $\eta_r$ ) is unity, the specific viscosity ( $\eta_{sp}$ ) which defines the relative increase in viscosity brought about by dissolved molecules (egs) is considered more important. The reduced viscosity ( $\eta_{red}$ ) is obtained by relating  $\eta_{sp}$  to concentration eg 6. More so, the limit  $\eta_{red}$  at zero concentration gives the intrinsic viscosity,  $[\eta]$ , eg 7 while the inherent viscosity ( $\eta_{inh}$ ) is the natural logarithm of  $\eta_r$  divided by the concentration eg 8. At  $c=0$ ,  $\eta_{inh} = [\eta]$ , hence  $[\eta]$  can be obtained from any of the viscosity. The intrinsic viscosity is related to polymer molecular weight according to eq 9  $\Rightarrow [\eta] = K \bar{M}_v^a$

$$\eta_r = \frac{\eta}{\eta_0} \quad \text{--- 4}, \quad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \quad \text{--- 5}$$

$$\eta_{red} = \frac{\eta_{sp}}{c} \quad \text{--- 6} \quad [\eta] = \lim_{c \rightarrow 0} \frac{\eta_{red}}{c} \quad \text{--- 7}$$

$$\eta_{inh} = \frac{\ln \eta_r}{c} \quad \text{--- 8}$$