contains the sample solution while lower part contains the solvent. The two parts are separated by means of a semi-permeable membrane. The movement of an air bubble inside the capillary indicates the solvent flow to the solution. Such movement of the air bubble is detected by a photocell. The servo mechanism is used to move the solvent reservoir in the upward or downward direction and also to adjust the hydrostatic pressure such that the solvent flow is totally stopped. The pressure head of the reservoir gives the osmotic head.

2.4.3. Light Scattering

If a strong beam of light is passed through vacuum, it is transmitted in the direction of travel and the path of the light cannot be detected. However, when light is passed through a medium containing discrete particles, it gets scattered in all directions in space. Light scattering accounts for many natural phenomenon such as rainbow, colourful dawn and dusk, the blue colour of the sky and the sea.

Light scattering method is used to determine the weight average molecular weight, $\overline{M}_w$, of the polymer sample. When a beam of light is passed through a polymer solution, it suffers scattering. It is due to scattering of light that most of the sols appear turbid. Turbidity, τ, may be defined as the fraction of incident light which is scattered per cm. length of the solution through which it passes. It is given by the expression,

$$\frac{I}{I_0} = e^{-\tau x}$$

where I_0 denotes the intensity of the incident light.

I denotes the intensity of light after passing through a thickness x of the medium.

According to Debye the turbidity (τ) of a solution is related to molecular weight ($\overline{M}_w$) of polymer (solute) by the following equation,

$$\frac{KC}{R_{\theta}} = \frac{HC}{\tau} = \frac{1}{\overline{M}_w} + 2BC \quad \ldots (i)$$

where B = virial coefficient

C = concentration of the solution

and R_{θ} = Rayleigh ratio at 90° observation angle.

The equation holds good only for particles which are smaller than the wavelength of light used. K and H are light-scattering calibration constants defined as :

$$K = \frac{2\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_0}$$

and

$$H = \frac{32\pi^3 n^2 (dn/dc)^2}{3\lambda^4 N_0}$$

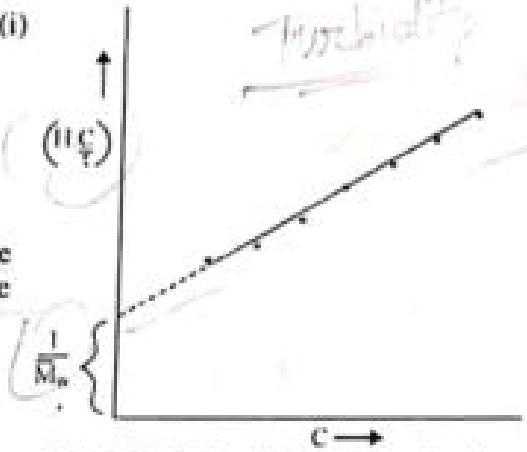


Fig. 2.11. Determination of molecular weight of polymers from turbidity measurement

where π has a numerical value of 3.14,

n is the refractive index of the solution,

$\frac{dn}{dc}$ is the specific refractive index increment (change of refractive index with concentration).

λ is the wavelength of the incident light and N_0 is the Avogadro's number.

Now equation (i) can be written as,

$$\left(\frac{KC}{R_{\theta}}\right)_{C \to 0} = \left(\frac{HC}{\tau}\right)_{C \to 0} = \frac{1}{\overline{M}_w} \quad \ldots (ii)$$

The significance of equation (ii) is that limiting value of $\left(H\frac{C}{\tau}\right)$ is equal to $1/\overline{M}_w$ when $C = 0$. Thus if a graph is plotted between $\left(\frac{HC}{\tau}\right)$ and C and then extrapolated to zero concentration, the intercept with y-axis will give the value of $1/\overline{M}_w$.

Further, polymer molecules are randomly coiled and the incident light is simultaneously scattered by different regions of the polymer coil. The result is that the scattered light emerging from different regions interfere with one another. Due to this, the intensity of the scattered light diminishes.

The value of Rayleigh ratio R_θ varies with θ and Debye equation can be modified as :

$$\frac{KC}{R_\theta} = \frac{HC}{\tau} = \frac{1}{\overline{M}_w P(0)} + 2BC \qquad \ldots \text{(iii)}$$

where $P(0)$ is the particle-scattering factor describing the angular dependence of the scattered light.

Now $$P(0) = 1 - \frac{1}{3} S^2 R_g^2$$

where $S = (4\pi/\lambda) \sin(\theta/2)$ and R_g is the radius of gyration. R_g is different for different shapes of polymer molecule in solution. Radius of gyration is defined as the average root mean square distance of the atoms from the centre of the mass.

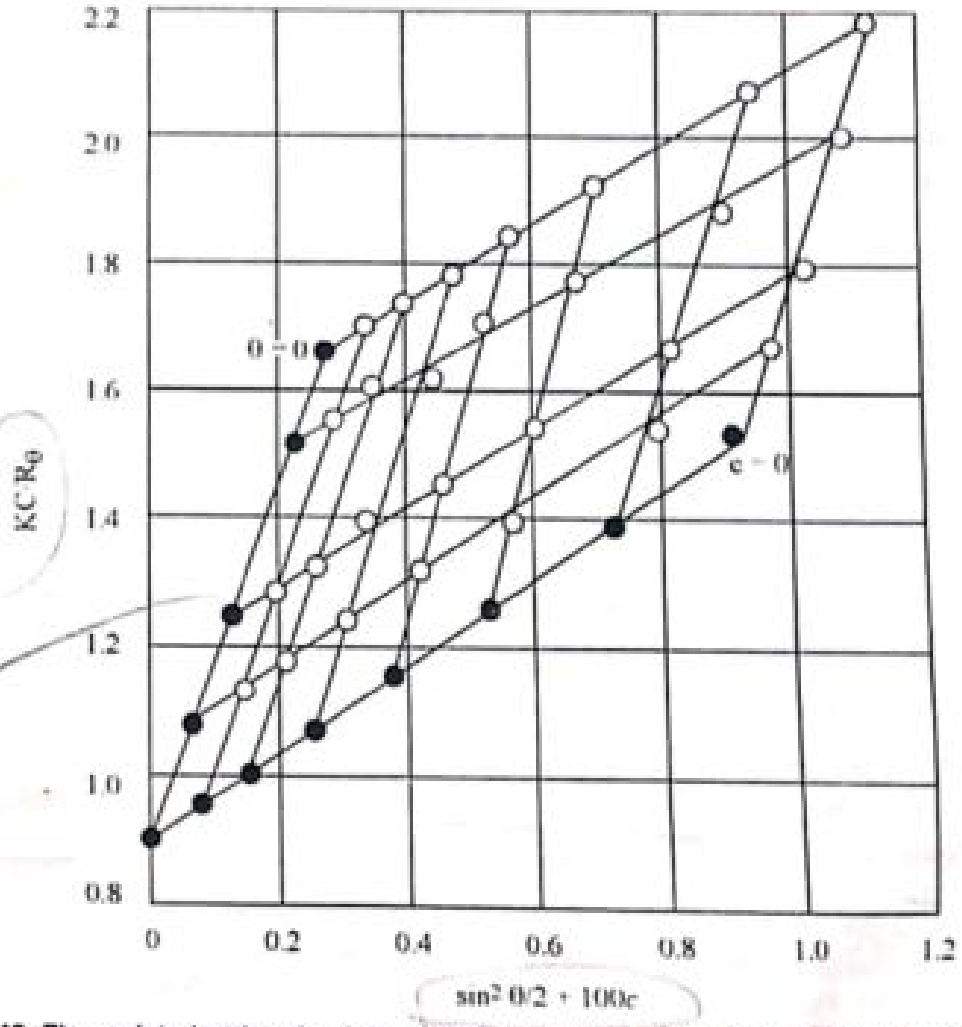


Fig. 2.12. Zimm plot showing the light scattering from a sample of polystyrene in butanone

If (iii) is incorporated in equation (ii) we get,

$$\frac{KC}{R_0} = \frac{1}{\overline{M}_w}\left[1 + 2BC + \frac{1}{3}S^2 R_g^2\right] \quad \ldots (iv)$$

Zimm utilized above equation to determine the molecular weight of a polymer. It involves double extrapolation of the plots of KC/R_0 versus $[\sin^2(\theta/2) + KC]$. Here K is the scattering constant which depends upon the refractive index of the solution; $\sin^2(\theta/2)$ is proportional to S^2. The experimental light scattering values are plotted over a wide range of concentrations C and angles θ. Lines are drawn through points at constant angle and extrapolated to zero concentration. Also, lines are drawn through points at constant concentration and extrapolated to zero angle. The two sets of limiting values are then extrapolated to common intercept at zero value of the abscissa from where we get the value of $\frac{1}{\overline{M}_w}$. This method of graphical extrapolation is called the Zimm plot.

By light scattering technique, molecular weight of polymers in the range of 10,000 to 10,000,000 can be easily determined. Various parameters used in this experiment like R_0 or τ can be determined using a light scattering photometer and n and dn/dc by differential refractometer.

Light Scattering Photometer

Modern light-scattering instruments use either a mercury arc or a laser as a source and detect the scattered light photoelectrically. The following (Fig. 2.13) is the experimental arrangement of a light scattering photometer.

L is the source of light. The light, after leaving the source, passes through a pair of lenses *K* and also through a monochromatising filter *IF*. It then passes through the slit *B* and strikes against a beam splitter *H*. After passing through the polariser *N*, the beam of light falls on the polymer solution kept in the cell C_p. After leaving the cell, the incident beam is absorbed by a light trap *LA*. The scattered light both from the cell and turbidity standard *St* reaches photocells Ph_1 and Ph_2 respectively. The photocell Ph_1 is mounted on a rotating arm to permit measurement of the light scattered at several angles.

Since the amount of light scattered by solution is very small, every care should be taken to see that the solution is free from impurities such as dust particles which would themselves scatter light considerably and introduce serious errors.

As we see from the equation

$$\overline{M}_w = \frac{1}{\lim_{c \to 0} H\frac{C}{\tau}}$$

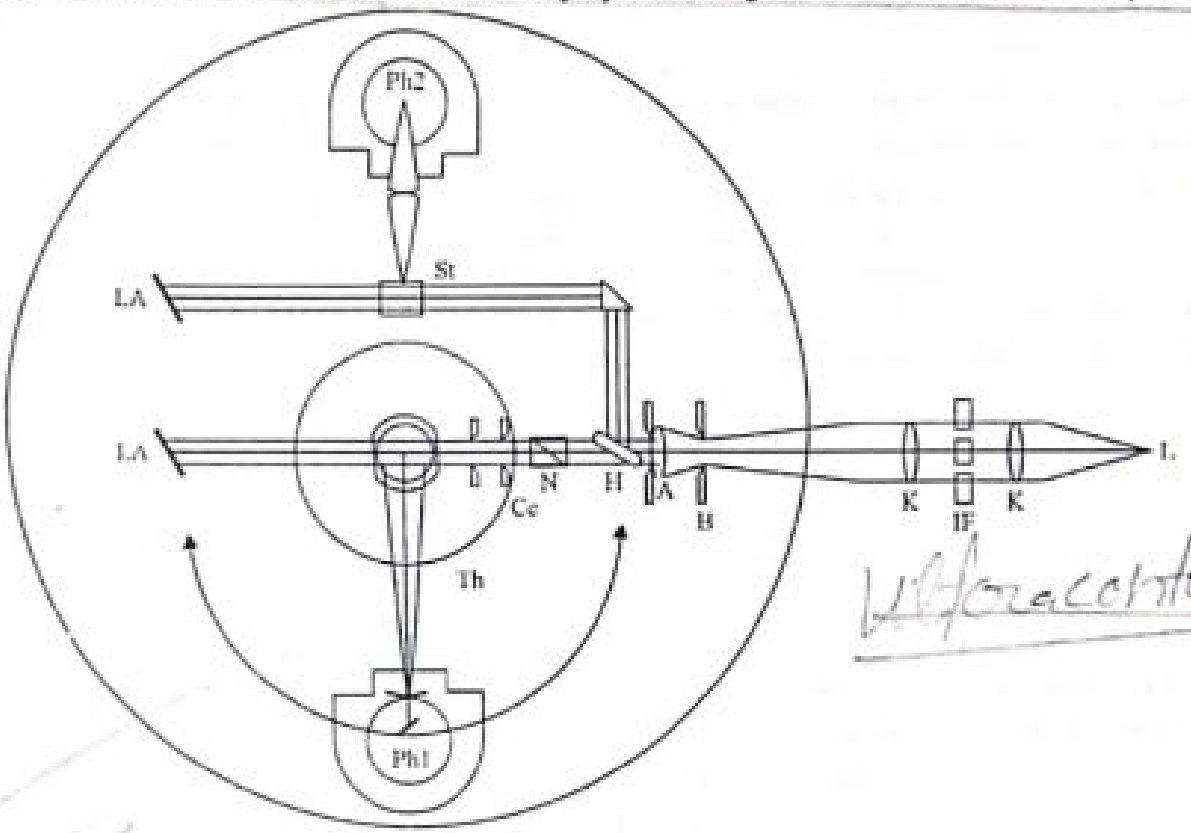
the turbidity of the solution of a given concentration increases with increase in molecular weight of macromolecule while the osmotic pressure decreases with increase in molecular weight, it is evident that the light scattering method is more accurate in the case of polymers of very high molecular weights particularly above 1,000,000 where osmotic pressure method gives inaccurate results.

2.4.4. Ultracentrifugation

This method is also known as sedimentation method. It is the most modern and widely used method to determine the molecular weight of high polymers. This method was developed by *T. Svedberg* and his coworkers (1925-31).

Sedimentation is the fall of colloidal particles in a viscous medium under the influence of gravity. The rate of sedimentation of suspended particles under the influence of gravity is small. However, it can be increased considerably by applying ultracentrifuge technique. When a polymer solution is subjected to a very high centrifugal force, it undergo sedimentation and molecules settle down. The rate of

sedimentation under the influence of a constant centrifugal force is related to their molecular weight. The rate of sedimentation can be increased considerably by increasing the number of revolutions per second.



Ph 1 Moveable photocell
Ph 2 Reference photocell
St Calibrated turbidity standard (translucent glass)
Ce Solution cell
Th Thermostat
N Polariser
H Light beam splitter
A Achromatic system
B Slit
K Condensing lenses
IF Interference filter
L Light source (high-pressure mercury lamp)
LA Light absorber (beam stop)

Fig. 2.13. Schematic diagram of an experimental set-up for light-scattering measurements

Two different methods based on the use of ultracentrifuge have been devised. They are (i) the sedimentation velocity method and (ii) the sedimentation equilibrium method. The first method yields the number-average molar mass, and the second method yields the mass-average molar mass.

(i) The Sedimentation Velocity Method

It is a quicker method in which the polymer solution is placed in a centrifuge tube under the influence of a very high gravitational field. Due to the high centifugal force, the polymer molecules will start sedimenting. By applying Stoke's law, it is possible to correlate the sedimentation coefficient with molecular weight by the following expression known as the Svedberg equation :

$$\overline{M}_n = \frac{S_0 RT}{D_0 (1 - \rho \overline{V})} \quad \ldots (i)$$

where S_0 and D_0 are the sedimentation and diffusion constants respectively.

A quantity called the sedimentation coefficient is denoted by S. It is the sedimentation rate for a unit centrifugal acceleration. For a given molecular species in a given solvent at a given temperature, S is a constant. It is expressed in the unit Svedberg, named after the Swedish chemist T. Svedberg, who did fundamental work on the development of centrifugal technique. Svedberg was awarded the Nobel Prize in Chemistry in 1926 for his work. Constants S_0 and D_0 can be obtained by extrapolating the sedimentation coefficient (S) and the diffusion coefficient (D) at different concentration to zero concentration. In the Svedberg equation $\bar{V}$ is the specific volume of the polymer in solution and ρ is the density of the solvent. Value of constant $R = 8.314\ JK^{-1}\ mol^{-1}$ and T is the temperature.

During ultracentrifugration, a polymer solution is under the influence of very strong gravitational field. The centrifugal force acting on the solute particle of mass m at a distance r from the centre of rotation is $m\omega^2 r$, where ω is the angular velocity. A buoyant force is also acting on the particle. So the resultant force

$$= \text{Centrifugal force} - \text{Buoyant force}$$

$$= m\omega^2 r - m_s\omega^2 r \qquad \ldots (i)$$

where m_s is the mass of dispiaced solvent. If ρ is the density of the solvent and v is the volume of the solute particle, then $m_s = v\rho$. But the measurement of v is very difficult. So another quantity called the partial specific volume $\bar{v}$ is generally used. It is defined as the increase in volume when one gram of a dry polymer solute is dissolved in a very large volume of the solvent. Hence, the quantity $m\bar{v}$ will be the increase in volume obtained when a solute particle of mass m is added to the solvent. Thus $m\bar{v} = v$. Now equation (i) can be written as :

$$\text{Resultant force} = m\omega^2 r - m\omega^2 r\bar{v}\rho$$

$$= m\omega^2 r(1 - \bar{v}\rho)$$

This resultant force will cause the particle to accelerate. But the medium is exerting a frictional force which is proportional to the sedimentation velocity dr/dt. Thus

$$\text{Frictional force} = f\left(\frac{dr}{dt}\right)$$

where f is the frictional coefficient.

The frictional force opposes the resultant force and the two forces are equal, when the steady state is reached, thus

$$\text{Frictional force} = \text{Resultant force}$$

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

Now, sedimentation coefficient S = sedimentation velocity/centrifugal acceleration

$$i.e., \qquad S = \frac{dr/dt}{\omega^2 r} = \frac{m(1 - \bar{v}\rho)}{f} = \frac{\overline{M}_N/N_A(1 - \bar{V}\rho)}{f}$$

$$\text{or} \qquad \overline{M}_N = \frac{S N_A f}{1 - \bar{v}\rho}$$

where N_A is the avogadro's number.

The diffusion coefficient D and frictional coefficient f are related by Stokes-Einstein diffusion equation :

$$D = RT/N_A f = kT/f$$

Hence

$$f = k\frac{T}{D}$$

$$\text{or} \quad S = \frac{1}{\omega^2 (t_2 - t_1)} \cdot \ln (r_2/r_1)$$

The angular velocity ω can be calculated by knowing the speed of rotation of ultracentrifuge. The beam of light, which is passing through the system and then falling on the photographic plate records the position of the boundary at various interval of time.

Problem 10 : *A polymer sample is placed in an ultracentrifuge which is operating at 50,000 rotations per minute (rpm). If the sedimentation coefficient of this polymer is 7.1×10^{-13} s, how far will the solution boundary move in 30 minutes at a distance of 6.5 cm. from the axis of rotation ?*

Solution : We know that

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

Hence,

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

$$\omega = 2\pi\nu = \frac{2 \times 3.14 \times 50.000}{60} = 5237 \text{ rad s}^{-1}$$

$$\therefore \quad \frac{dr}{dt} = (7.1 \times 10^{-13} \text{ s})\,(5237 \text{ rad s}^{-1})^2\,(6.5 \text{ cm})$$

$$= 1.27 \times 10^{-4} \text{ cm s}^{-1}$$

$$\therefore \quad \Delta r = (1.27 \times 10^{-4} \text{ cm } s^{-1})\,(30 \times 60s)$$

$$= 0.229 \text{ cm.}$$

Problem 11 : *A sample of solution of a bovine serum albumin is placed in an ultracentrifuge which is operating at a speed of 45,000 rpm. If the boundary position of the solution moves from an initial r-value of 6.15 cm to a final r-value of 6.83 cm in a time interval of 157 min., calculate the sedimentation coefficient of bovine serum albumin.*

Solution : From the equation

$$S = \frac{1}{\omega^2 (t_2 - t_1)} \ln (r_2/r_1)$$

We have,

$$S = \frac{\ln (6.83/6.15)}{\left(2\pi \times \dfrac{45000 \text{ rpm}}{60s \text{ m}^{-1}}\right)^2 \left(157 \text{ min} \times 60\, s \text{ m}^{-1}\right)}$$

$$= 5.01 \times 10^{-3}\, s$$

(ii) Sedimentation Equilibrium Method

In this method, the rotor speed is lower (about 10,000 rpm) than in the sedimentation velocity method, where the rotor speed is of the order of 60,000 rpm. When an equilibrium between sedimentation and diffusion is reached, there is no net flow. In other words an equilibrium is said to be established under the influence of gravity in a sedimenting column when the amount of material driven outward by centrifugal force is exactly balanced by the amount diffused in opposite direction due to Brownian and thermal motions. The experiment takes several days to reach the equilibrium state.

During ultracentrifugation, polymer molecules get distributed according to their molecular weights under the influence of centrifugal force. An equilibrium concentration gradient is established along the cell. Thus at this stage, when the sedimentation and diffusion balance out

molecular weights is given by the equation

$$\overline{M}_W = \frac{2RT \ln (C_2/C_1)}{\omega^2 (1 - \bar{v}\rho)(r_2^2 - r_1^2)}$$

where $\overline{M}_W$ is the weight-average molecular weight, ω is the angular velocity of the rotor (in radians s^{-1}), ρ is the density of the solution, c_1 is the concentration at distance r_1 and c_2 is the concentration at distance r_2 from the axis. The concentration ratio (c_2/c_1) is determined by photometric measurement. If we plot a graph between ln c and r^2, it should be a straight line with slope equal to $\overline{M}_W \omega^2 (1 - \bar{v}\rho)/2RT$. Thus weight-average molecular weight can be calculated from the measurement of slope.

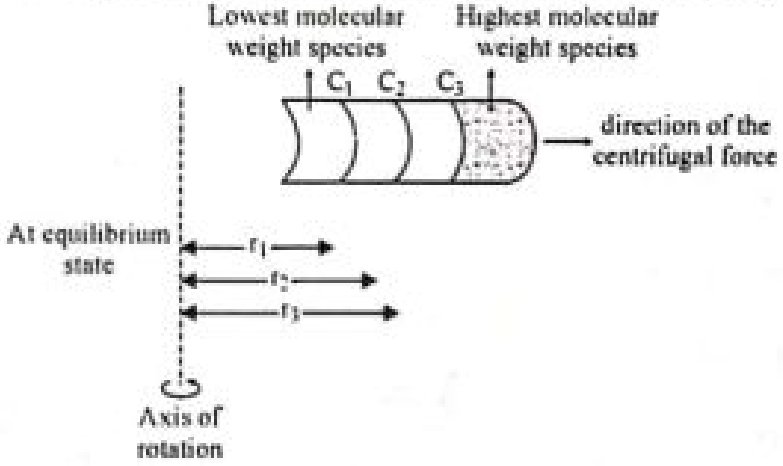


Fig. 2.16. Distribution of polymer molecules at various distances from axis of rotation under influence of equilibrium centrifugal force

The commonly used ultracentrifuge set up has an aluminium or titanium alloy rotor which can operate from 2000 rpm to 65000 rpm. It is operated electrically and a camera is used to photograph the solution cell at different times.

The solvent should be dust-free and should have relatively low viscosity. The density and refractive index of the solvent must be quite different from that of the polymer sample. This will be good for effective sedimentation. The main drawback of this method is that it is rather laborious and time consuming.

2.4.6. Viscometry

Viscometry is an useful technique for determining the viscometry-average molecular weight, $\overline{M}_v$. The viscosity of a polymer solution is considerably higher than that of the pure solvent. It is due to the presence of macromolecules which raises the viscosity of the solvent because of the inhomogenieties introduced by large molecules.

This method was introduced by H. Staudinger. If η_0 is the viscosity of pure solvent and η that of solution of a given macromolecule, then η/η_0 is known as the relative viscosity (η_r) of the solution, *i.e.*,

$$\eta_r = \frac{\eta}{\eta_0}$$

Specific viscosity (η_{sp}) may be defined as the relative increase in viscosity and is given by

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1 = \eta_r - 1$$

The ratio η_{sp}/c *i.e.*, the relative increase in specific viscosity per unit concentration of macromolecule is known as reduced viscosity. As reduced viscosity is not independent of concentration, it becomes necessary to extrapolate a plot of η_{sp}/c against c to zero concentration. This extrapolated value is known as the intrinsic viscosity (η_i). This may be expressed by the following expression :

$$\eta_i = \lim_{c \to 0}\left(\frac{\eta_{sp}}{c}\right)$$

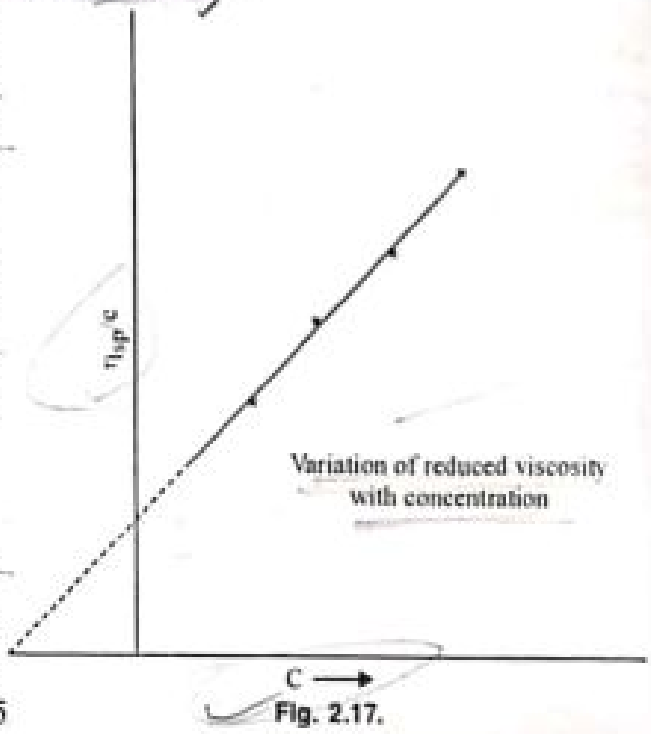
where c is the concentration of the macromolecule in gms per 100 ml.

Intrinsic viscosity is also known as the Staudinger index or limiting viscosity number. In order to get intrinsic viscosity of a macromolecule, it becomes necessary to determine specific viscosity of the solution of macromolecule of different concentrations in a given solvent.

Staudinger observed, in 1950, that for a series of samples of the same polymer in a given solvent and at a constant temperature, the intrinsic viscosity is related to the molar mass of the polymer by the following equation, known as Mark-Houwink equation, or Staudinger equation :

$$\eta_i = K\left(\overline{M}_{visc}\right)^a$$

where $\overline{M}_{visc}$ is the viscosity-average molecular weight of the polymer and K and a are constants for a particular polymer/solvent/temperature system. The value of 'a' depends upon the geometry or shape of the polymer molecule. The values of a vary from 0.5 to 1. For polymers behaving as random coils, a is about 0.8 and for globular proteins having a compact structure, it is about 0.5.



Variation of reduced viscosity with concentration

Fig. 2.17.

For an unknown polymer system, the K and a values have to be generated. This is done by fractionating the polymer sample into several fractions and for each fraction, the molecular weight is determined either by osmometry or by the light scattering method and the corresponding intrinsic viscosities are also measured.

Again if logs of both sides of Staudinger equation is taken, we have

$$\ln [\eta_i] = \log k + a \ln \overline{M}_{visc}$$

Table

Fraction number	Molecular weight $\overline{M}_n \times 10^{-5}$	η_i
1	8.237	1.65
2	11.390	2.19
3	13.890	2.49
4	15.120	2.65
5	19.720	3.20

Molecular weight and viscosity data for a polymethyl acrylate sample in benzene solution.

A log-log plot of $[\eta_i]$ versus $\overline{M}_{visc}$ gives a straight line with slope equal to a and intercept equal to ln K. Thus, the constants a and K can be easily determined.

Problem 12 : *The intrinsic viscosity of myosin is 217 $cm^3\ gm^{-1}$. Calculate the approximate concentration of myosin in water which would have a relative viscosity of 1.5.*

Solution : We know that $\eta_i = \lim_{c \to 0}\left(\frac{\eta_{sp}}{c}\right)$

There are two types of viscometers used for this purpose :

(a) The Ostwald viscometer

(b) The Ubbelohde suspended level viscometer (USLV).

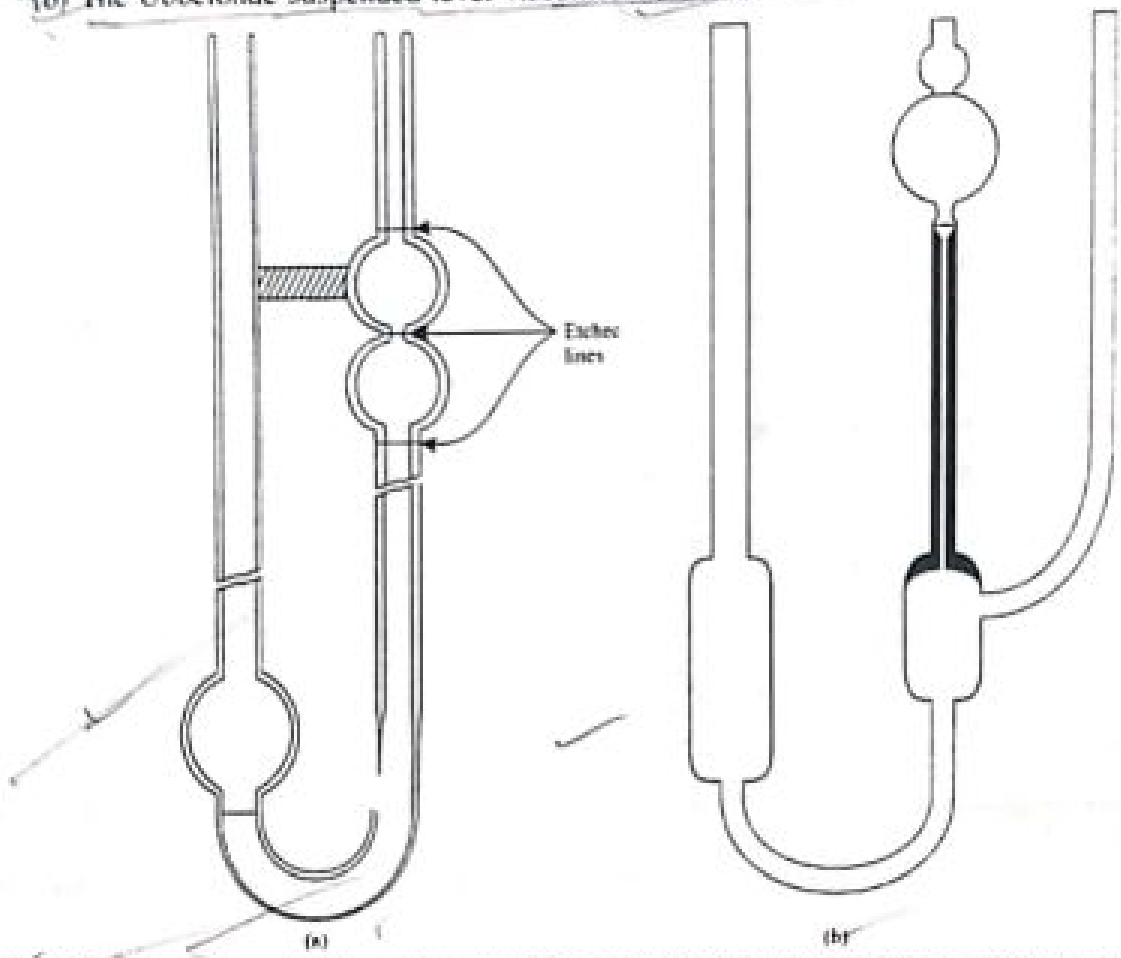


Fig. 2.18. The two types of viscometers used for measuring viscosities of dilute polymer solutions : (a) the Ostwald viscometer and (b) the Ubbelohde suspended level viscometer

(a) Ostwald viscometer : It is a simple glass capillary device. The viscometer is dried and the same volume of the solution under examination is taken. Otherwise, the effective pressure head will vary from one solution to another. The process is repeated and flow times of various sample solutions are taken.

The experimental procedure with respect to the Ostwald viscometer is rather tedious as each time, we have to empty, clean and refill the viscometer with a fresh solution before measuring the flow time.

(b) USLV : The main advantage of this apparatus is that only a single solution of the known concentration is required to start the experiment. A known volume of polymer solution is taken in the viscometer and the flow time is measured. Subsequent concentrations can be obtained by adding known volumes of pure solvent and mixing inside the viscometer itself.

There are certain precautions which are strictly followed to get the correct result.

(i) All measurements should be done at constant temperature because the viscosity is highly dependent on temperature.

(ii) The apparatus should be hold perfectly vertical during the experiment otherwise, even with the same volume of the solution, the pressure head will vary.

(iii) All solutions should be free from suspended impurities because it will obstruct the free flow of the solution with in the capillary and will give incorrect flow times.

(iv) The flow time for a particular volume of the solution or solvent must be sufficiently long so that the difference in flow time between two successive concentrations is at least of the order of 3 to 5 seconds.

2.5. ANALYSIS AND TESTING OF POLYMERS :

There are various standard methods of physical and chemical analysis of polymers. Some of them are described below :

(i) Chemical analysis of polymers
(ii) Spectroscopic methods
(iii) X-ray diffraction analysis
(iv) Microscopy
(v) Thermal analysis
and (vi) Physical testing.

2.5.1. Chemical analysis of polymers :

The chemical analysis of polymer is similar to analysis of low-molecular weight organic compounds. There are many standard analytical techniques other than usual methods, for analysis of elements and functional groups. There are many specific books available for identification and analysis of plastics. Chemical reactions such as degradation reactions of polymers provide additional means of chemical analysis. Mass spectroscopy and gas chromatography are two powerful techniques for analysing low molecular weight products of reactions (usually degradation) of polymers.

(a) Mass spectroscopy : The polymer is allowed to react to form low molecular weight fragments. They are condensed at liquid-air temperature, then volatilized, ionized and separated in a mass spectrometer. From the abundance of the various ionic species found, the structures of low molecular weight species can be elucidated.

(b) Gas chromatography : Gas chromatography is a special form of the general chromatographic technique, in which the moving phase is a gas and the stationary phase may be either liquid or solid. The technique is suitable for separation of materials which are votatile without decomposition.

In gas-chromatography the sample is introduced into the moving carrier gas stream (nitrogen or hydrogen) and is carried by it through the column. The column contains either the active solid (gas-solid chromatography) or a liquid of low vapour pressure held upon an inert support or only liquid in a capillary column (gas-liquid chromatography). The active solid or non-volatile liquid forms the stationary phase whereas the carrier gas forms the mobile phase. The components of the mixture sample distribute them selves between the two phases. The adsorption or solubility in the fixed phase would differ from substance to substance, therefore these components are carried along the column at different rates and finally they emerge at the end of the column in distinct zones separated by the carrier gas. On emerging the vapours of the components are detected by suitable instrumental methods accompained by an automatic recording.

2.5.2. Spectroscopic Methods :

Spectroscopic methods like IR, NMR, EPR are helpful in the analysis of polymers.

2.5.3. X-ray diffraction study :

It was suggested by M.Von Laue, in 1913, that it might be possible to diffract X-rays by means of crystals. The reason of this suggestion was that the wavelength of X-rays was of about the same order (10^{-3} cm) as the inter-atomic distances in a crystal. X-ray diffraction study has proved to be highly useful in determining structures and dimensions of the crystals.

W. H. Bragg pointed out that scattering of X-rays by crystals could be considered as reflection from successive planes of atoms in the crystals. However, unlike reflection of ordinary light, the reflection of X-rays can take place only at certain angles, which are determined by the wavelength of the X-rays and the distance between the planes in the crystal. The fundamental equation, which gives a simple relation between the wavelength of the X-rays (λ), the interplanar distance in the crystal (d) and the angle of reflection (θ), is known as the Bragg equation.

$$2d \sin \theta = \eta \lambda$$

Bragg eqn

The wavelenghts of X-rays are comparable to interatomic distances in crystals; the information obtained from scattering at wide angles shows the spatial arrangements of the atoms. Low-angle X-ray scattering is useful in detecting larger periodicities.

There are two types of the X-ray diffraction techniques used in the study and analysis of polymeric crystals.

(i) Rotating crystal technique (i) Powder technique.

(i) Rotating crystal technique : X-rays are usually produced by bombarding a metal target with a beam of high voltage electrons. This is done inside a vacuum tube *T*. The X-rays generated in the tube T are now passed through a slit so as to obtain a narrow beam which is then allowed to strike a single crystal *C* mounted on the turn-table. The crystal is rotated gradually by means of the turn-table so as to increase the glancing angle at which the X-rays are incident at the exposed face of the crystal.

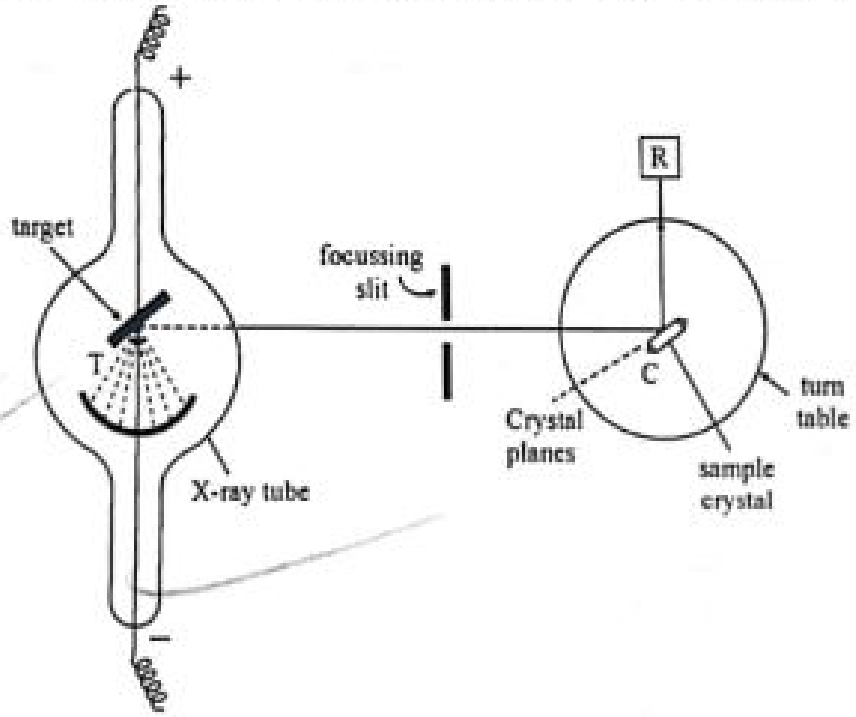


Fig. 2.19. An X-ray Spectrometer

The wavelength of X-rays produced depends on the target metal and the applied voltage. The intensities of diffracted X-rays, angles and distances may be detected by their action on photographic films or plates. The angles for which diffractions are maximum give the value of θ. The process is carried out for each plane of the crystal. X-rays of a given wavelength are diffracted only for certain specific orientations of the single crystal sample. Therefore it must be placed in all possible orientations during the experiment, usually by rotating the crystal about one of its axis to achieve the desired orientations with respect to the X-ray beam.

(ii) Power technique (The Debye–Scherrer method) : This method is more convenient, but gives less information than the single crystal (rotating-crystal) method. The powder, infact, consists of many small crystals which are oriented in all possible directions. As a result of this, X-rays are scattered from all sets of planes. The sample is kept in the form of a cylinder inside a thin glass tube. The intensity of diffracted rays are detected by means of photographic film arranged in the form of a circular arch. In this method, no rotation is necessary since the powder sample already contains microcrystals arranged in all possible orientations.

Application to Polymers :

The crystal structure of a polymer is determined from X-ray patterns of a fibre drawn from the polymer. Because of the alignment of the crystalline regions with the long axis of the molecules parallel

to the fibre axis, the pattern is essentially identical to a rotation pattern from a single crystal. In such a pattern diffraction maxima occur in rows perpendicular to the fibre axis, called layer lines.

Chain Conformations : As the periodicity of molecular structure of a polymer is characterised by the existance of a repeat unit, so the periodicity of its crystal is characterised by a repeat distance. The repeat distance is directly determined by measuring the distance between the layer lines. The repeat distance of 2.55 A° in the crystals of polyethylene is readily identified with a single repeat unit in the planar zig-zag conformation. The position of the atoms in the unit cell are then derived from the relative intensities of the diffracted beams. The diffraction patterns of polymers, do not give all information. The bond lenghts, bond angles and arrangements of atoms along the chain are determined from other sources.

Methods for analysing the diffraction patterns from helical structures is highly versatile technique for the determination of the repeat unit.

Chain packing : The packing of the chains is described in terms of the unit cell and its contents. The volume occupied in the crystal by a single repeat unit is the volume of the unit cell. The volume of the unit cell is obtained from the repeat distance and the positions of the diffraction spots on the layer lines. This volume measures the density of the crystals, which is useful in determining the degree of crystallinity.

Disorder in the Crystal Structure :

X-ray diffraction also give the information about the disorder in the crystal structure. This disordering results in the broadening of the diffraction maxima. However, the distortion of perfect crystals into paracrystals is now considered important in many polymers.

Orientations :

Unless the crystalline regions in polymers are oriented, as by drawing a fibre, the diffraction maxima merge into rings, made up of the maxima from a large number of crystallites in many different orientations. If orientation is intermediate between these extremes, the rings split into arcs, and a quantitative evaluation of the crystallite orientation is made by measuring the angular spread and intensity of these arcs.

2.5.4. Microscopy :

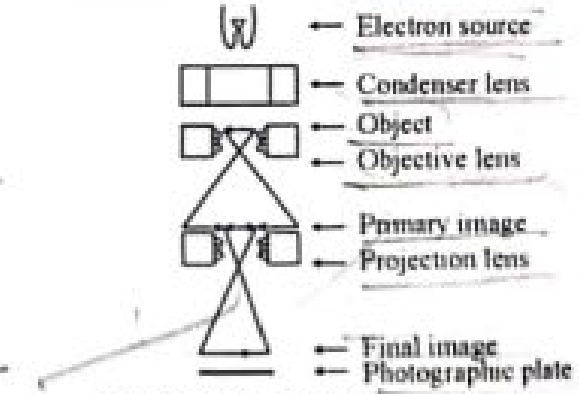
There are various techniques used for polymer analysis.

1. Light Microscopy : Reflected-light microscopy has been used for examining the texture of solid opaque polymers. The polymer is taken in the form of thin film and light is transmitted through it. There are two common techniques of light microscopy, one is polarized light microscopy and other is phase- contrast microscopy. In polarized light microscopy, crystalline materials rotate the plane of polarized light. The morphology of spherulites in some polymers is complicated which is observed in the light microscope between crossed polarizers. When using a hot-stage polarizing microscope, crystalline melting point is taken as the temperature of disappearance of the last traces of crystallinity.

In second technique *i.e.*, phase-contrast microscopy, observation of structural features involve difference in refractive index rather than absorption of light.

Interference microscopy allowing measurement of thickness as low as a few angstrom units has proved valuable in the study of polymer single crystals.

2. Electron Microscopy : It is a powerful tool for the study of the morphology of crystalline



An Electron microscope

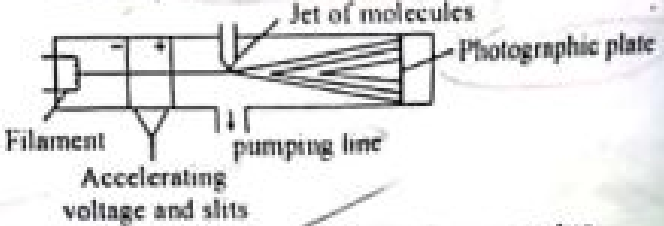


Fig. 2.20. An electron diffraction apparatus

polymers. Resolution of smaller objects can be achieved in electron microscopy, the practical limit of resolution is a few angstrom units.

The electron microscope is an optical instrument. The image forming radiation in a electron microscope is a beam of electrons, the lenses are either in magnetic or electrostatic field and the image is made visible either photographically or by means of a fluorescent screen.

The diffraction pattern is characteristic of the structure of individual molecules. The principle of this procedure is much similar to that of powder method of X-ray analysis. The disadvantage of this microscopy is that the intense electron beam acting for a considerable length of time destroys the specimen in many cases. As the electron beam is unable to penetrate through metallic surface, a very thin film replica of the surface is made and analysed with electron microscope. The specimen undergoes changes caused by heating during the bombardment of electrons in its evacuated environment. Inspite of these limitations, the electron microscope on account of its inherent high resolution power and great depth of focus, gives promise to striking developments in near future.

Scanning Electron Microscopy : In scanning electron microscopy, a fine beam of electrons is scanned across the surface of an opaque specimen to which a light conducting film has been applied by evaporation. Secondary electrons or X-ray photons emitted when the beam hits the specimen are collected to provide a signal. The resolution is the order of 100 A°.

2.5.5. Thermal Analysis :

There are various thermal analytical methods for the analysis of polymers, such as

(i) Thermogravimetric analysis (ii) Thermo mechanical analysis
(iii) Electrical thermal analysis (iv) Differential thermal analysis
and (v) Differential scanning colourimetery

In these methods some property of the system is measured as a function of the temperature. We shall discuss here only differential thermal analysis and differential scanning colourimetery.

(iv) Differential thermal analysis (DTA) :

In DTA the sample and an inert reference substance, undergoing no thermal transition in the temperature range of interest, are heated at the same rate. The temperature difference between the sample

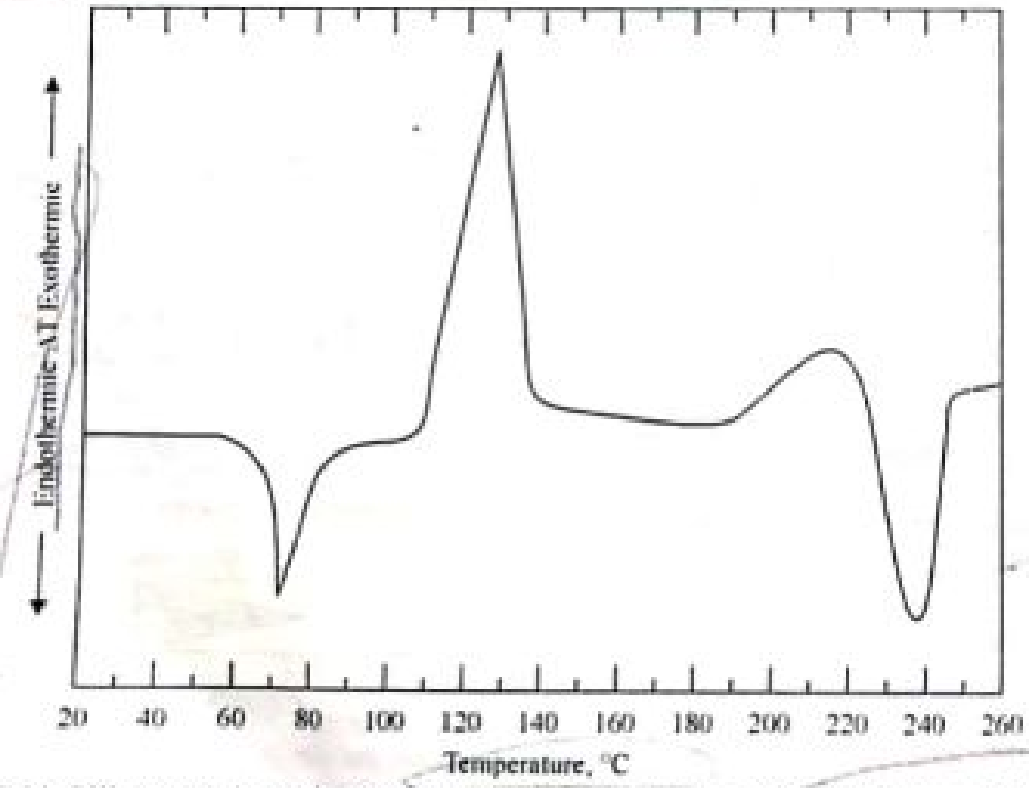


Fig. 2.21. Differential thermal analysis curve for amorphous poly (ethylene terephthalate)

2.5.6. Physical Testing :

There are various test methods for measuring the physical properties of polymers. A brief description of some mechanical properties are given below :

(a) Tensile Strength : (Stress-Strain Properties in Tension) One of the most informative mechanical experiments for any material is the determination of its stress-strain curve in tension. This is usually done by measuring continuously the force developed as the sample is elongated at constant rate of extension. The tensile strength curve for plastics shows modulus or stiffness, yield stress and strength and elongation at break. This type of curve is typical of a plastic such as polyethylene. Tensile properties are usually measured at rates of strain of 1–100% per min. At higher rates of strain, tensile stength and modulus usually increases while elongation decreases.

(b) Fatigue Tests : When subjected to cyclic mechanical stresses, most materials fail at a stress considerably lower than that required to cause rupture in a single stress cycle. This phenomenon is called fatigue. Alternating tensile, compressive stress and cyclic flexural stress are the various modes of fatigue testing in common use. Results are reported as plots of stress versus number of cycles to fail. Fatigue failure may arise from the absorption of energy in a material that is not perfectly elastic. This energy is manifested as heat, leading to a temperature rise, a lower modulus, and rapid failure.

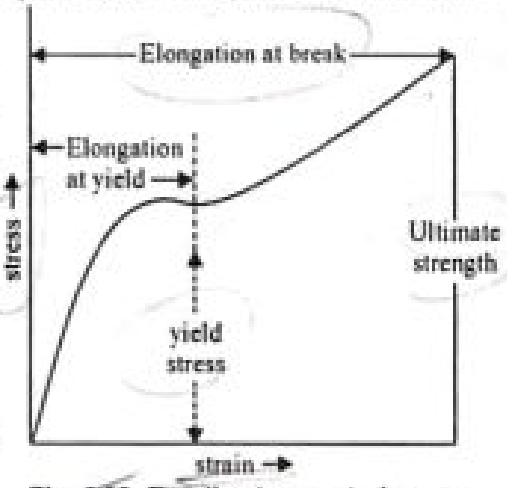


Fig. 2.23. Tensile stress- strain curve for plastics

(c) Impact Tests : The rupturing in polymer samples may be divided into two classes :

(i) Brittle rupture

(ii) Ductile rupture.

(i) Brittle rupture : In brittle rupture the specimen is broken into pieces. Brittle failure is charactrised by lack of distortion of the broken parts. There are two aspects of brittle rupture. The temperatrue below which brittle failure occurs under a given set of experimental conditions and measures of the toughness of materials at ambient temperature. The test methods used to obtain both types of information are highly empirical. Since the specimen is destroyed, multiple testing is usually applied to allow statistical evaluation of the results. The brittle point is determined by subjecting a specimen to impact in a standardised but empirical way. The temperature of the test is varied until that temperature is found where, statistically, half the specimens fail by brittle rupture. The brittle point is roughly related to the glass transition temperature.

(ii) Ductile rupture : In ductile rupture the specimen is permanently distorted near the point of failure.

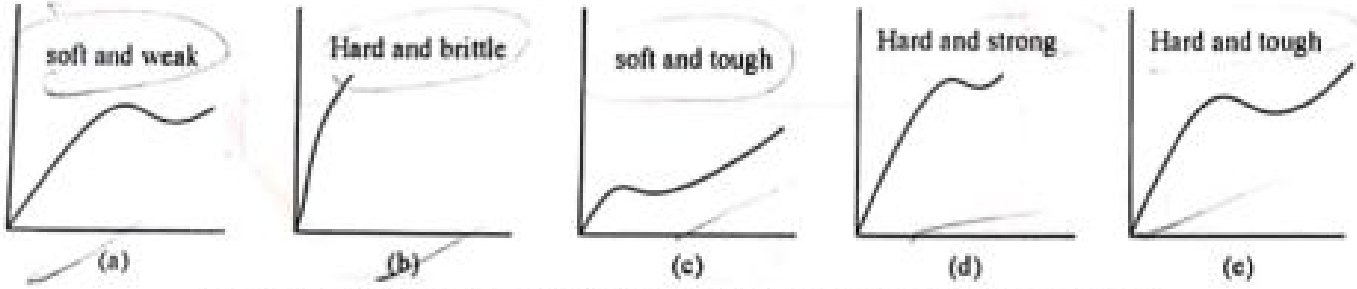


Fig. 2.24. Tensile stress-strain curves for several types of polymeric materials

Impact strength of plastics is measured by tests in which a pendulum with a massive striking edge is allowed to hit the specimen. From the travel of the pendulum after breaking the specimen can be calculated the energy required to cause the break.