

# MOLECULAR WEIGHTS OF MACROMOLECULES (POLYMERS)

The molecular weight of a single macromolecule will be equal to molecular weight of repeat unit multiplied by degree of polymerization. But a macromolecular substance may not contain the macromolecules of same size and same length, hence macromolecules will have different molecular weights. Macromolecules, therefore, cannot be assigned definite molecular weights. Hence we take average molecular weight for such macromolecular substances.

Two types of average molecular weights of macromolecular substances have been defined :

(i) The number average molecular weight ( $\bar{M}_n$ )

(ii) The weight average molecular weight ( $\bar{M}_w$ )

**(i) Definition of the Number Average Molecular Weight ( $\bar{M}_n$ ).** It is equal to the weight of macromolecular substance divided by total number of moles present. Let  $n_1, n_2, n_3, \dots$  be the number of moles of particles of macromolecules having molecular weights  $M_1, M_2, M_3, \dots$ , respectively.

Now, 
$$\text{Mole} = \frac{\text{Weight}}{\text{Molecular weight}}$$

or 
$$\text{Weight} = \text{Mole} \times \text{Molecular weight.}$$

Total weight of all macromolecules present  

$$= n_1 M_1 + n_2 M_2 + n_3 M_3$$

Now, 
$$M \bar{n} = \frac{\text{Total weight}}{\text{Total number of moles}}$$

$$M \bar{n} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

**(ii) Definition of the Weight Average Molecular Weight ( $\bar{M}_w$ )**

It is defined as :

$$M \bar{w} = \frac{w_1 M_1 + w_2 M_2 + w_3 M_3 + \dots}{w_1 + w_2 + w_3 + \dots}$$

where,  $w_1, w_2, w_3, \dots =$  Weights of macromolecules having molecular weights  $M_1, M_2, M_3, \dots$ , respectively

Now, 
$$\text{Weight} = \text{Mole times mol. wt.}$$

$$w_1 = n_1 M_1; w_2 = n_2 M_2; w_3 = n_3 M_3$$

Hence 
$$M \bar{w} = \frac{(n_1 M_1) M_1 + (n_2 M_2) M_2 + (n_3 M_3) M_3 + \dots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}$$

$$M \bar{w} = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \dots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}$$

## METHODS OF MOLECULAR WEIGHT DETERMINATION OF MACROMOLECULES (POLYMERS)

The following methods are generally used to determine the molecular weight of macromolecules :

- (i) Osmotic pressure method
- (ii) Viscosity method
- (iii) Light scattering method
- (iv) Sedimentation (ultra centrifuge method)

(i) **Osmotic Pressure Method.** The osmotic pressures of solution of macromolecules, even at very low concentration, are significant and can be easily measured. Hence measurement of osmotic pressure of macromolecular solution can be used to determine the molecular weight of such substances. According to Van't Hoff Equation

$$PV = nRT$$

$$PV = (w/m)RT$$

$$P = (w/V) RT/m$$

$$P = CRT/m$$

or 
$$\frac{P}{C} = \frac{RT}{m} \quad \dots (1)$$

where  $P =$  O.P. of solution macromolecular substance at  $T^{\circ}A$

$C =$  Concentration of solution (gm/cc)

$P/C =$  Reduced osmotic pressure

$m =$  Molecular wt. of macromolecule

$R =$  Gas constant

Equation (1) holds good only at infinite dilution. Therefore, equation (1) becomes

$$\left( \frac{P}{C} \right)_{C \rightarrow 0} = \frac{RT}{m} \quad \dots (2)$$

where  $\left( \frac{P}{C} \right)_{C \rightarrow 0} =$  Limiting or reduced osmotic pressure

The osmotic pressure of dilute solution of polymer is measured at decreasing concentrations. If a graph is plotted between  $P/C$  and  $C$ , a straight line is obtained (Fig. 5.7). When this line is

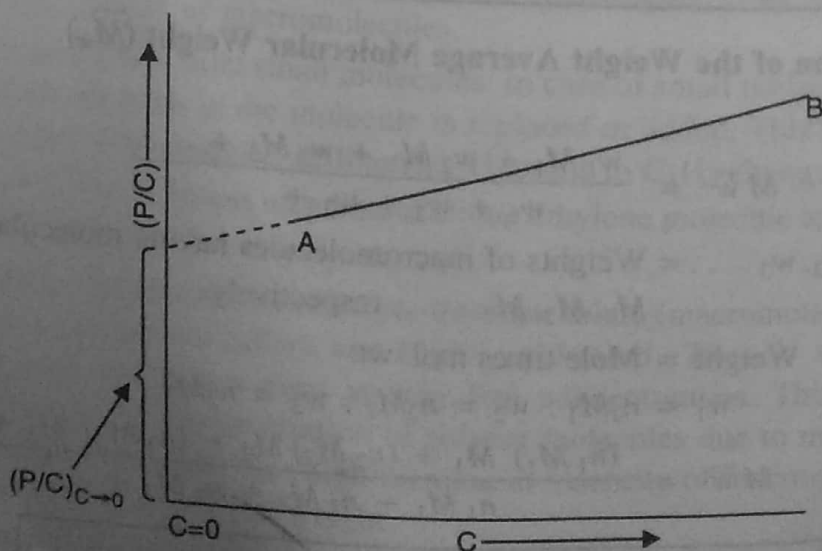


Fig. 5.7. Determination of limiting viscosity pressure.

extrapolated to  $C = 0$ , the intercept on  $P/C$  axis gives the value of  $(P/C)_{C \rightarrow 0}$ . On substituting this value in equation (2), the molecular weight of polymer is calculated.

Since osmotic pressure is a colligative property *i.e.*, depends on the number of particles, the value of molecular weight obtained by osmotic pressure method will be number average molecular weight  $\bar{M}_n$ .

(ii) **Viscosity Method.** This method is simple and widely used for molecular weight determination of polymers. The viscosity of polymer solution can be accurately measured and is different from that of solvent.

Let, Viscosity of pure solvent =  $\eta_0$

Viscosity of polymer soln. =  $\eta$

- Then 1. Relative viscosity ( $\eta_r$ ) of polymer soln. =  $\frac{\eta}{\eta_0}$
2. Specific viscosity ( $\eta_{sp}$ ) of polymer soln. =  $\frac{\eta}{\eta_0} - 1 = \frac{\eta - \eta_0}{\eta_0}$
3. Reduced viscosity ( $\eta_{red}$ ) = Sp. viscosity per unit concentration.  

$$= \frac{\eta_{sp}}{C}$$
4. Intrinsic viscosity  $[\eta]$  = Reduced viscosity when  $C \rightarrow 0$   

$$= (\eta_{red})_{C \rightarrow 0}$$
  

$$= \left( \frac{\eta_{sp}}{C} \right)_{C \rightarrow 0}$$

The intrinsic viscosity is related to molecular weight of polymer according to following equation :

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

where  
 $K, a =$  Constants  
 $M =$  Molecular weight

If a graph is plotted between  $\eta_{red}$  and  $C$ , a straight line is obtained (Fig. 5.8).

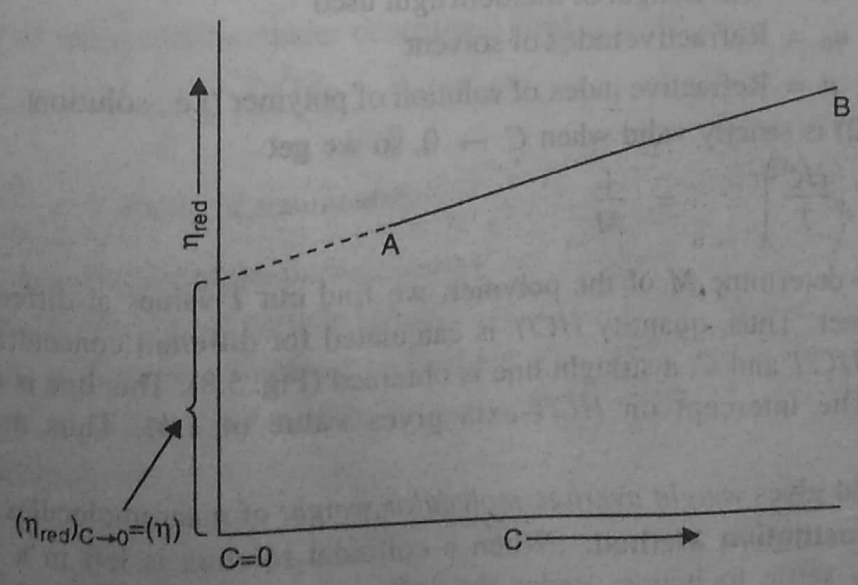


Fig. 5.8. Determination of intrinsic viscosity.

This line, when extrapolated to  $C = 0$ , the intercept on  $\eta_{red}$ -axis gives  $[\eta]$ . Thus knowing  $K, a$  and  $[\eta]$ , molecular weight ( $M$ ) of polymer is calculated.

Molecular weight of polymer obtained by Viscosity Method lies between  $M \bar{n}$  and  $M \bar{w}$  and is called *viscosity average molecular weight*.

(iii) **Light Scattering Method.** This method is useful in case of polymers of very high molecular weights, particularly above 10,00,000. The results obtained are quite accurate.

This method is based on the scattering of light by a colloidal solution, *i.e.*, Tyndall effect. The portion of incident light scattered increases with the increase in the number and size of particles in the solution. The intensity of transmitted light ( $I$ ) is given by

$$I = I_0 \cdot e^{-Tl} \quad \dots (1)$$

- where
- $I_0$  = Intensity of incident light falling on solution column.
  - $I$  = Intensity of transmitted light after travelling length  $l$  in solution column.
  - $T$  = Solution turbidity.

*Sol. turbidity is defined as the fraction of incident light scattered per centimeter length of solution through which it passes.* The solution turbidity can be determined by measuring the decrease in intensity of transmitted light.

Turbidity of a solution is related to molecular weight of the macromolecule by the equation

$$T = HCM$$

or

$$\frac{HC}{T} = \frac{1}{M} \quad \dots (2)$$

- where
- $T$  = Solution turbidity
  - $M$  = Molecular weight of macromolecule
  - $C$  = Concentration of solution (gm/cc)
  - $H$  = Constant. Its value depends on the wavelength of light used.

Constant  $H$  is defined as

$$H = \frac{32\pi^3 n_0^2 \left( \frac{n - n_0}{C} \right)^2}{3N \lambda^4} \quad \dots (3)$$

- where
- $N$  = Avogadro's number
  - $\lambda$  = Wavelength of incident light used
  - $n_0$  = Refractive index of solvent
  - $n$  = Refractive index of solution of polymer (*i.e.*, solution)

Equation (2) is strictly valid when  $C \rightarrow 0$ , so we get

$$\left( \frac{HC}{T} \right)_{C \rightarrow 0} = \frac{1}{M} \quad \dots (4)$$

In order to determine  $M$  of the polymer, we find out  $T$ -values at different dilutions of the solution of polymer. Thus, quantity  $HC/T$  is calculated for different concentrations. If a graph is plotted between  $HC/T$  and  $C$ , a straight line is obtained (Fig. 5.8). This line is extrapolated to zero concentration. The intercept on  $HC/T$ -axis gives value of  $1/M$ . Thus molecular weight is calculated.