MODULE 2

Polymer Morphology—Introduction

Studies of physical form, arrangement and structure of the molecules of a material system relates to its morphology. Polymer morphology covers the study of the arrangement of macromolecules into amorphous and crystalline regions and the overall physical structure of the molecular aggregates.

In molecules including those of polymers, fixed arrangements of atoms that remain normally unaltered and which can be altered only by breaking and reforming of primary valence bonds, are commonly referred to as *configurations*. On the other hand, arrangements of molecular segments that can be altered by rotation of segments or groups of atoms around single bonds are referred to as *conformations*. Different modes of chain growth (and sometimes chain termination) give rise to different configurations including head-to-tail, head-to-head or tail-to-tail arrange-ments (Sec. 6.2), stereospecific or random arrangements given by isotactic, syndiotactic and atactic structures (Sec. 1.5.6) in vinyl polymers, and structures arising from 3, 4, or 1, 2 addition and *cis* and *trans* isomers from 1, 4 addition in diene polymers (Sec. 5.9).

7.22. Development of Crystallinity

Morphological studies about polymers are primarily related to the molecular pattern and physical behaviour of the crystalline regions of crystallizable polymers. Amorphous, semicrystalline and highly crystalline polymers are known, but it is difficult or even impossible to attain 100% crystallinity in bulk polymers. It is also difficult, if not impossible, according to the latest studies based on electron microscopy and other approaches, to obtain solid amorphous polymers completely devoid of any degree of molecular order or crystallinity. A whole spectrum of structures ranging from total disorder, and different kinds and degrees of order to very high degree of (if not total) order may describe the physical state of a given polymeric system depending on test environment, thermomechanical treatment to which the polymer has been subjected and the chemical environment from which the polymer has been isolated. Moreover, the collected data for the degree of crystallinity may vary according to the employed method of estimation. The crystallinity data given in Table 7.2 must, therefore, be regarded as approximate.

Table 7.2. Approximate degree of crystallinity (%) for different polymers

Polyethylene (low density)	60–80
Polyethylene (high density)	80–98
Polypropylene (fibre)	55–60
Nylon (polyamide fibre)	55–60
Terylene (polyester fibre)	55–60
Cellulose (cotton fibre)	65–70
Cellulose (viscose rayon fibre)	35–40
Gutta percha	50–60
Natural rubber (crystallized)	20–30

Polymers having crystallites in excess of 50% are generally recognized to be crystalline. Cellulose derivatives used as fibres have crystallinity lower than that shown by cellulose. The predominantly linear chains of high density polyethylene (HDPE) exhibit crystallinity much higher than any other polymer known, even substantially higher than that exhibited by the low density variety; and for the HDPE, the attainable crystallinity is very much close to the upper limit (100%). On the other hand, atactic polymers in general (including those of styrene and methyl methacrylate bearing bulky side-groups) having irregular configurations fail to meaningfully crystallize under any circumstances.

Figure 7.22 gives an idea of the rate of crystallization of a highly crystallizable polymer, polyethylene, at different temperatures, studied by following volume changes.[11] As the temperature is lowered, the rate of crystallization rapidly increases and well below the melting point (<127°C), it soon becomes so rapid as to make observations practically impossible. The practical consequence of the very high rate of crystallization in polyethylene is that it is not possible to obtain the polymer in the amorphous state at room temperature or under ambient conditions. Sudden quenching of the melt to below room temperature yields a material which is still crystalline (though usually with the likelihood of a lower degree of crystallinity than that developed on normal cooling of the melt). This is because the time required for crystallization is far shorter than the time taken in cooling the test sample.

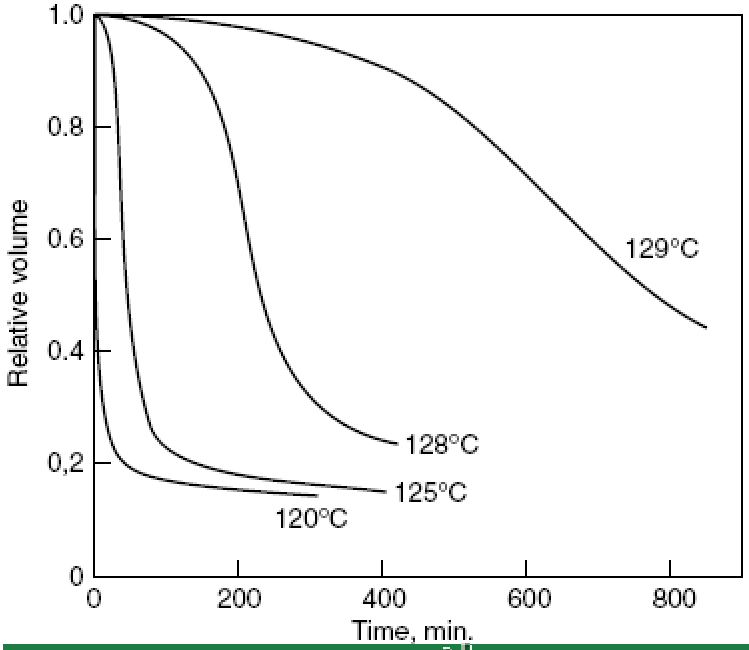

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Figure 7.22. Progress of densification or development of crystallinity with time in polyethylene held at different temperatures. The ordinate is the ratio of actual volume change to the ultimate change in volume after an indefinitely long time period (Mandelkern, 1964; Courtesy, McGraw Hill, New York)

For practical reasons, therefore, the phenomenon of polymer crystallization is conveniently studied and measured using an amorphous polymer, such as natural rubber. The advantage of using rubber as a kind of model material for the study of crystallization is that crystallization process is quite slow in the substance and it takes place in a convenient range of temperature. The manipulation of the crystallization process for experimental purposes is done with much greater ease with rubber than with a crystalline polymer which crystallizes at rates too high for easy and precise measurements, and that also at much higher temperatures.

All rubbers are, however, not crystallizable. Only those built up of chains characterized by chemically identical and regular repeating units, such as natural rubber, are capable of crystallization.

Natural rubber may be conveniently crystallized by cooling below room temperature, preferably below 0°C or by simply stretching at room temperature.

7.23. Crystallization of Rubber on Cooling

When unvulcanized natural rubber is held at a fixed low temperature such as 0°C, it slowly gets somewhat stiffened and hard and loses flexibility proportionately. However, the material still retains a good degree of flexibility and toughness. The change is also associated with some gain in density or lowering of volume, and it is understood to be due to development of crystallinity in the material.

Crystallization in ordinary low molecular weight liquid on cooling to the freezing point or below takes place very rapidly by the required molecular rearrangement from a disordered to a very regular state of packing. A polymer melt system is somewhat more complicated due to complex chain entanglements restricting free mobility of the chain segments and thus hindering and delaying the desired rearrangement process on cooling. For polymers the time scale for crystallization is usually much longer than for liquids of low molecular weight.

Trends of change in relative volume of rubber taking place during crystallization at several temperatures are shown[12] in Fig. 7.23. The maximum attainable crystallinity and the time required for this is very much dependent on the temperature. In each case the rate of volume reduction is initially quite slow; the rate gradually builds up, passes through a steady zone and then finally decays giving a limiting maximum development of crystallinity. Lowering of temperature leads to enhancement of the steady rate of crystallization till about –25°C at which point the steady rate passes through a maximum and on further reduction in temperature the crystallization rate follows a decreasing trend. The dependence of rate on temperature is shown[12] in Fig. 7.24.

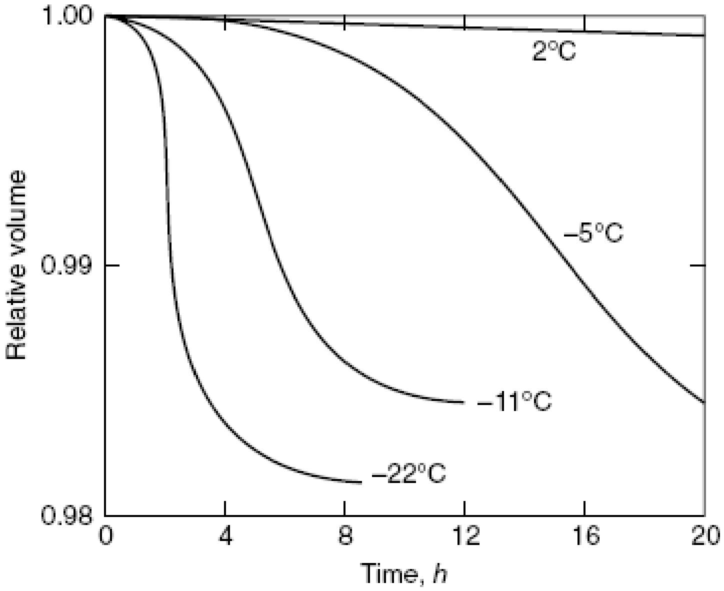

Figure 7.23. Crystallization of natural rubber; plot showing trends of change in relative volume vs time at different temperatures[12]

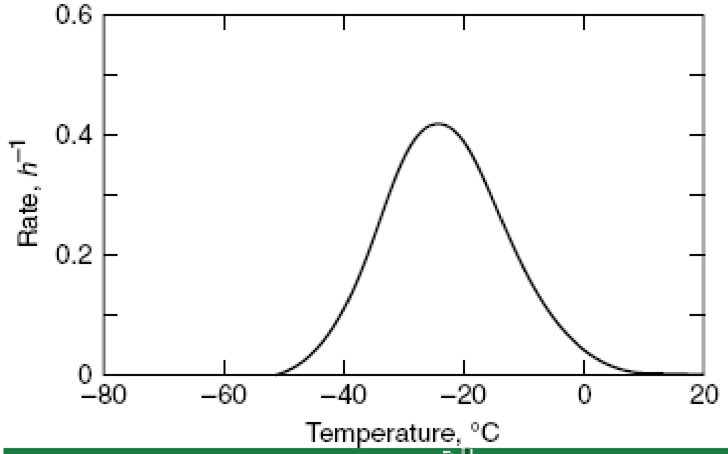

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Figure 7.24. Plot showing variation of rate of crystallization with variation of temperature for natural rubber[12] *(Wood, 1946; Courtesy, Wiley-Interscience, New York)*

The crystallization is completed in about five hours at –25°C. In natural rubber, the extent of crystallinity developed does not exceed 30%.

7.24. Mechanism of Crystallization

As the polymer melt is held at a temperature close to or slightly above its melting range, the initial delay in crystallization rate build-up is linked with the initial process of *nucleation*. Growth of crystallites is contingent upon the development and existence of a certain number of very small growth centres or nuclei for the deposition of oriented chain segments. The centres are initially formed on extended cooling or holding of the melt at the given temperature by coming together of a small number of molecular segments in the course of their random motion (micro Brownian motion) under the prevalent thermal condition. Nucleation, however, is common to all processes that turn an initially homogeneous medium into a heterogeneous system due to deposition of a separate phase.

The tiny nuclei formed initially are rather unstable and probably many of them will disappear soon after formation. But they become more stable if they survive and grow in size and finally may reach a size that assures them a permanent life and permits further growth by more deposition of the material on their surface. Larger the surface area of a nucleus, faster is the rate of deposition of the oriented segments on the surface. This explains the rapid rise in rate of crystallization just beyond the initial stage of development of crystallinity (Figs 7.22 and 7.23).

As the growth continues, the opposing effect of entanglements between molecular chains attached to neighbouring crystallites becomes more and more serious and ultimately critical, putting severe restrictions on the mobility of chain segments and thus making it difficult for them to get to a position for attachment to any one of the crystallites formed. Beyond this stage, the rate of crystallization sharply diminishes and finally the process dies down.

Lowering of temperature favours nucleation and lower thermal energy of the chain segments makes it less likely that a nucleus once formed will again disappear, the overall result being a gain in the number of nuclei and an increase in the overall rate of crystallization as the temperature is progressively lowered. However, at a very low temperature, the overall energy of the system and that available to a chain segment are so much diminished that the segments lose much of their mobility and hence their deposition on a nucleus generated is hindered more effectively. For natural rubber the crystallization process is practically frozen out below –50°C (Fig. 7.24).

7.25. Stress-Induced Crystallization

It is well known and a matter of wide experience that stretching of a strip of vulcanized rubber makes it develop a temporary crystallinity which disappears instantly on removal of the stretching force. A strip of raw or unvulcanized rubber also develops crystallinity when subjected to high extensions on application of a stretching force, but it remains in the extended state without retraction to its original state on stress release. However, when heated carefully in the subsequent stage, such as by dipping the strip into hot water, the crystals melt and the strip reverts to its unstrained state. The cross-links in the vulcanized material are responsible for accumulation of the strong restoring or retracting force which breaks the stress-induced orientation or the crystalline structure when the stress is withdrawn. In the unvulcanized form, the absence of cross-links allows varied degrees of chain slippage on extension and whatever elastic restoring force accumulates is far too insufficient to break the crystalline structure. Raising the temperature to about 30°C or to a slightly higher level to melt the crystallites allows the rubber strip to return to its original state. Time dependency of crystallization of unvulcanized rubber at a low temperature, 0°C by stretching to different fixed extensions can be studied by following density changes with time and the trends of change are shown in Fig. 7.25.

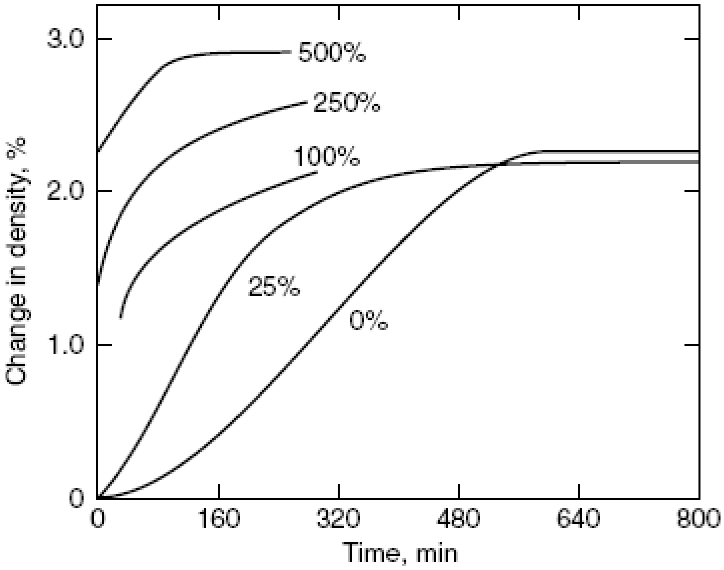


Figure 7.25. Time dependency of stress-induced crystallization (densification) of unvulcanized rubber held at a low temperature (0°C) for different orders of fixed extensions as indicated

Moderate extensions produce effects comparable to those produced by lowering of temperature. However, for extensions greater than 100%, the crystallization rates are very high and only the final stages of the process can be practically observed.

Polymer Single Crystals

Single crystals of different polymers can be grown by slow precipitation from very dilute solutions. They appear in the form of very thin plates or lamellae, usually diamond-shaped with spiral growth pattern and showing step-like formation on the surface (Fig. 7.29).

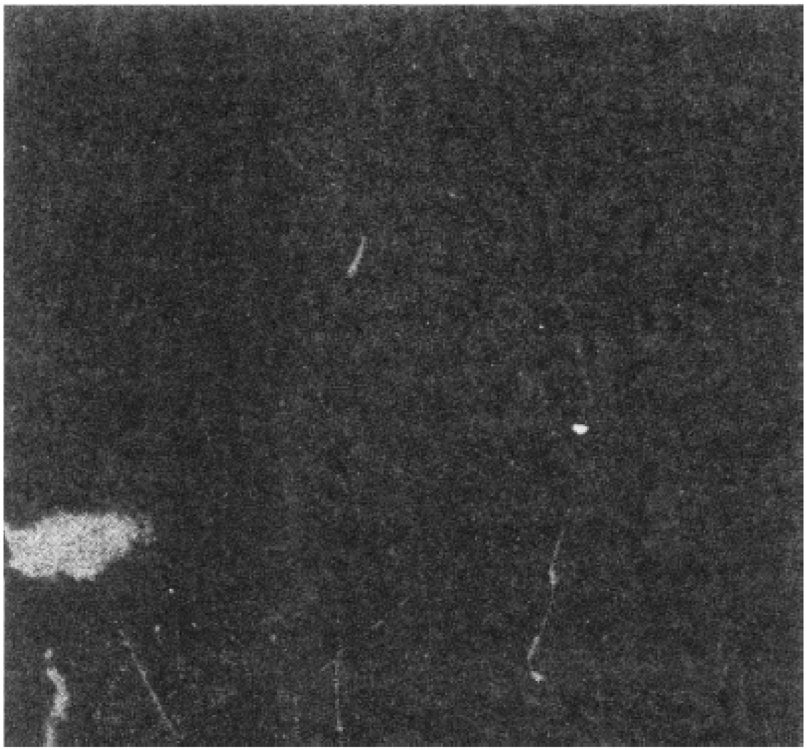


Figure 7.29. Electron micrograph of single crystals of polyethylene.[14] *(Reneker and Geil, 1960; Courtesy, American Institute of Physics, New York)*

The single crystals are very small in size and cannot be examined by X-ray diffraction. However, they are readily and conveniently studied by electron microscopy. Electron diffraction pattern and electron micrographs reveal certain interesting features about the single crystals. The thickness of the lamellae is very small (100–200 Å) compared to the length of the polymer chain. The diffraction pattern indicates without uncertainty that the chain axis is perpendicular to the plane of the lamellae. The structural pattern of the single crystal is then understood well on the basis of what is known as the folded chain theory which envisages that a single molecule of the polymer must bend or fold forwards and backwards many number of times across the thickness of the lamellae. Such folded chains can be stacked in the crystal lattice without much difficulty. It is widely believed that the single crystal comprises an array of folded chains packed individually and successively between the top and bottom surfaces, or planes, and on the growing edges of the lamellae (Fig. 7.30).

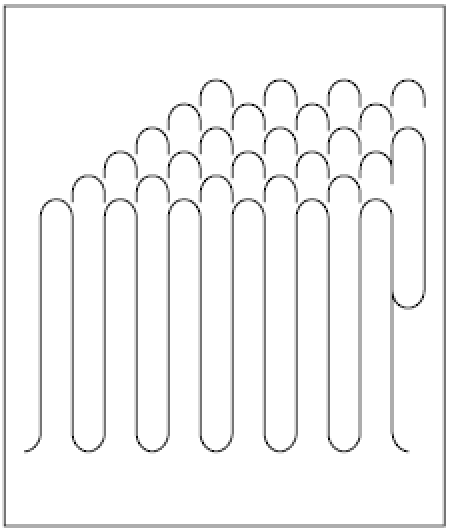


Figure 7.30. Schematic representation of chain folding in the formation of a single crystal

Crystallization of this nature involving whole individual polymer molecules discretely without interference of other molecules is made possible due to large distances that separate the individual molecules in the very dilute solution (Fig. 7.31). This wide separation ensures near elimination of chain entanglement. Thus, when one segment of a polymer molecule gets attached to one of the thin edges of the growing crystal, it faces no competition from other far away molecules for occupation of the adjacent lattice site. There will be no hindrance to the successive occupation of immediately adjacent sites by the segments of the same molecule by a chain folding mechanism until the whole molecule is used up.

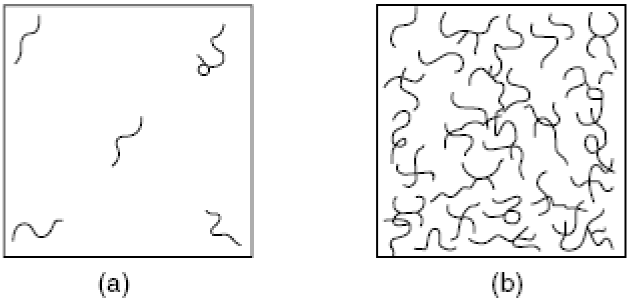


Figure 7.31. Separation between polymer molecules in (a) very dilute solution, and (b) concentrated solution (schematic representation)

7.28. Structure of Bulk Polymers

Crystalline polymers obtained on cooling of their melts also produce electron micrographs showing the lamellae structure for the crystallites[15] and giving little direct evidence for the presence of major amorphous regions (Fig. 7.32). An idealized model representation of the lamellae structure shown in Fig. 7.33(a), however, may not be applicable to all types of polymers. Most polymers (other than the different types of polyethylenes) contain amorphous regions to the tune of 20–50% distributed in the material along with the crystalline zones. In the structural model, a provision has to be made to accommodate the amorphous material. In a fringed-micelle or fringed-crystallite model [Fig. 7.33(b)], the amorphous material is interspaced between the randomly distributed crystallites. This model explains well the morphological features in such materials as rubber and some cellulosic polymers. For other polymers of intermediate orders of crystallinity, different structures combining the fringed micelle and regularly stacked lamellae model may represent the overall structural pattern. These structural concepts allow for imperfections commonly encountered, such as the interlamellar entanglements, molecular loops of varying dimensions, irregular fold lengths, and interconnecting chains passing through different lamellae.

Figure 7.32. Electron micrograph of the surface of polyoxymethylene crystallized by melt cooling[15,16] *(Geil, 1960; Courtesy, Wiley-Interscience, New York)*

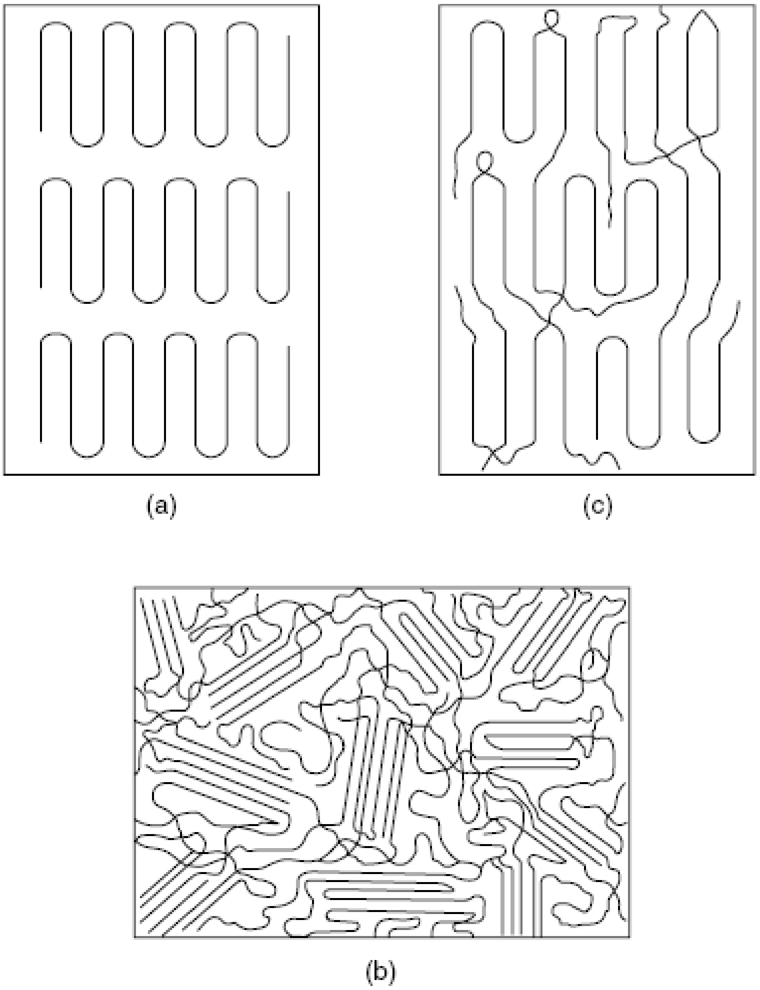
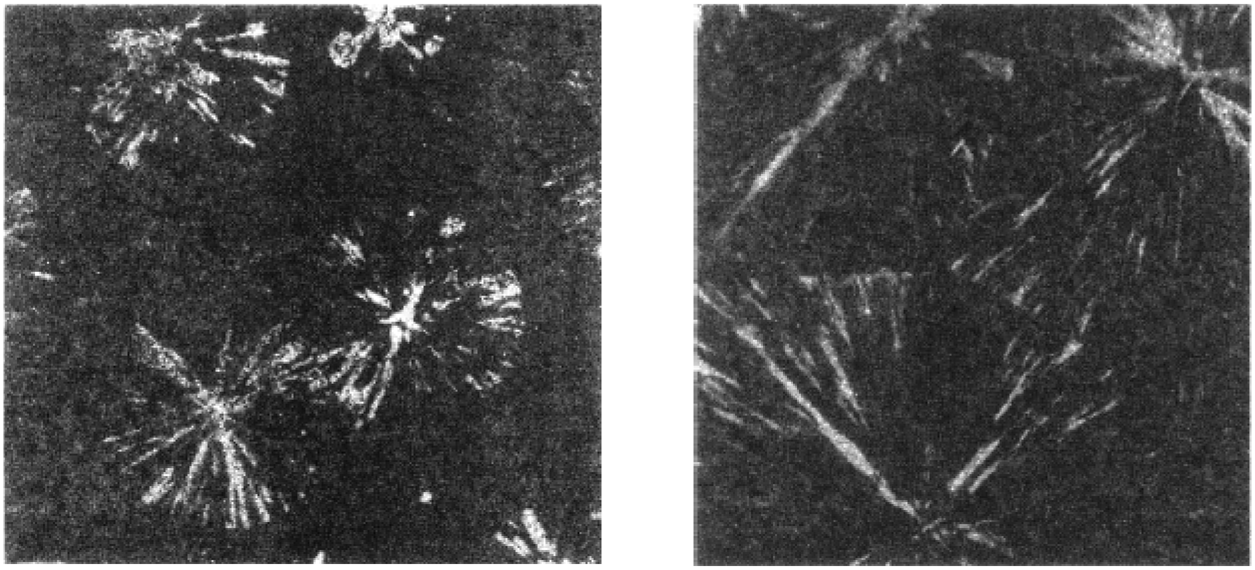


Figure 7.33. Schematic representation of: (a) ideal stacking of lamellar crystals, (b) fringed-micelle model of randomly distributed crystallites, and (c) interlamellar amorphous model

Any model consisting of stacks of lamellae interspaced with and connected by amorphous regions may be referred to as the interlamellar amorphous model [Fig. 7.33(c)]. This model provides the most useful approach to understanding the mechanical properties of bulk crystallized polymers of moderate to high degrees of crystallinity. The ductility and cohesive character is a direct consequence of the interlamellar ties. Much like stacks of bricks without mortar, stacks of lamellae (crystals) without measurable presence of tie molecules, such as those obtained by slow cooling of a very dilute solution, would prove relatively brittle. The tie molecules reduce brittleness and induce ductility.

7.29. Spherulites

The most common and prominent feature in bulk crystallized polymers is the spherulite or spherical crystallite. A spherulite is usually constituted of a symmetrical structure arising as a consequence of the cooperative growth of crystallites radially outward from a core or nucleus in three dimensions (Fig. 7.34). Bulk crystallized polymers are not merely a series of stacked lamellae separated and interconnected by amorphous regions. The lamellae units are organized radially within the spherulites (Fig. 7.35). The crystallization process through which spherulites are formed follows sequential steps of nucleation of spherulite growth. Nucleation may be aided by intentional addition of a foreign substance, called the nucleating agent. Nucleating agents reduce the size of spherulites by increasing the number of nuclei. Growth of large spherulites contributes to brittleness.



(a) (b)

Figure 7.34. Stages of spherulite growth in melt crystallized polypropylene: (a) the spherulites begin to grow from point sources, (b) their gain in size may continue until they impinge on one another

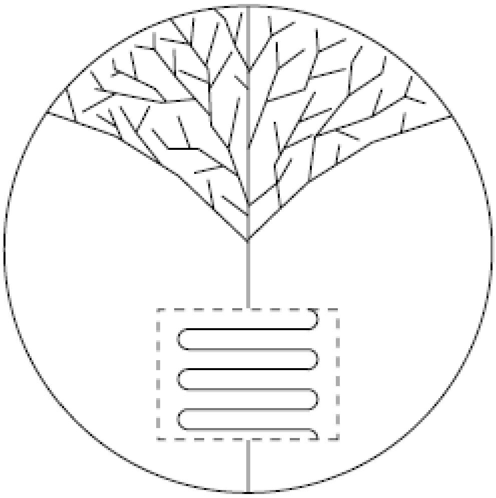


Figure 7.35. Spherulitic structure shown schematically: (1) radial growth and branching of the lamellae, (2) portion of a lamellae enlarged to indicate a folded chain structure showing chain axis perpendicular to the radius of the spherulite

Most polymers continue to increase in density long after spherulite growth is complete. The post-primary crystallization densification takes place both in the inter- and intra-spherulitic regions. The densification due to secondary crystallization taking place after the primary process of spherulite growth, leads to thickening of the lamellae as chain segments are gradually pulled in from the amorphous regions. Another consequence of secondary crystallization may be increase in brittleness. However, the process of secondary crystallization and its effect on mechanical properties are recognized to be complex and they depend largely on many factors including the rate and span of cooling, annealing and cold drawing or orientation by stretching.

Transition Phenomena in High Polymers

Raising or lowering of temperature, just as application or withdrawal of stress, greatly influences the physical structure and properties of polymers. As temperature is changed, a high polymer material usually passes two transitions characterized by (i) melting point or first order transition corresponding to the melting temperature denoted by T_m, and (ii) the second order transition or the glass transition corresponding to the temperature denoted by T_g.

7.20.1. Melting Point and First Order Transition

Melting of a crystalline solid or boiling of a liquid is associated with change of phase. Many high polymers possess enough molecular symmetry and/or structural regularity that they crystallize sufficiently to produce a solid–liquid phase transition phenomenon or melting, i.e., they have a crystalline melting point, T_m. The melting is quite sharp for a few polymers such as, the nylons, while in most other cases as for polystyrene, different rubbers, etc., the phase change takes place over a range of temperature. Phase transitions of this kind, particularly in low molecular weight materials, being associated with sharp discontinuities in some primary physical properties such as the density or volume, V, $[V = (\partial G/\partial P)_T]$ and entropy, S, $[-S = (\partial G/\partial T)_p]$, which are first derivatives of free energy, are commonly called first order transitions, (Fig. 7.16). Although we observe melting, a true first order transition or ideal melting in high polymers is frequently absent primarily in view of the distribution of molecular weight and entanglements of chain molecules in the material system.

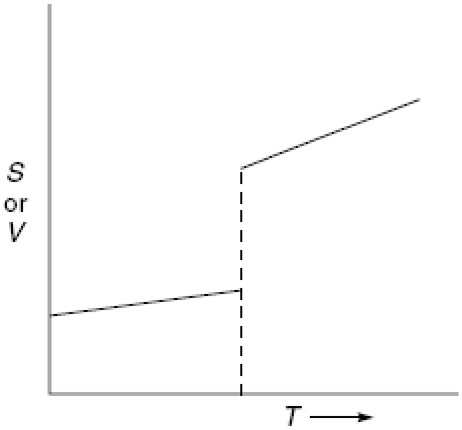


Figure 7.16. First order transition showing an idealized phase transition: Trend of change of entropy (S) or volume (V) with temperature (T)

7.20.2. Glass Transition or Second Order Transition

Glass transition or second order transition is not a phase transition and almost each polymeric or high polymeric material is characterized by a specific glass transition temperature (T_g), appearing well below its (crystaline) melting point T_m.

At T_g, the variables S, V and H merely undergo change of slope when plotted against temperature without showing sharp changes or discontinuities as observed in case of first order transitions. The properties which undergo discontinuities at the glass transition temperature are: heat capacity C_p, $[C_p = (\partial H/\partial T)_p]$, coefficient of thermal expansion α, $\left[\alpha = \frac{1}{V}(\partial V/\partial T)_P = \frac{1}{V}\,\frac{\partial}{\partial T}\{(\partial G/\partial P)_T\}_P\right]$ and isothermal compressibility K, $\left[K = -\frac{1}{V}(\partial V/\partial P)_T = -\frac{1}{V}(\partial^2 G/\partial P^2)_T\right]$ which are second derivatives of free energy, and it is for this reason that the glass transition temperature, T_g is commonly referred to as the second order transition temperature (Fig. 7.17).

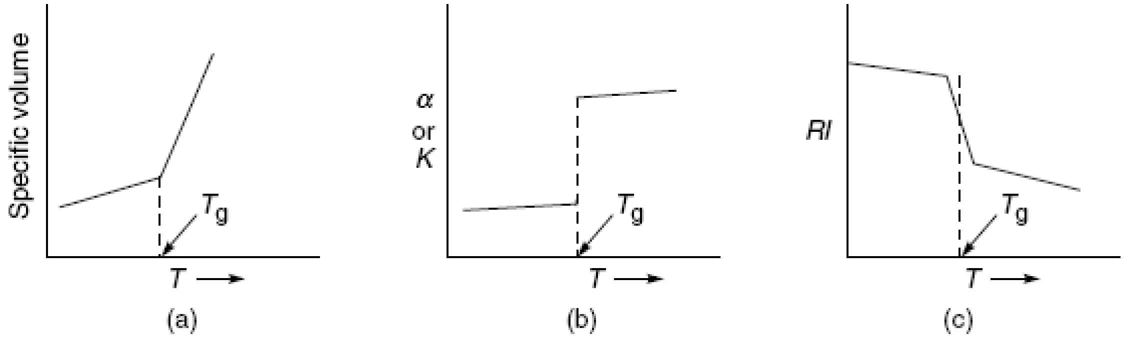


Figure 7.17. Trend of change of (a) specific volume, (b) coefficient of thermal expansion (α) or isothermal compressibility (K), and (c) refractive index (RI) with temperature indicating the glass transition point (T_g)

The glass transition is not a phase transition and so, it involves no latent heat. Below this temperature normally rubber-like polymers become rigid, hard and dimensionally stable and they are considered to be in a glassy state while above this temperature, all normally rigid, hard and stiff polymers become soft, and readily susceptible to cold flow or creep, and they turn into a rubbery state. The difference between the glassy and rubbery states of the polymer lies not in their geometrical structure, but in the state and level of molecular motion. Below the glass transition temperature, T_g, the molecular segments or groups constituting the chain backbone can undergo only limited degrees of vibration and they do not possess the energy required to rotate about bonds and change their positions with respect to segments of neighbouring chains. At or slightly above T_g, rotation sets in and it is conceivable that only the molecular segments rather than the entire high polymer molecule would rotate at this stage of transition. The much higher coefficient of thermal expansion just beyond T_g points to the greater degree of freedom of rotation.

At their respective glass transition or second order transition temperatures, different polymers may be considered to be in an isoviscous state, and as such, T_g is a common reference point for polymers of diverse nature, below which they behave as rigid plastics (glassy polymer) and above which they are rubbery in nature. For us, a useful rubber is provided by a polymer whose T_g is well below the ambient temperature and a useful plastic is one whose T_g is far above the ambient temperature. Table 7.1 gives a list of some common polymers and their T_m and T_g values.

*Table 7.1. T_m and T_g values of some polymers**

Polymer	**Repeat Unit**	**T_m °C**	**T_g °C**
**See also Table 1.3*			
Polyethylene	—CH_2—CH_2—	137	–115, –60
Polyoxymethylene	—CH_2O—	181	–85, –50
Polypropylene (isotactic)	—CH_2—$CH(CH_3)$—	176	–20
Polyisobutylene	—CH_2—$C(CH_3)_2$—	44	–73
Polybutadiene (1, 4-*cis*)	—CH_2—CH=CH—CH_2—	2	–108
Polyisoprene (1, 4-*cis*) (natural rubber)	—CH_2—$CH(CH_3)$=CH—CH_2—	14	–73
Poly(dimethyl siloxane)	—$OSi(CH_3)_2$—	–85	–123

Polymer	Repeat Unit	T_m °C	T_g °C
Poly(vinyl acetate)	—CH_2—CH($OCOCH_3$)—		28
Poly(vinyl chloride)	—CH_2—CH·Cl—	212	81
Poly(methy methacrylate)	—CH_2—C(CH_3)($COOCH_3$)—	200	105
Polytetrafluoroethylene	—CF_2—CF_2—	327	126
Poly(Caprolactam)	—$(CH_2)_5$CONH—	215, 223	50
Poly(hexamethylene adipamide)	—HN$(CH_2)_6$—NHCO— $(CH_2)_4$CO—	264	53
Poly(ethylene terephthalate)	—O$(CH_2)_2$—O·CO—(C_6H_4)CO—	254	69
Poly(ethylene adipate)	—O$(CH_2)_2$—OCO—$(CH_2)_4$CO—	50	–70

Molecular weight, external tension or pressure, plasticizer incorporation, copolymerization and cross-linking are some of the more important factors that influence the glass transition temperature and the melting point of polymers. The comparative lowering of T_m and T_g for polymer modification by plasticizer incorporation and by copolymerization (comonomer incorporation) is shown in Fig. 7.18. In general, a comonomer incorporation, i.e., copolymerization is more effective than plasticization in lowering the melting point, while plasticization is normally more effective than copolymerization in lowering the glass transition point. Cross-linking tends to increase the glass transition temperature as the cross-links inhibit the freedom of the chain segments to rotate, necessitating a higher temperature for inception of rotation. Similarly, higher molecular weight of linear chains restricts scope for segmental rotation and hence causes rise in T_g, with a levelling off effect in the higher molecular weight range, however.

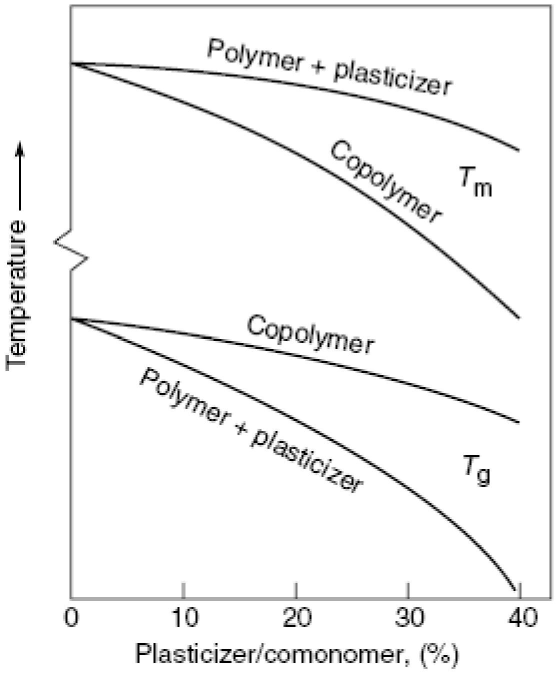


Figure 7.18. Schematic plots showing comparative lowering of T_m and T_g of a polymer by separately incorporating: (i) a plasticizer and (ii) a comonomer by copolymerization

7.20.3. Measurement of Glass Transition Temperature

The glass transition temperature, T_g, is conveniently measured in the laboratory by taking help of dilatometry (Fig. 7.19). The polymer appropriately confined in the bulb at the bottom is kept immersed in a suitable liquid, usually mercury so as to give a column of the liquid in the capillary up to a convenient height for measurement. The positioning of the glass plug, as shown, enables heating the test specimens avoiding overheating. The dilatometer placed in an outer bath may be heated at a preset rate and pattern. From the rise of the liquid in the capillary on heating and consequent rise in temperature, the change in volume of the specimen (taking into account the volume expansion of the liquid, etc.) may be conveniently obtained. A typical plot showing variation of specific volume with change of temperature for polystyrene is shown in Fig. 7.20.

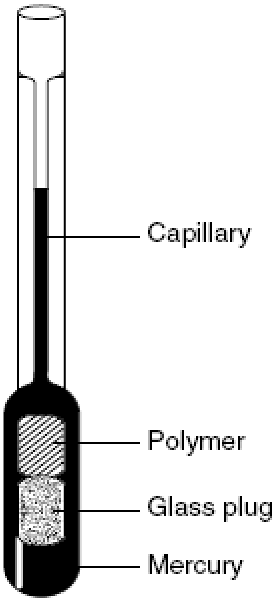


Figure 7.19. A dilatometric set up for measurement of change in volume of a polymer with change in temperature

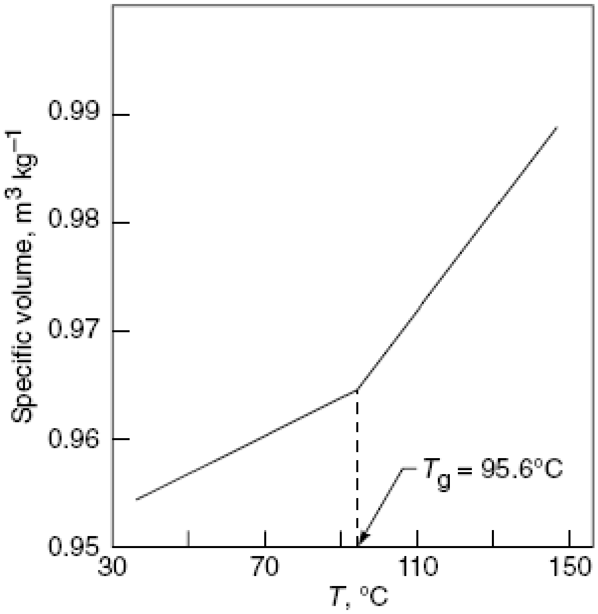


Figure 7.20. Volume expansion of polystyrene with rise in temperature: the inflection point corresponds to T_g

The Concept of Average Molecular Weight

A given polymer material is mostly a mixture of molecules of (nearly) identical chemical structure but varying in chain length or molecular weight. The molecules produced in polymerization reactions have lengths that are distributed in accordance with a probability function which is governed by the mechanism of the reaction and by the conditions under which it has been carried out. The concept of average molecular weight is, therefore, important and relevant and the assignment of a numerical value to the molecular weight of polymer requires the definition of a particular average. An average molecular weight $\overline{M}$ may be generally expressed as

$$\overline{M} = f_1M_1 + f_2M_2 + f_3M_3 + \ldots = \Sigma f_iM_i$$

(6.13)

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

$$\overline{M} = \frac{\Sigma N_iM_i^a}{\Sigma N_iM_i^{(a-1)}}$$

(6.14)

where N_i is the number of molecules with molecular weight M_i and the index 'a' may have any real value. Two most important averages are: (i) number average molecular weight and (ii) weight average molecular weight. Setting $a = 1$, one obtains the expression for number average moleclar weight, $(\overline{M}_n)$ from Eq. (6.14), i.e.

$$\overline{M}_n = \frac{\Sigma N_iM_i}{\Sigma N_i}$$

(6.15)

Equation (6.15), in effect, can be expressed as a summation series resembling Eq. (6.13) where the fractional coefficients represent mole fractions of the respective molecular species present in the system, knowing that total weight $W = \Sigma N_iM_i$ and total number of molecules $N = \Sigma N_i$. Thus,

$$\overline{M}_n = \frac{W}{N} = \frac{\Sigma N_iM_i}{\Sigma N_i} = \frac{N_1}{N}\cdot M_1 + \frac{N_2}{N}\cdot M_2 + \frac{N_3}{N}\cdot M_3 + \ldots$$
$$= f_1M_1 + f_2M_2 + f_3M_3 + \ldots$$

(6.16)

On the other hand, setting $a = 2$ in Eq. (6.14), one obtains the expression for weight average molecular weight $(\overline{M}_w)$, i.e.

$$\overline{M}_w = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$$

(6.17)

Equation (6.17) may also be rearranged and expressed as a summation series as given by Eq. (6.13), but in this case the fractional coefficients correspond to weight fractions of different molecular species present. Thus,

$$\bar{M}_w = \frac{\Sigma N_i M_i \cdot M_i}{\Sigma N_i M_i} = \frac{\Sigma w_i M_i}{\Sigma w_i} = \frac{\Sigma w_i M_i}{W}$$

$$= \frac{w_1}{W} \cdot M_1 + \frac{w_2}{W} \cdot M_2 + \frac{w_3}{W} \cdot M_3 + \ldots$$
$$= f_1 M_1 + f_2 M_2 + f_3 M_3 + \cdots$$
(6.18)

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

The consequence of definitions given above is that $\bar{M}_w \geq \bar{M}_n$; the equality, however, corresponds to the limiting case of a perfectly monodisperse sample. The deviation from unity of the ratio $\bar{M}_w / \bar{M}_n$, known as the distribution ratio, is taken as a measure of polydispersity of polymer samples, a higher value of the ratio indicating greater polydispersity.

Evaluation of number average molecular weight is useful in understanding the polymerization mechanism and kinetics. The evaluation of $\bar{M}_n$ is also useful in the analysis of kinetic data to examine the effects of many side reactions including chain transfer, inhibition and retardation, and autoacceleration or gel effect in vinyl polymerization. The number average molecular weight also assumes prime importance in determining the solution properties of the polymer, commonly known as the colligative properties. Polymer molecules of lower molecular weight contribute equally and enjoy equal status with those of higher molecular weight in determining these properties.

Weight average molecular weight, on the other hand, is important in relation to bulk properties of polymers that reflect their load bearing capacity. Softening, hot deformation, tensile and compressive strength, modulus and elongation, toughness and impact resistance and some other related bulk properties of polymer 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 sample and other related factors in this context.

6.6. Viscosity Average Molecular Weight

The viscosity of a polymer solution (η) is higher than that of the pure solvent (η_0) at a given temperature and the gain in medium viscosity on dissolving the polymer in the solvent is a function of both molecular weight and concentration of the polymer solute. Even though the solution viscosity is easy to measure, it does not give a direct and absolute value of molecular weight. If the polymer solution is very dilute and consequently the density change of the solvent due to dissolved polymer is negligible, then the viscosities of the solution and solvent at a given temperature would be proportional to their flow times in a capillary viscometer such that the relative viscosity, η_r expressed as the ratio, η/η_0 would be given by the flow time ratio t/t_0 where t and t_0 are the flow times of the solution and solvent respectively. Both relative viscosity (η_r) and specific viscosity (η_{sp}) defined as $\eta_{sp} = (\eta - \eta_0)/\eta_0$ are dimensionless. If the solute macromolecules do not interfere with one another during flow, the viscosity gain is proportional to their concentration and η_{sp}/c, commonly known as the reduced viscosity, would be a constant. But for polymer solutions, η_{sp}/c is generally found to increase with increase in c. 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 plot of η_{sp}/c vs c when the linear experimental plot is extrapolated to zero concentration, or more precisely, to infinite dilution condition. The concentration dependence of polymer solution viscosity is conveniently expressed by two empirical equations, known as Huggins' Equation[16] given by Eq. (6.19) and Kraemer's Equation[17]given by Eq. (6.20), i.e.

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2 c$$
(6.19)

and

$$\ln \eta_r/c = [\eta] + k_2[\eta]^2 c$$
(6.20)

The term ln η_r/c is commonly termed as inherent viscosity. The reduced viscosity, inherent viscosity and intrinsic viscosity are expressed in units of reciprocal concentration and usually in decilitre per gram (*c*, expressed in g/100 cc). The constants, k_1 and k_2 are known as the Huggins constant and Kraemer constant respectively. For most cases, k_2 is negative and in a general manner $k_1 - k_2 = 0.5$. The slope of each plot, left hand side vs *c* based on Eqs (6.19) and (6.20) are proportional to square of the intercept, i.e., of the intrinsic viscosity, and the two plots made using common ordinate and abscissa would extrapolate to a common point on the ordinate, thus enabling a precise determination of the [η] value (Fig. 6.1).

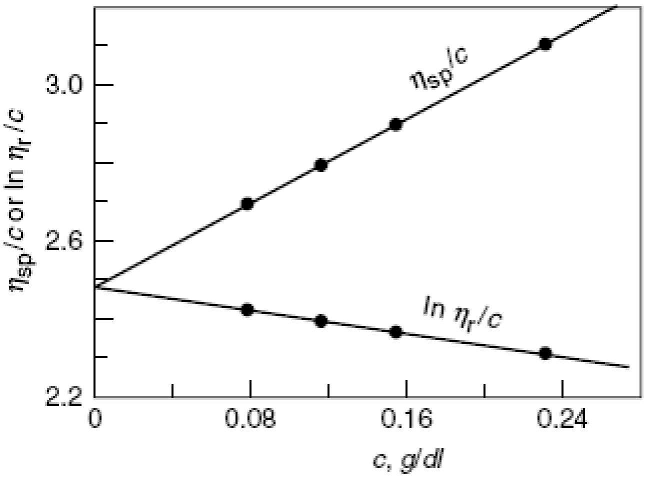


Figure 6.1. Typical plots showing η_{sp}/c vs c and ln η_r/c vs c using common ordinate and abscissa for the determination of intrinsic viscosity [η] of a given polymer–solvent system at a given temperature

The relationship between [η] and the viscosity average molecular weight $\bar{M}_v$ is given by the semi-empirical Mark-Houwink equation:

$$(\eta_{sp}/c)_{c \to 0} = [\eta] = K \bar{M}_v^a$$
(6.21)

where *K* and *a* are constants for a particular polymer–solvent system at a given temperature. This equation provides a basis for determining molecular weight from viscosity measurements. The values of $\bar{M}_v$ obtained are not absolute in view of incomplete interpretations of *K* and *a*. The values of *K* and *a* must normally be determined by measuring the [η] values of monodisperse polymer samples whose molecular weights have been obtained from one of the absolute methods such as osmometry and light scattering and making use of a plot[18] of log [η] vs log *M* (Fig. 6.2). The exponent *a* varies with both the polymer and the solvent; its value usually ranges between 0.5 and 0.8. It does not fall below 0.5 in any case and exceeds 0.8 in exceptional cases particularly for polyelectrolytes in the absence of added salts.

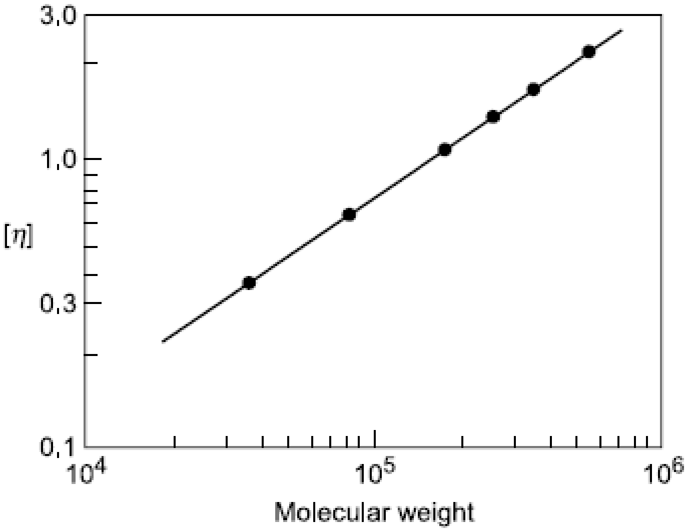


Figure 6.2. Intrinsic viscosity–molecular weight relationship at 30° for polyisobutylene in cyclohexane[18] *(Krigbaum and Flory, 1953; Courtesy, American Chemical Society, Washington)*

For most systems, K and a are best understood when $[\eta]$ is determined in a solvent at what is known as the theta (θ) temperature. The value of a is then equal to 0.5 and K depends on the temperature while remaining independent of the solvent, keeping in mind, however, that the solvent fixes the temperature of measurements. At the θ temperature, the chemical potential due to polymer (segment)–solvent interactions is zero and the deviations from ideality just vanish. Therefore, the free energy of interactions of the segments within a volume element is also zero. In fact, θ temperature is the lowest temperature for complete miscibility in the poor solvent used at the limit of infinite molecular weight. The ideality is struck at the θ temperature because the molecular dimensions are unperturbed by intramolecular interactions (*See* Sec. 6.15).

6.6.1. General Expression for Viscosity Average Molecular Weight

For determination of the intrinsic viscosity, it is necessary to extrapolate the η_{sp}/c vs c plot to infinite dilution ($c \rightarrow 0$), since it is only under this condition that 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 degree of swelling is higher in a better solvent. Likewise, the intrinsic viscosity is also higher in a good solvent than in a poor solvent. What it really means is that in a better solvent, as the polymer goes into solution, a unit mass of polymer expands more to give a higher hydrodynamic volume.

Let us now consider a heterogeneous polymer in dilute solution of concentration c behaving ideally in that the individual molecules contribute to viscosity independently of one another. In that event, if $(\eta_{sp})_i$ is the specific viscosity contribution due to species of size i, then one may write:

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

(6.22)

considering c_i and M_i as the concentration and molecular weight of the said species and in view of the ideal specific viscosity component $(\eta_{sp})_i = KM_i^a c_i$, one further obtains

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

(6.23)

and hence,

$$\eta_{\mathrm{sp}}/c = [\eta] = K\,\Sigma M_i^a c_i/c$$
(6.24)

where, $c = \Sigma\, c_i$, stands for the total concentration of all polymer species. Taking $c = \Sigma N_i M_i$ and $c_i = N_i M_i$, Eq. (6.24) may be expressed as:

$$[\eta] = K\,\frac{\Sigma N_i M_i^{(1+a)}}{\Sigma N_i M_i}$$
(6.25)

Combining Eq. (6.25) with the Mark–Houwink equation, the general expression for the viscosity average molecular weight becomes:

$$\overline{M}_v = \left\{\frac{\Sigma N_i M_i^{(1+a)}}{\Sigma N_i M_i}\right\}^{1/a}$$
(6.26)

Clearly, for a approaching the value of unity, $\overline{M}_v$ approaches $\overline{M}_w$ and in the limiting case of $a = 1$, $\overline{M}_v = \overline{M}_w$.

The viscometric studies of polymer solutions as a means of molecular characterization of polymers are well recognized and widely practised because of simplicity in terms of experimental approach and the apparatus needed. Dilute solution viscosity is conveniently measured in capillary viscometers of different kinds such as the Ostwald type or the Ubbelohde type (Fig. 6.3). Ubbelohde viscometer is a suspended level viscometer and it has the advantage that the flow time measurements are not dependent on the volume of liquid (solution or solvent) in the viscometer and hence, measurements at a series of concentrations can be conveniently made by successive dilution within the viscometer. All flow time measurements for the solvent and solutions of different concentrations are made in a thermostat bath regulated within ±0.1°C. The flow time data should then be treated graphically according to Eq. (6.19) or (6.20) and then extrapolated to infinite dilution ($c \rightarrow 0$) to obtain the value of the intrinsic viscosity, $[\eta]$ as described earlier. $\overline{M}_v$ can then be evaluated using the Mark–Houwink equation and using the appropriate K and a values from the literature, if available, or from an independent determination as described earlier in this section.

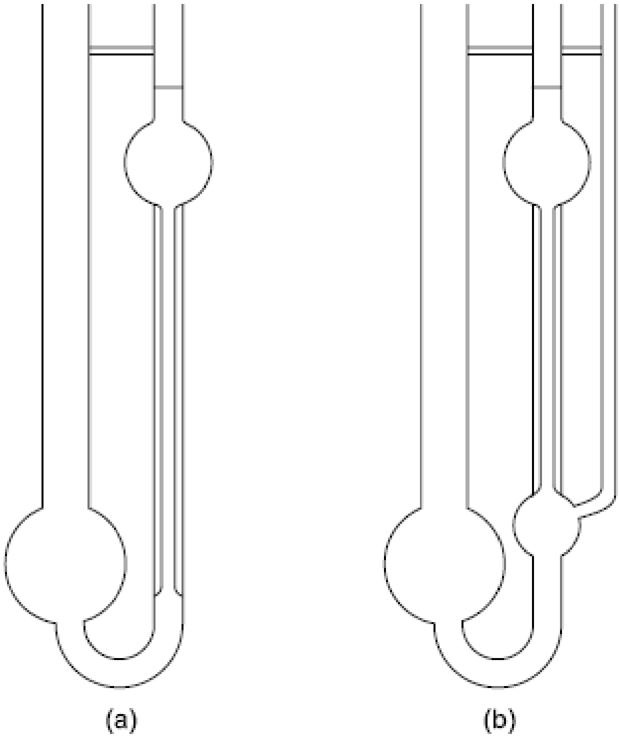


Figure 6.3. Capillary viscometers: (a) Ostwald type, (b) Ubbelohde type

6.7. Number Average Molecular Weight

Number average molecular weight can be conveniently evaluated using a polymer solution and taking recourse to ebulliometric, cryoscopic and osmometric measurements. Direct measurement of vapour pressure lowering in dilute polymer solutions lacks precision and hence often leads to uncertain results. However, vapour-phase osmometry permits indirect utilization of vapour pressure lowering and this technique led to development of equipment which can measure a temperature difference that is proportional to the vapour pressure lowering of polymer solution at equilibrium, as can be related through the Clapeyron equation. Temperature differences thus noted are of the same order of magnitude as those to be observed in cryoscopy or ebulliometry; these methods customarily require calibration with low molecular weight standards and usually give reliable results for molecular weight up to 30,000. However, lack of development of equipment for ebulliometric and cryoscopic techniques has turned them much less relevant and useful.

6.8. Membrane Osmometry

Consider a solution of a polymer separated from the pure solvent by a semipermeable membrane; the chemical potential of the solvent, in solution (μ_s) is less than that of the pure solvent (μ_0) and consequently, to keep the system in equilibrium, the chemical potential of the solvent on either side of the membrane must be balanced or made equal. This may be conveniently done by applying an excess pressure, called the osmotic pressure π to the solution side to compensate for the deficiency in chemical potential. Thus, the condition of equilibrium for the chemical potential of the solvent on the two sides of the osmometer membrane gives

$$\mu_0 - \mu_s = \Delta\mu_1 = -\pi\overline{V}_1$$

(6.27)

or,

$$RT \ln f_1 x_1 = -\pi \overline{V}_1$$
(6.28)

where, *R* is the universal gas constant, *T*, the absolute temperature, $\overline{V}_1$ the partial molar volume and f_1 the activity coefficient of the solvent in solution. For a very dilute solution, $f_1 \rightarrow 1$ and $\overline{V}_1$ may be taken as equal to the molar volume, V^0_1 of the pure solvent. Replacing solvent mole fraction x_1 by $(1 - x_2)$ where $x_2$is the mole fraction of the solute in solution, and expanding the logarithm factor, one obtains for a very dilute solution:

$$\pi \overline{V}_1^0 = RT \left(x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \ldots \right)$$
(6.29)

If *c* is the concentration in gram per unit volume of solution, then x_2 is given by

$$x_2 = \frac{c/\overline{M}_n}{1/V_1^0 + c/\overline{M}_n} \simeq \frac{V_1^0 c}{\overline{M}_n}$$
(6.30)

combining Eqs (6.29) and (6.30), one obtains

$$\pi/c = \frac{RT}{\overline{M}_n} \left\{ 1 + \frac{1}{2} \cdot \left(\frac{V_1^0}{\overline{M}_n} \right) c + \frac{1}{3} \cdot \left(\frac{V_1^0}{\overline{M}_n} \right)^2 c^2 + \ldots \right\}$$
(6.31)

Polymer solutions largely deviate from ideality and the activity coefficient *f*, is less than unity even at the lowest concentration at which accurate osmometric measurements can be made. The real coefficients of the concentration terms are somewhat higher in magnitude than those in the equation above. Even then, π/c may be expressed as a power series in *c* using empirical coefficients, viz.,

$$\pi/c = RT(A_1 + A_2 c + A_3 c^2 + \ldots)$$
(6.32)

or alternatively,

$$\pi/c = \frac{RT}{\overline{M}_n} (1 + \Gamma_2 c + \Gamma_3 c^2 + \ldots)$$
(6.32a)

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

The coefficients A_2, A_3, etc. are known as the second, third etc. virial coefficients. In most cases, the term in c^2 and higher powers of *c* may be neglected. Thus, π/c is measured as a function of *c* and plotted on a graph paper (Fig. 6.4a) and extrapolation[19] of the plot to $c \rightarrow 0$ gives an intercept on the π/c axis which is equal to $RT/\overline{M}_n$. Alternatively, (π/RTc) may be plotted against *c* (Fig. 6.4b). Evaluation of the number average molecular weight then readily follows from the intercept. The plots are usually linear and in each case, the slope allows evaluation of the second virial coefficient. In good solvents and at high concentrations, the plots may deviate from straight line and tend to become concave upward. In that event, a plot of $(\pi/RTc)^{1/2}$ vs c gives a linear plot. The slopes of plots shown in Fig. 6.4 or the values of the second virial coefficient allow evaluation of the respective polymer solvent interaction. Both slope and curvature are zero at θ temperature. The membrane osmometry is based on the principle illustrated in Fig. 6.5. The membrane is critically important. It should offer high permeability for solvent molecules and practically no permeability to the smallest macromolecules present in the polymer under study. All measurements must be made at a specified and constant temperature. The thermodynamic drive to reach equilibrium causes the liquid level in the capillary in the solution side to rise till the hydrostatic pressure on the membrane in the solution side balances the osmotic pressure on the same in the solvent side. A measure of the difference in liquid levels in the two capillaries after attainment of equilibrium is used to calculate the osmotic pressure. Among the different kinds of membrane, those based on cellulose such as regenerated cellulose (gel cellophane), are used most widely; other suitable membrane materials are collodion (nitrocellulose, 11–13.5% N_2) and denitrated collodion, poly(vinyl alcohol), poly(vinyl butyral) etc. Among the different types of osmometer cells and assembly, the one based on Zimm-Meyerson design (Fig. 6.6), is more popular because of its simplicity.[20] Typical time period required for the attainment of equilibrium in classical osmometers using dilute polymer solutions is in the range of 10–20 h.

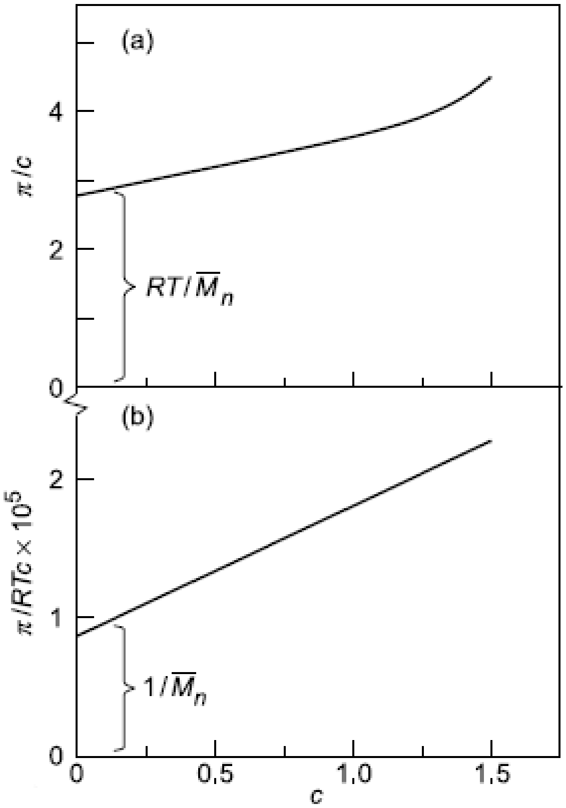


Figure 6.4. Typical plots showing (a) π/c vs and (b) π/RTc vsc for determination of M-macr$_n$.

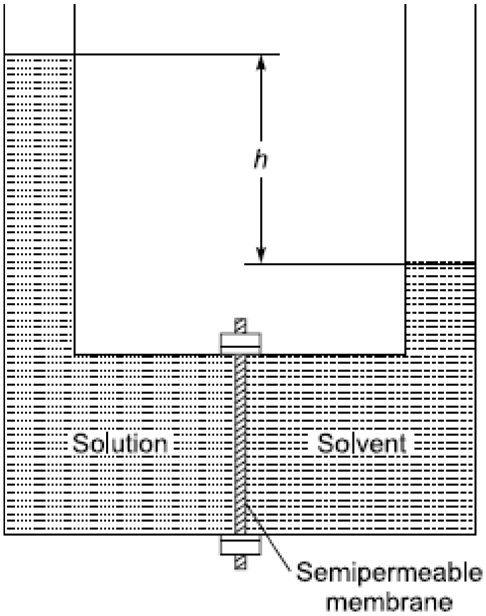


Figure 6.5. Operating principle of a membrane osmometer

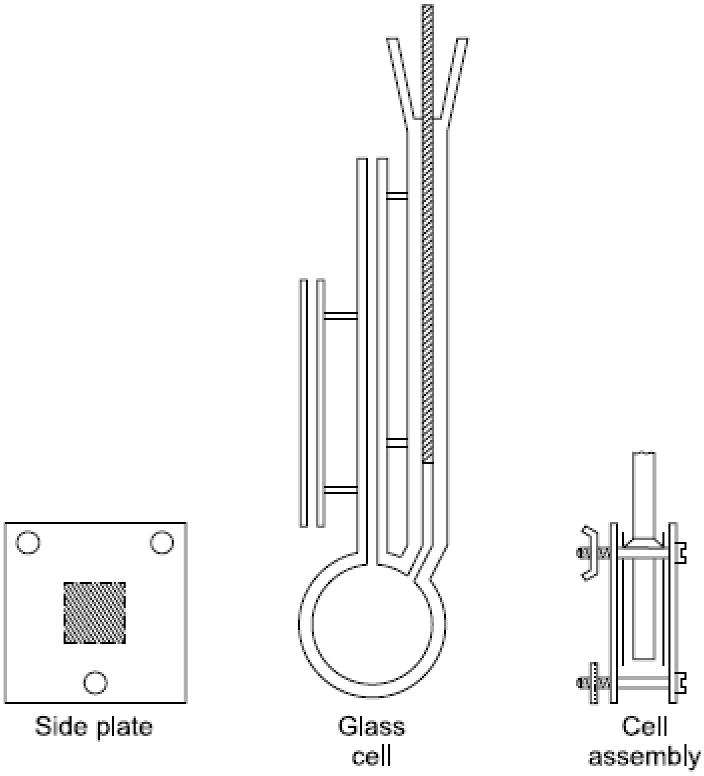


Figure 6.6. Sketch of a Zimm-Meyerson osmometer

However, different models of high speed osmometers are now-a-days available. Their design features closed solvent compartment gadgeted with a sensitive pressure-sensing device without the use of a capillary. The equipment may use a photoelectric or capacitance detecting device using a servo mechanism, or else a strain gauge for direct pressure detection. The high speed equipments allow attainment of equilibrium often in less than 5 min.

6.9. Weight Average Molecular Weight: Light Scattering by Polymer Solutions

The phenomenon of scattering of light[21] by the molecules of a gas (Rayleigh scattering) or by colloidal particles suspended in a liquid medium (Tyndall scattering) is well known. The intensity of the scattered light depends on the polarizability of the molecules or particles compared with that of the medium in which they are contained, i.e. dissolved or suspended. It also depends on the molecular or particle size and on their concentration. If the solution/suspension is sufficiently dilute, the intensity of scattered light is equal to the sum of the contributions from the individual molecules/particles, each being unaffected by the others in the medium.

Light passing through an optically inhomogeneous medium is scattered in all directions and the intensity of the transmitted beam decreases exponentially. The turbidity τ is simply defined by

$$I = I_0 e^{-\tau l}$$
(6.33)

where I_0 and I are the intensities of the beam before and after passing through a path of length, l, of the medium.

Let us consider a polymer solution. Thermal agitation of the molecules in solution causes instantaneous local fluctuations of density and concentration. If the solute and solvent have different polarizabilities, the intensity of light scattered by a tiny volume element varies with these fluctuations continuously and arbitrarily. Consequent to these variations in intensity, the rays scattered by two volume elements so situated as to produce interference at a point of observation, will not cancel each other.

In a dilute solution, the work needed to produce a concentration fluctuation is less than that required to produce a density fluctuation corresponding to equal scattering power. Concentration fluctuations are the main origin of scattered light from a dilute polymer solution. The effect due to 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 required to produce a given concentration fluctuation is related directly to the free energy of dilution, ΔG_1. The intensity of scattered light can therefore be used to measure the thermodynamic properties. The scattered light intensity from a solution is commonly expressed in terms of its turbidity, which is the fraction by which the intensity of the scattered beam is reduced over 1 cm path length of solution as related by Eq. (6.33). For polymer molecules small in comparison with the wavelength of light used, τ is also expressed as

$$\tau = \frac{32\pi^3 kTn^2 c(\partial n/\partial c)^2 \overline{V}_1}{3\lambda^4 (-\partial \Delta G_1/\partial c)}$$
(6.34)

Here, k is Boltzman's constant, n, the refractive index of the medium, $(\partial n/\partial c)$, the change in refractive index with concentration where c is the concentration, λ, the wavelength of the incident beam and ΔG_1signifies the difference between the molar free energy of the pure solvent and the partial molar free energy of the solvent in solution. Now, $\Delta G_1 = -\pi \overline{V}_1$ where π is osmotic pressure, and using the relation between osmotic pressure and molecular weight one may write

$$-(\partial \Delta G_1/\partial c) = \frac{RT\overline{V}_1}{M}(1 + \Gamma_2 c + \ldots)$$
(6.35)

Combining Eqs (6.35) and (6.34) one gets

$$H \cdot \frac{c}{\tau} = \frac{1}{M}\ (1 + \Gamma_2 c + \ldots)$$
(6.36)

where $H = (32\pi^3 n^2 / 3\lambda^4 N)(\partial n/\partial c)^2$, and $N = R/k$ is the Avogadro number. If τ is determined as a function of c and Hc/τ is then plotted against c, then the intercept on the Hc/τ axis obtained by extrapolation to zero concentration (Fig. 6.7) allows ready calculation of the molecular weigh M, which can be shown to be the weight average molecular weight, $\overline{M}_w$.

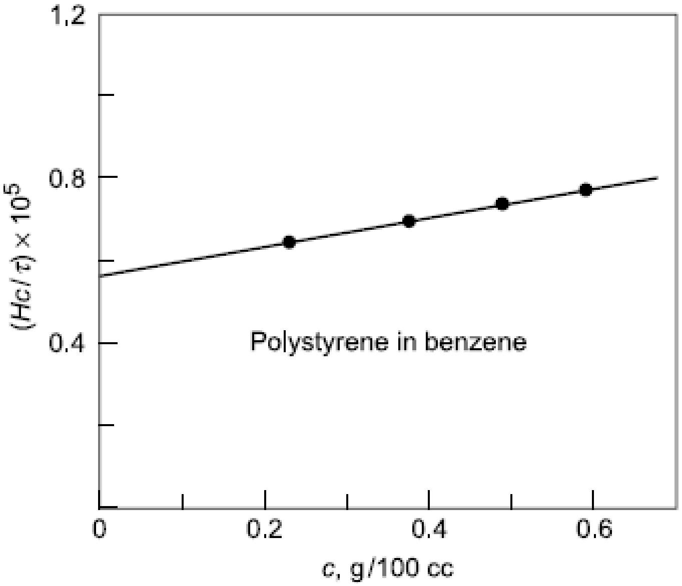


Figure 6.7. A typical plot of Hc/τ vs c for determination of M-macr$_w$

The polarizability of a molecule is a function of the number and kinds of atoms constituting the molecule. It is obvious then that the polarizability of a molecule made up of many identical units, i.e. of a polymer molecule is proportional to the number of units and therefore, the degree of polymerization and hence the molecular weight. The intensity of light scattered by a molecule is proportional to the square of its molecular weight. The intensity of light scattered by N_i molecules of molecular weight M_i in a unit volume of solution is, thus, proportional to $N_i M_i^2$ and the total intensity of light scattered by all the molecules in the unit volume is proportional to $\Sigma N_i M_i^2$ and the total weight of the polymer molecules contained in the unit volume is given by $c = \Sigma N_i M_i$. Hence,

$$\tau/c \propto \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \simeq \overline{M}_w$$
(6.37)

According to Rayleigh's law, the angular variation of the intensity of unpolarized light scattered by a molecule much smaller than the wavelength, λ of the incident light is proportional to $(1 + \cos^2\theta)$, where θ is the angle between the incident and scattered beam. It is, however, necessary to measure the scattered intensity i_θ at only one angle, θ for calculation of τ, and according to Rayleigh

$$\tau = \frac{16\pi i_\theta r^2}{3I_0(1+\cos^2\theta)} = \frac{16\pi}{3} \cdot R_\theta$$

(6.38)

where $(i_\theta r^2)/I_0\ (1 + \cos^2 \theta) = R_\theta$ is known as the Rayleigh ratio and it is independent of θ. Here, I_0 is the incident intensity and r is the distance from the scattering particle to the point of observation. Normally, if the scattered intensity at zero angle, i_0 (along the direction of the incident beam) could be measured, one could obtain the value of τ using Eq. (6.38). However, direct observation of i_0 is not practically possible as the much more intense incident beam would also be observed at the same time. R_θ may also be expressed as

$$R_\theta = \frac{Kc}{1/M + A_2c + \ldots}$$

(6.39)

and K is an optical constant given by the expression:

$$K = \frac{2\pi^2 n^2 (\partial n/\partial c)^2}{\lambda^4 N}$$

(6.40)

Equation (6.39) may be rearranged for the determination of molecular weight in the following form to allow a plot of (Kc/R_θ) vs c.

$$\frac{Kc}{R_\theta} = \frac{1}{M} + A_2c + \ldots$$

(6.41)

The intercept at $c = 0$ gives the molecular weight and the limiting slope gives a measure of the second virial coefficient, A_2. The above relationship is particularly applicable for particles much smaller than λ, but it applies to larger solute particles as well for values of Kc/R_θ extrapolated to $\theta = 0°$. The effect of large size may, however, be described by a function, $P(\theta)$:

$$P(\theta) = \frac{\text{Scattered intensity (with intraparticle interference) for large particles}}{\text{scattered intensity without interference}}$$

$$= i_\theta/i_\theta^0 = R_\theta/R_\theta^0$$

(6.42)

$P(\theta)$ is usually much less than 1 when θ is large and its value increases as θ becomes smaller. For $\theta = 0°$, $P(\theta)$ is unity, and Eq. (6.41) is applicable in this limiting condition. For large particles, equation (6.41) is modified to

$$(Kc/R_\theta) = (1/M \cdot P(\theta)) + A_2c + \ldots$$

(6.43)

In view of difficulty in direct measurement of i_θ for $\theta = 0°$ and in view of the fact that any equation for $P(\theta)$ is valid only at very high dilutions, it is necessary to extrapolate the appropriate scattering data at each angle to zero concentration, before one does the extrapolation to $\theta \to 0°$ to use $P(\theta)$ data for evaluation of molecular weight. At the same instance, it is required to extrapolate the data at each concentration to zero angle for evaluation of the weight average molecular weight $(\overline{M}_w)$ and the second virial coefficient using Eq. (6.41), which for polymer (large) molecules is valid only at zero angle.

The two objectives are combined in one graphical plot as developed by Zimm.[22] The scattered intensity is measured as a function of angle for several solutions of successively decreasing concentrations. A plot is then prepared using Kc/R_θ as the ordinate and $\sin^2(\theta/2) + kc$ as the abscissa where k is an arbitrary constant so chosen as to permit a suitable spread of the data on the piece of graph paper (Fig. 6.8). From such graphical presentation of data, two types of limiting plots are obtained; (i) through extrapolation to $\theta = 0°$, at constant c, and (ii) through extrapolation to $c = 0$, at constant θ. Each set of extrapolated points thus obtained are joined by a curve or line which can be extrapolated to give an intercept on the Kc/R_θaxis, and the intercept gives the value of $1/\overline{M}_w$. The fact that both curves should extrapolate to the same point on the ordinate increases the precision of the determination of $\overline{M}_w$. From the Zimm plot, the slope of the limiting curve corresponding to $\theta = 0°$ gives the second virial coefficient. The mean square radius of gyration, S^2_z of the particles is given by the slope and intercept corresponding to the other limiting curve in the Zimm plot (for $c = 0$), according to the relationship:

$$S_z^2 = (3\lambda^2/16\pi^2 n^2) \cdot (\text{slope}/\text{intercept})$$

(6.44)

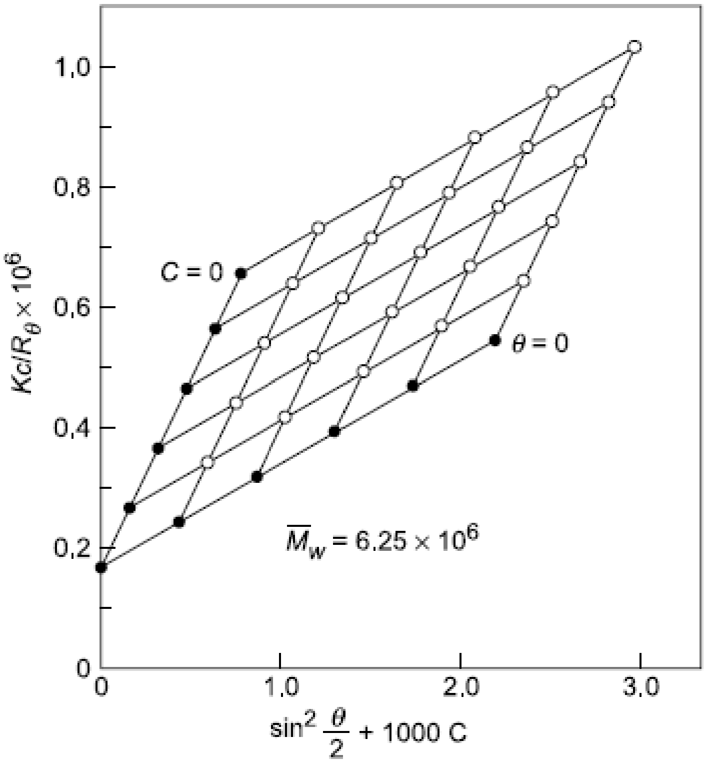


Figure 6.8. A typical Zimm plot, Kc/R_θ vs. $\sin^2(\theta/2) + kc$ from light scattering measurements for sodium amylose xanthate in 1 M NaOH solution at 30°C

Light scattering photometers based on photoelectric measurements are used for measurements of scattering data. A simple measurement principle and approach is shown in Fig. 6.9. It is absolutely necessary to keep the measuring chamber dust free. The scattering glass cell is centred on the axis of rotation of the receiver photomultiplier tube assembly which can be rotated with controlled and measurable angular positions. Besides the measurement of τ or R_θ, it is necessary to determine the refractive index $n$and the parameter $(\partial n/\partial c)$, whch is a constant for a given polymer–solvent combination at a given temperature. It is measured with the help of a differential refractometer. The choice of solvent is important. The difference in refractive index between the polymer and the solvent should be as large as possible. A solvent of low second virial coefficient allows a more precise evaluation of $\overline{M}_w$ by extrapolation. Dust free solvents and solutions preferably obtained by pressure filtration should be used.

The solvent and solutions must be free from all extraneous scattering material. Molecular weight range of 10,000 to 10,000,000 are measurable by this technique.

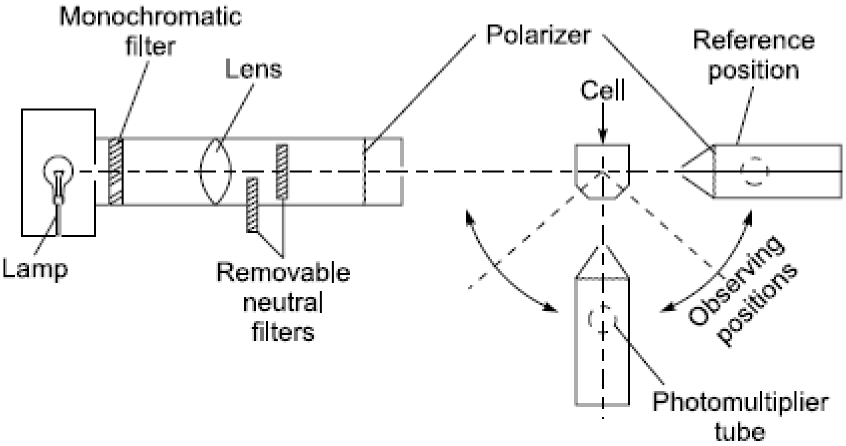


Figure 6.9. Principle of light scattering measurements

6.9.1. Dissymmetry

For polymer molecules much smaller than the wavelength of the incident light, the scatterings in the forward and backward directions measured at two angles symmetrical about 90° (say, 45° and 135°) are not appreciably different, but for particles larger than about a tenth of the wavelength of light, the intensity of the scattered light follows a decreasing trend from front to rear. The ratio $(i_{45^\circ}/i_{135^\circ})$, known as the dissymmetry, *z* of light scattering is unity for small particles and it increases with size. Evaluation of the dissymmetry is conveniently used to estimate particle size which is the effective expanse of the particle with respect to the wave. length. If the particle weight is also known, the measure of dissymmetry gives an indication of the shape of the particles as to whether they are spherical, rod-like, disc-like or random coils. There are, however, limitations to this approach of particle shape determination.[23]

6.10. End-Group Analysis

Analysis of functional groups in polymers, particularly of those incorporated at chain ends is a very important means of polymer characterization. Polymer characterization by this approach is meaningful specially when it is a clear-cut case with well-defined mechanism of polymer growth under a specified condition, and purification from low molecular weight monomers, additives and spurious contaminants has been meticulously accomplished. For high polymers, desired purifications are satisfactorily accomplished by repeated precipitations.[24,25]

In well-defined polymer systems, a knowledge of the number of a specific end-group in a given mass of polymer permits determination of number average molecular weight from the results of end-group analysis, which in effect, gives a count of the molecules in a given weight of the sample. Or else, if the number average molecular weight is determined by an independent technique, end-group analysis gives an idea of the number of a specific end-group per polymer chain which further throws light on the detailed mechanism of polymerization, including initiation and termination. Meaningful information about chain transfer or radical transfer reactions may also be obtained from well-designed experiments.[26–28] Titrimetric methods are particularly useful to estimate such groups as —NH_2, —COOH, etc. in relatively low molecular weight polyamide, polyester and related polymers.[29,30]

Spectroscopic methods (*UV*, visible and IR absorption spectroscopy) have been conveniently used for polymer end-group characterization on many occasions.[31–34] Radioactive tracer technique has also been used for some systems (limited though they are) for studies of the mechanism of polymerization and for end-group characterization.[35–38] Sensitive colourimetric methods[39–41] of selective nature have also been extensively used for characterization of end-groups.

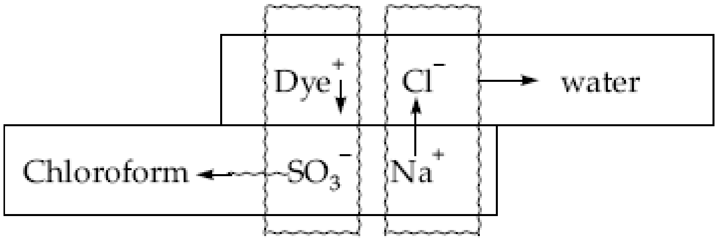
The dye-partition technique and the dye-interaction technique introduced by Palit[40,41] and developed for quantitative characterization of polymer microstructure by Palit, Ghosh and coworkers[24,25,42] have been quite suitable for the analysis of —COOH, —OH, —NH_2, —Cl, —Br, $—OSO_3^-$, $—SO_3^-$ groups or end groups in high polymer systems.

The general chemical methods of analysis of functional end-groups suited for characterization of condensation polymers are prohibitively difficult for a vinyl polymer because of the latter's much higher molecular weight in general. Introduction of highly sensitive methods is therefore necessary to enable easy detection (and possible estimation) of groups or atoms present as end groups in macromolecules of very high molecular weight. The dye techniques, viz. the dye-partition technique and the dye-interaction technique provide simple solutions to these problems.

6.10.1. Dye-Partition Technique

In the analytical chemistry of detergents and surfactants in general, the colourimetic methods involving the use of ionic dyes of various kinds have been widely employed.[43–45] Large surfactant ions and large dye ions of opposite charge react to produce compounds having very low or little solubility in water. The ionic dyes soluble in water are so selected that they are ordinarily insoluble in such organic solvents as benzene and chloroform. As a result, in a two-phase system involving one such immiscible solvent with an aqueous solution of a dye, little colour is seen in the organic layer. If some detergent bearing an ionic group of a specific kind and charge is present along with excess of a suitable dye of opposite charge, the dye-detergent salt formed, usually being more soluble in the organic solvent, is partitioned preferentially in the organic layer.[46]

According to the principle of dye-partition technique, ionizable groups present in polymers easily undergo metathetic reactions with suitable dyes. In case the dye is water soluble and insoluble in a water immiscible organic solvent and the polymer has the reverse characteristics, i.e. the polymer dissolves in the organic solvent but not in water, in any partition experiment, the dye ion would combine with the polymer counterion and as a result, the coloured dye ion would pass into the non-aqueous phase; or in other words, colouration of the nonaqueous phase would indicate the presence of ionizable end-groups in the polymer.



(6.45)

A possible source of complication, namely the adsorption of the dye by the polymer, is practically negligible in view of the fact that a purely thermal polymer such as polystyrene or poly(methyl methacrylate) having no ionizable end group, solubilizes little dye in such partition experiments. Moreover, the polymer in most cases is insoluble in aqueous phase and so there is little complication due to its distribution in both the phases, as in the case of detergents.

Carboxyl ($—COO^-$) end-group is detected by doing the partition test using the cationic dye pynacyanol (chloride) in neutral or mildly alkaline aqueous solution (pH 8) and the polymer in benzene solution.[47]Strong acid end-groups such as sulphate ($—OSO_3^-$), sulphonate ($—SO_3^-$) etc., also respond to this test but they are easily distinguished by carrying out the partition test under acid condition, preferably using methylene blue (chloride) as the basic or cationic dye in aqueous centinormal HCl solution and the polymer in chloroform solution. Under this condition —COOH groups fail to respond to the dye-partition test. Similarly, basic end-groups such as the amino end-groups and quaternary ammonium (cationic) end-groups are readily detected and estimated using an acid or anionic dye such as disulphine blue VN150 or bromophenol blue dye in aqueous acidic (0.01 N HCl) solution and taking the polymer in chloroform solution. For quantitative purposes, equal volumes of the aqueous dye solutions (10 mg/litre) and dilute solution of a polymer in the appropriate organic solvent (0.05–0.5%) are intimately shaken together in a stoppered tube, allowed to settle for distinct separation of layers (centrifuged if necessary) and the colour developed in the organic layer is then measured spectrophotometrically with the help of a calibration curve prepared for a relatively low molecular weight appropriate model compound such as stearic acid, sodium lauryl sulphate, cetyl trimethyl ammonium bromide or lauryl amine.

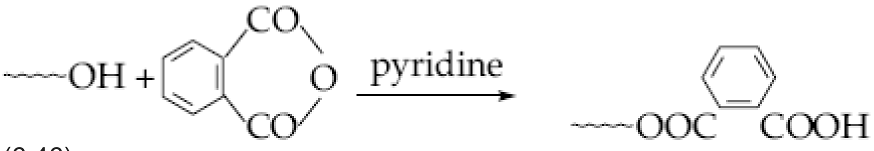
6.10.2. Dye-Interaction Technique

Solution of a number of basic and acid dyes in aqueous buffer solutions when extracted with benzene, toluene and similar solvents, yields an organo extract of the dye base of dye acid, whose colour depends on the pH of the solution extracted, though the colour of the dye in the aqueous layer may not be pH sensitive. A simple example is the well-known basic dye methyl violet 3B (gentian violet) which, though practically insoluble in benzene is but little extracted by benzene from aqueous solution of pH up to about 7.0. It gives a light violet extract at pH 7.0 and an unstable deep brown extract at about pH 9.0. A strongly alkaline solution produces brown yellow benzene extract of the dye. The dye shows practically no colour change in aqueous solution over the whole pH range. The most sensitive extracts are obtained from more strongly alkaline solutions. Traces of a compound bearing $—COO^-$, $—OSO_3^-$ or $—SO_3^-$ functional groups sharply change the colour of the benzene extract to violet. Basic dyes of the rhodamine 6G class extracted in benzene from aqueous solution (10 mg/litre) at pH 10–12 also give yellow extracts of high acid sensitivity. Micronormal acid solutions in benzene e.g. formic acid, stearic acid, etc.) can be easily detected by these reagents. The colour change for the sensitive rhodamine dye reagents in the dye interaction test is from yellow to pink [often with fluorescence if the concentration of the (acid) anionic groups is relatively high]. The basic dye reagents (benzene extracts) are quite stable and retain their sensitivity if preserved over NaOH pellets in the dark. For quantitative purposes, equal volumes of the dye reagent and dilute (benzene) solution of an acid or of a polymer purified appropriately are mixed together and the extent of colour change brought about, depending on the nature and concentration of the acid present[41], is measured spectrophotometrically taking the help of a suitable calibration curve.[24]

For the detection of bases such as amines or basic end-groups (amino end-groups) in polymers, almost all phthalein dyes, particularly the halogenated ones are highly sensitive and they can be successfully used after extraction with benzene from their aqueous solution (50 mg/litre) at pH 3–4. Eosin A, eosin saure L neu, erythrosin J or erythrosin pur and rose Bengal give sensitive benzene extracts as dye reagents for detection of basic and cationic end-groups. For quantitative measurements, equal volumes of a selected dye reagent and benzene solution of a polymer are mixed together. The colour change (colourless to pink/yellow to pink/pale brown to pink, as the case may be) brought about in proportion to the concentration of the base or basic end-group present is measured spectrophotometrically using a calibration curve given by a long chain model compound such as lauryl amine or cetyl trimethyl ammonium bromide. For end-group analysis by the dye techniques, tests for acid end-groups are not interfered with by the presence of basic end-groups and vice versa.

The dye techniques suited for the analysis of selected ionic (acidic or basic) end-groups can also be used for the analysis of non-ionizable end-groups after conveniently modifying them to ionizable groups. Before subjecting the polymers to dye tests using the highly sensitive dye reagents, it is necessary that they are scrupulously purified by a process of repeated precipitation to free them from low molecular weight (ionic) acidic or basic contaminants.

Hydroxyl (OH) end-groups in a polymer are not responsive to dye tests. They can be conveniently transformed into dye test responsive carboxyl (—COOH) groups by phthalation[25] (heating 0.2–0.5 g of polymer dissolved in 5 ml pyridine with excess of phthalic anhydride at 90–100°C for 6 h).



(6.46)

On the other hand, OH end-groups in a polymer can also be transformed into dye test responsive anionic $—OSO_3^-$ (sulphate) end-groups by sulphation[42] (heating the polymer with chlorosulphonic acid in pyridine medium at 90°C for 4–6 h)

$$\sim\sim\sim OH + ClSO_3H \xrightarrow{\text{pyridine}} \sim\sim\sim O \cdot SO_3H + HCl$$

(6.47)

The sulphur atom of the anionic sulphate end-group is attached to the polymer chain through an oxygen atom (C–O–S linkage); the anionic sulphonate end-group ($—SO_3^-$) is, however, attached to the polymer chain through a C–S linkage. Sulphate end-roups are readily hydrolyzable to —OH groups under acidic conditions and they are distinguishable from sulphonate end-groups as the latter are non-hydrolyzable under similar conditions.[48]

Halogen (Cl, Br, I) end-groups or atoms present in a polymer are not responsive to the dye tests, but they can be conveniently transformed into dye test responsive cationic groups (pyridinium halide) by quaternization using pyridine as the quaternizing base (heating 0.5 g polymer dissolved in 5 ml pyridine at 95°C for 24 h).

$C{=}C$ unsaturation (as a polymer end-group) may be conveniently traced and detected and possibly estimated by converting the (chain end) unsaturation into an amine (end) group. This is done by heating the polymer in benzene solution with excess of a primary amine (*n*-butylamine) in a sealed tube for 24 h, when addition of the amine takes place at the unsaturation.[49] The polymer is then purified and tested for amine end group by the application of the appropriate dye techniques.

Employing different dye reagents and the two dye techniques in appropriate sequence and following a well-designed approach, one can readily characterize polymers bearing different functional end-groups at the same time. Ordinary chemical or physico-chemical methods of end-group analysis are normally applicable with good degree of precision for polymers of molecular weight up to about 30,000, but highly sensitive microchemical techniques such as the dye techniques for end-group analysis are generally applicable to characterize end-groups of benzene or chloroform soluble polymers of molecular weight up to about 5×10^5.

6.11. The *Z* Average Molecular Weight

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

$$\overline{M}_z = \frac{\Sigma N_i M_i^3}{\Sigma N_i M_i^2}$$

(6.48)

The use of the weighting factor $N_i M_i^2$ for the determination of the *Z* average molecular weight clearly indicates that the higher molecular weight molecules are weighted even more heavily in this case than in the case of the weight average molecular weight. For a given distribution, the order of the averages is clearly $\overline{M}_z > \overline{M}_w \geq \overline{M}_v > \overline{M}_n$. The *Z* average molecular weight is conveniently measured by sedimentation equilibrium method in an ultracentrifuge.

The ultracentrifugation techniques are relatively complicated and are much less commonly employed for molecular weight measurements of synthetic high polymers. They are, however, more commonly used for characterization of biological polymers such as proteins.

Using a relatively low speed of rotation with the polymer solution in the cell held in position, and operating the centrifuge under constant conditions over long periods, thus avoiding convection and related disturbances within the cell, a state of equilibrium is reached in which the polymer is distributed in the cell according to its molecular weight and molecular weight distribution. The force of sedimentation on a species in solution is just balanced by its tendency to diffuse out. For a dilute solution closely approaching ideal thermodynamic behaviour and for a monodisperse polymer, the molecular weight, *M* is given by the expression

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

(6.49)

where c_1 and c_2 are the concentrations 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. A solvent chosen should preferably be a poor solvent and it should be quite different in density from the polymer so as to allow good sedimentation, and also in refractive index so as to facilitate measurement. If the polymer is polydisperse in nature, then different approaches for measuring the concentration as a function of r yield different molecular weight averages ($\overline{M}_w$, $\overline{M}_z$, etc.). Measurements based on refractive index yield $\overline{M}_z$. Preparative ultracentrifuges are useful in fractionating polymer samples and in separating them from easily sedimented contaminants.

6.12. General Requirement of Extrapolation to Infinite Dilution

The process of dissolution of a polymer is usually slow and it mostly occurs in two characteristic stages: (i) an initial phase of swelling and (ii) gradual formation of a molecular solution if it is not a cross-linked system. The second stage is often aided and accomplished quicker by stirring or agitation and by warming or heating. Solubility features in polymer systems are far more complex than those for low molecular weight substances. The polymer molecules are usually far bigger in size than the solvent molecules, and this factor along with the extent of interactions between polymer segments (intramolecular and intermolecular) and between the polymer and the solvent under a given set of conditions are important considerations to understand and analyze solubility of polymers and their solution properties.

A simple theory considers a polymer chain as an assemblage of a large number of points (chain units or segments) on a lattice work which are joined or tied together by flexible (chemical) bonds of equal lengths. The polymer chain may assume any specific arrangement on the lattice out of many statistically possible arrangements. For ideal solution behaviour, there should be no interaction between segments of different chains, which can be approached and possibly attained only with infinitely dilute solution. But actual measurements of any solution property at such vanishing concentrations are practically impossible to make, thereby necessitating extrapolation of measured properties at finite concentrations to infinite dilution. For finite concentration, howsoever dilute, the interactions between chains cannot be altogether ignored because of chain entanglements.

6.13. Polymer Fractionation and Molecular Weight Distribution

In a very poor solvent, or more appropriately, in a non-solvent, the polymer will not dissolve. On gradual or dropwise addition of a non-solvent to a dilute solution of the polymer in a good solvent, some polymer will be thrown out of solution and will appear as a precipitate at certain point. It has been found that polymer molecules of the highest molecular weight or molecular weight range get precipitated first. On separation of the precipitate, further addition of the non-solvent in a similar manner throws out at a subsequent point a second fraction of polymer with a somewhat lower molecular weight or molecular weight range. The separation into fractions may be made sharper if after adding the requisite amount of the non-solvent the mixture is warmed to make the system just homogeneous and then the polymer fraction is allowed to precipitate as the mixture is cooled. The process is repeated to isolate successive fractions of decreasing molecular weight or molecular weight range. Each of the successive fractions is carefully isolated, dried, weighed and its molecular weight determined by one of the techniques discussed in the preceding sections. It is then possible to draw an integral molecular weight distribution curve as given in Fig. 6.10 showing cumulative weight per cent plotted against molecular weight. Another useful curve based on differential molecular weight distribution shown in Fig. 6.11 is obtained by differentiating the integral distribution curve. The relative positions of $\overline{M}_n$, $\overline{M}_v$, $\overline{M}_w$ and $\overline{M}_z$ are shown on this curve.

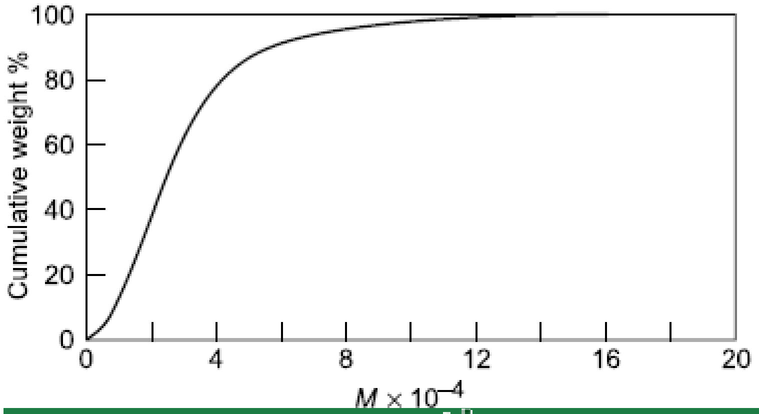


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Figure 6.10. A typical integral molecular weight distribution curve: plot of cumulative weight % vs molecular weight

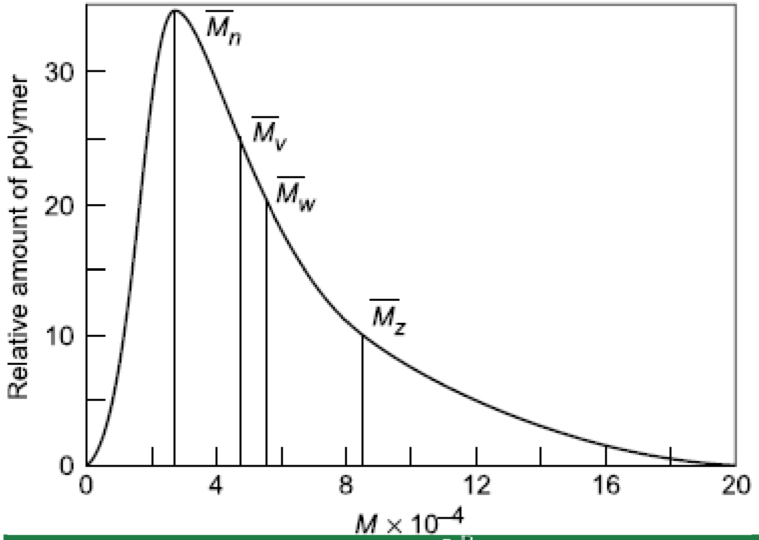

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Figure 6.11. A typical differential molecular weight distribution curve: plot of relative amount of polymer vs molecular weight

Fractionation based on the above approach separates the various molecular species in a given polymer sample mainly on the basis of their solubility characteristics rather than on the basis of their molecular weight. For a given polymer, the solubility characteristics are, however, dependent not only on chain length, but also on branching (including its nature and frequency), cross-linking, end-groups present and on changes in chemical structure on aging.

6.14. Gel Permeation Chromatography

A chromatographic process is one in which the solute is transferred between two phases, one of which is stationary while the other is moving, and the transfer is often allowed to take place in a long column. In gel permeation chromatography the same solvent or liquid is allowed to form the two phases in the column packed with a microporous gel such that the stationary phase is that part of the solvent which is inside the porous gel particles and the mobile phase is made by the solvent remaining outside. The driving force behind the transfer of solute polymer molecules between the two phases is diffusional in nature and it gives rise to a difference in concentrations of solute in the two phases, the transfer process being also largely restricted by the solute molecules' capacity to penetrate or permeate through the pore structure of the gel. The gels used are typically hard, incompressible polymers, those most commonly used being microporous polystyrene (cross-linked with divinyl benzene) prepared by a suspension technique using a suitable inert solvent–non-solvent media. Another material commonly used is porous glass. The pores in the gels used are nearly of the same size as that of the polymer molecules.

A known amount of polymer in a known volume of dilute solution is injected into a solvent stream flowing down the column. The solute polymer molecules flow past the porous beads of the gel and at the same time diffuse into their inner pore structures according to size distribution of the solute polymer molecules and the pore size distribution of the gel. A fractionation of the polymers is achieved in the process in view of the fact that the entry of the larger molecules into the pores of the gel are more restricted or completely hindred due to relatively low pore sizes, and they flow out of the gel column faster, spending less time inside the gel. The smaller molecules follow just the opposite trend as they spend more time inside the gel. The largest among the solute molecules emerge first while the smallest of them emerge last from the gel column. The technique, very commonly known as the "gel permeation chromatography" (GPC), allows separation of polymer molecules by their size. For a properly selected gel, the smallest of the solute polymer molecules find most of the stationary phase accessible.

The method initially requires empirical calibration of a column or a set of columns with gels of graded pore size to yield a calibration curve[50] such as the one shown in Fig. 6.12 relating a molecular size parameter, $[\eta]M$, [see Eq. (6.50) in Sec. 6.15] and retention volume such that with its help a plot of amount of solute versus retention volume of a test polymer known as its chromatogram, Fig. 6.13, can be transformed into a molecular size distribution curve from which a molecular weight distribution curve can be drawn. The GPC is a neat and fast technique for both analytical and preparative work applicable to both linear and branched polymers, requiring a sample size of only a few milligrams and the analysis is usually complete in a time scale of 2–5 h.

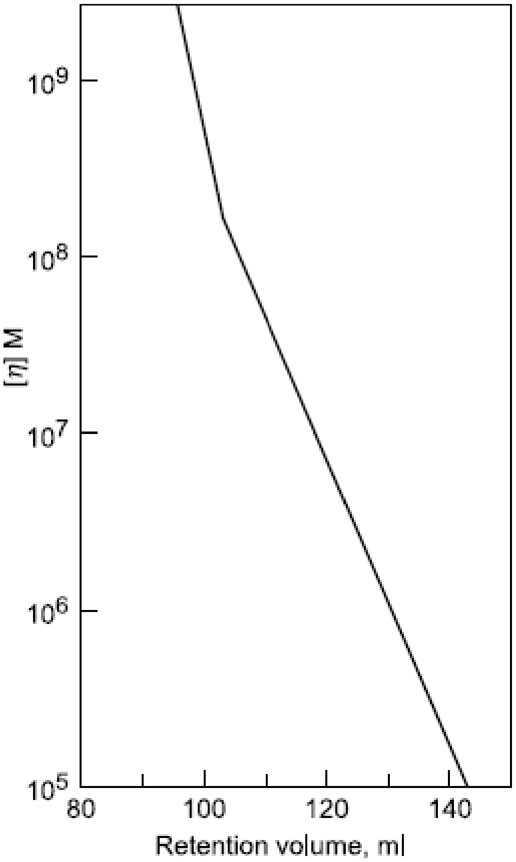

Figure 6.12. Calibration curve for gel permeation chromatography: plot of [η]M vs retention volume[50] *(Grubisic, Remp and Benoit, 1967;Courtesy, Wiley-Interscience, New York)*

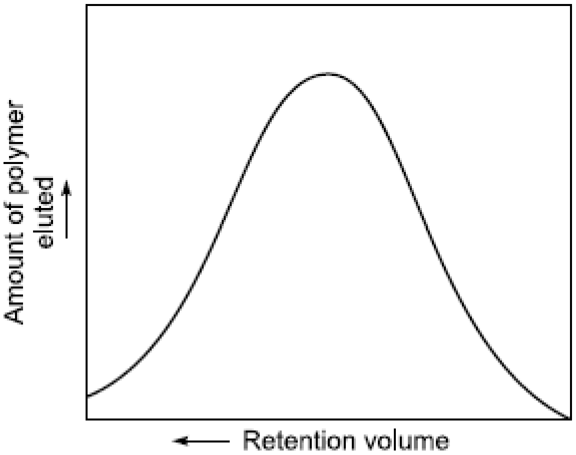

Figure 6.13. A typical GPC chromatogram

Gel permeation chromatography separates molecules in a given polymer sample according to their molecular sizes (or hydrodynamic volumes). Any extraneous physico-chemical factor that contributes to the perturbation of the hydrodynamic volumes of the dissolved polymer molecules and also brings about changes in their rate of elution would not only complicate measurements and interpretations but also may lead to erroneous results and conclusions. For example, in case of non-polar polymers with limited number of charged groups ($—SO_3^-$, $—COO^-$, etc.) such as the ionomers or even in case of those having end groups only as the charged groups in their structure, the macromolecules are absorbed on the surface of the microgels as they pass through the columns, thus offering somewhat enhanced resistance to elution as a consequence and then, the size exclusion basis of GPC separation loses its relevance. Such a phenomenon would lead to larger elution volumes and to relatively low molecular weights than actual. The ion-containing polymers tend to aggregate in solvents of low polarity and in case of such macromolecular aggregation, fractionation and molecular weight determination based on separation according to molecular size in solution are largely affected. Analysis of such polymers by GPC can be reliably done only if the charged groups are turned non-ionic or by selecting an eluent solvent system which would prevent adsorption of polymers in the gel columns and would also eliminate macromolecular aggregation. It is important to have a good knowledge about the history of a polymer including its method of synthesis and its microstructure particularly with reference to the presence of charged groups (end groups or branch or repeat units) before attempting to know more about it by employing gel permeation chromatography