

THIS METHOD GIVES WEIGHT AVERAGE MOLECULAR WEIGHT OF MACROMOLECULES.

(iv) **Sedimentation Method.** When a colloidal solution is left in a vessel, the particles tend to settle to bottom under the influence of gravity. This phenomenon is called *sedimentation*. Unless the solution particles are large, the sedimentation under gravity is at a very slow rate. However, rate of sedimentation can be highly increased if the solution is subjected to a very large gravitational force, which can be artificially created by means of *ultracentrifugation*. This technique was introduced by Svedberg. Ultracentrifuge is a very high speed centrifuge in which

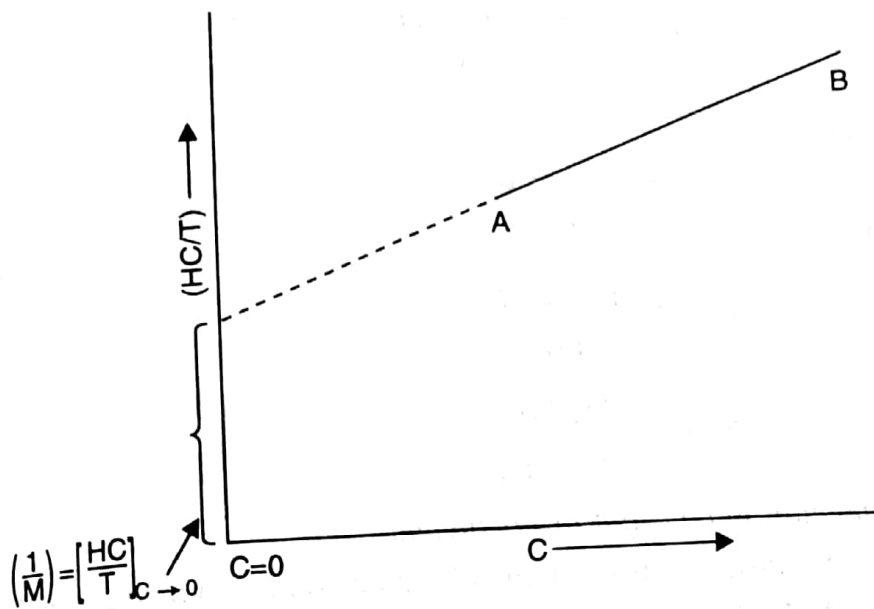


Fig. 5.9. Determination of molecular weight of polymer by light scattering method.

sedimentation occurs under very high centrifugal force of rotation. The speed of rotation is so high that an acceleration as high as million times that of gravity is attained. The polymer solution is kept in ultracentrifuge and rate of sedimentation is noted. Knowing rate of sedimentation, it is possible to calculate the molecular weight of polymer.

The determination of molecular weight of polymers by ultracentrifuge can be done by two methods :

- (a) Sedimentation velocity method
- (b) Sedimentation equilibrium method

(a) *Sedimentation velocity method.* The acceleration in a centrifugal field is given by ... (1)

$$\text{Acceleration in centrifugal field} = \omega^2 x$$

where

$\omega$  = Angular velocity (radian/sec.)

=  $2\pi \times$  Revolutions per second.

$x$  = Distance of setting particle the axis of rotation.

The velocity of sedimentation under centrifugal field is given by

$$\frac{dx}{dt} = \frac{2r^2(d_p - d_m)\omega^2 \cdot x}{9\eta} \quad \dots (2)$$

where

$\frac{dx}{dt}$  = Velocity of sedimentation

$r$  = Radius of the particle (cm)

$d_p$  = Density of particle (gm/cc)

$d_m$  = Density of medium (solvent)

$\eta$  = Viscosity of medium (poise)

Rewriting equation (2),

$$\frac{dx}{x} = \frac{2r^2(d_p - d_m)\omega^2 \cdot dt}{9\eta}$$

On integration

$$\int_{x_1}^{x_2} \frac{dx}{x} = \frac{2r^2(d_p - d_m)\omega^2}{9\eta} \int_{t_1}^{t_2} dt$$

$$\ln x_2 - \ln x_1 = \frac{2r^2(d_p - d_m)\omega^2(t_2 - t_1)}{9\eta}$$

or

$$\frac{\ln\left(\frac{x_2}{x_1}\right)}{\omega^2(t_2 - t_1)} = \frac{2r^2(d_p - d_m)}{9\eta}$$

or

$$S = \frac{2r^2(d_p - d_m)}{9\eta}$$

or

$$S = \frac{\ln(x_2/x_1)}{\omega^2(t_2 - t_1)}$$

where

$S$  is called *sedimentation constant or coefficient*.

The sedimentation constant  $S$  is calculated by equation (4) knowing  $x$  and  $t$  at two stages of sedimentation and speed of rotation of centrifuge ( $\omega$ ). Knowing  $S$ , the radius of particle ( $r$ ) can be calculated by equation (3).

Assuming the polymer particle to be spherical, the mass of the particle will be given by

$$m = \frac{4}{3}\pi r^3 d_p$$

Molecular wt. = Mass of a particle  $\times N$

$$M = \frac{4}{3}\pi r^3 d_p N$$

$N$  = Avogadro's Number

This method gives *weight average molecular weight* of polymer. It is important to note that equation (3) applies to uniform spherical particles of polymer.

(b) *Sedimentation Equilibrium Method*. When the solution of polymer is rotated for a long time in an ultracentrifuge, a stage comes at which the particles no longer sediment (settle down). This stage is known as equilibrium point. At equilibrium point, rate of sedimentation and rate of diffusion of particles (due to thermal and Brownian motions) back to medium are equal and opposite. At this stage the following equation holds good :

$$\ln(C_2/C_1) = \frac{M\omega^2(d_p - d_m)(x_2^2 - x_1^2)}{2RT d_p}$$

$$M = \frac{2RT d_p \ln(C_2/C_1)}{\omega^2(d_p - d_m)(x_2^2 - x_1^2)}$$

where

$C_1$  = Concentration of particles at point  $x_1$  from centre of rotation

$C_2$  = Concentration of particles at point  $x_2$  from centre of rotation

$M$  = Molecular weight of polymer

$d_p$  and  $d_m$  = Densities of particles and medium respectively.

$\omega$  = Speed of rotation of ultracentrifuge

$T$  = Temperature

$R$  = Gas constant

From equation (1) the molecular weight of polymer can be calculated. This method gives *weight average molecular weight*. Equation (1) is applicable to dilute dispersions of particles of any shape but all of the same size.

## 6. CONFIGURATION OF MACROMOLECULES (POLYMERS)

Polymers are said to be *linear* if the repeating units are joined together like links in a chain. The chains may be *branched* or joined together by cross-links or both. More extensive cross-linking may lead to the formation of three-dimensional cross-linked polymers.

If we consider the polymerization of the monomer  $\text{CH}_2 = \text{CHZ}$ , then there are three stereoisomers possible (See Fig. 5.10).

- (i) All the Z groups are on the same side of chain; this is called *isotactic polymer*.
- (ii) Z groups lie alternatively on each side of the chain; this is the *syndiotactic polymer*.
- (iii) Z groups are randomly situated along the two sides of the chain, this is *atactic polymer*.

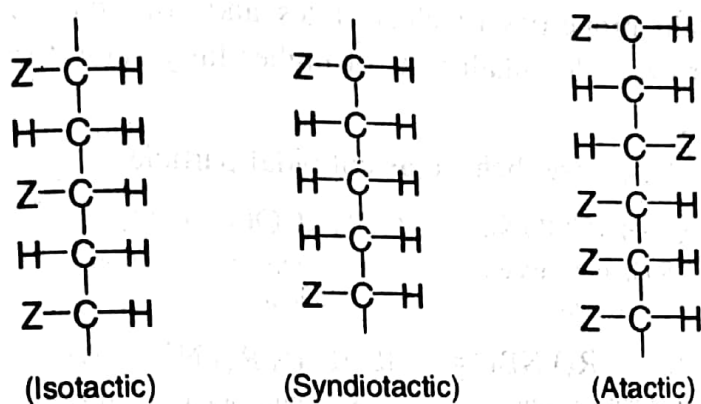


Fig. 5.10. Stereoisomeric addition polymers.

The polymer chain may have enormous number of configurations of identical energy. The simple theory of polymer configurations is very much similar to the theory of random flight of gas molecules with constant free path, which corresponds to the bond distance in the polymer. The physical character of macromolecules primarily depends on their shape and size.

The shape of macromolecules also varies, some of them are nearly spherical, some of them are rod-like, again many of them have *coiled chains* repeatedly folded. When there are cross-linkings between the repeat units or chains, the macromolecules become *rigid insoluble* material such as bakelite, vulcanised rubber etc. When a polymer is dissolved in *good solvent* in which the interaction between monomer units and solvent molecules are as strong as those between monomer units, the polymer molecules show an *extended random coil configuration*. When the polymer is dissolved in a *poor solvent* in which the interactions between monomer units and solvent molecules are weaker than those between monomer units, the polymer molecules show a *compact configuration*. For example, *random chain configurations* are assumed by polypeptide (protein) molecules in solution. Hydrogen bonds are not formed in this situation. The chains can rotate round carbon atoms to which side groups are attached. Reversible transitions can occur between alpha helix structure and random chain configurations of polypeptides depending on the pH of solution.

## 7. COLLAPSE OF POLYMERS