IBasic Concepts of High Polymer Systems

1. Basic Concepts of High Polymer Systems

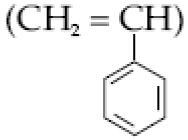
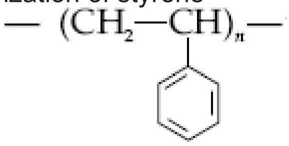
1.1. Introduction and Historical Background

The quest for new materials has been with us from ancient times. Polymers, though introduced in the materials field in a meaningful manner only very recently, occupy a major place and pivotal position in the materials field today. In performance characteristics and application prospects and diversity, they offer novelty and versatility not found in any other kind of materials.

Till about the first two decades of the twentieth century, confusion prevailed over the basic understanding of polymer molecules. They were recognized more as colloids or associated molecules. Attempts to determine their molecular weights using solutions in suitable solvents by cryoscopy often gave confusive, irreproducible, uncertain and sometimes very high values. For starch, natural rubber and cellulose derivatives, molecular weights ranging up to 40,000–50,000 or even more were obtained. Such high values implied existence of very large molecules. But this was not accepted in view of the total lack of structural concept about such large molecules. The chemists continued to favour the concept of large association of much smaller molecules of short chain or cyclic structures.

1.2. Macromolecular Concept

The realization of the macromolecular concept of polymeric materials in 1920s proved to be a vital turning point. Accumulated confused ideas of the earlier decades became meaningful and they were then translated into the production of a large variety of materials of hitherto unknown structures through polymerization and copolymerization of olefinic, diolefinic and vinylic compounds and combinations thereof, and through polycondensation reactions between a large variety of bi- or polyfunctional compounds bearing well characterized chemical functional groups.

The macromolecular concept came into wide acceptance and appreciation soon after it was propounded by Staudinger[1] in 1920. He advanced long-chain structural formulas for polystyrene, natural rubber, etc. Long sequences of simple chemical units linked with each other with covalent bonds came into recognition as the basic structural feature of a polymer molecule. The polystyrene molecule obtained from polymerization of styrene  $(CH_2=CH)$ came to be recognized to have the formula  $-(CH_2-CH)_n-$ where *n* had a large value. Staudinger was not sure about the terminal points or end groups of the long-chain polymer molecules. He was of the view that there was no need to saturate the terminal valences and suggested[2] that no end groups were needed. However, development and elucidation of the chain reaction theory and mechanism of vinyl and related polymerization by Flory[3] and others[4] clearly established that polymer materials consisted of long-chain molecules with well characterized end groups. Another distinctive feature of the same decade was the pioneering work of Carothers[5] in the area of polycondensation and towards the first rational synthesis of linear macromolecules, polyesters and polyamides.

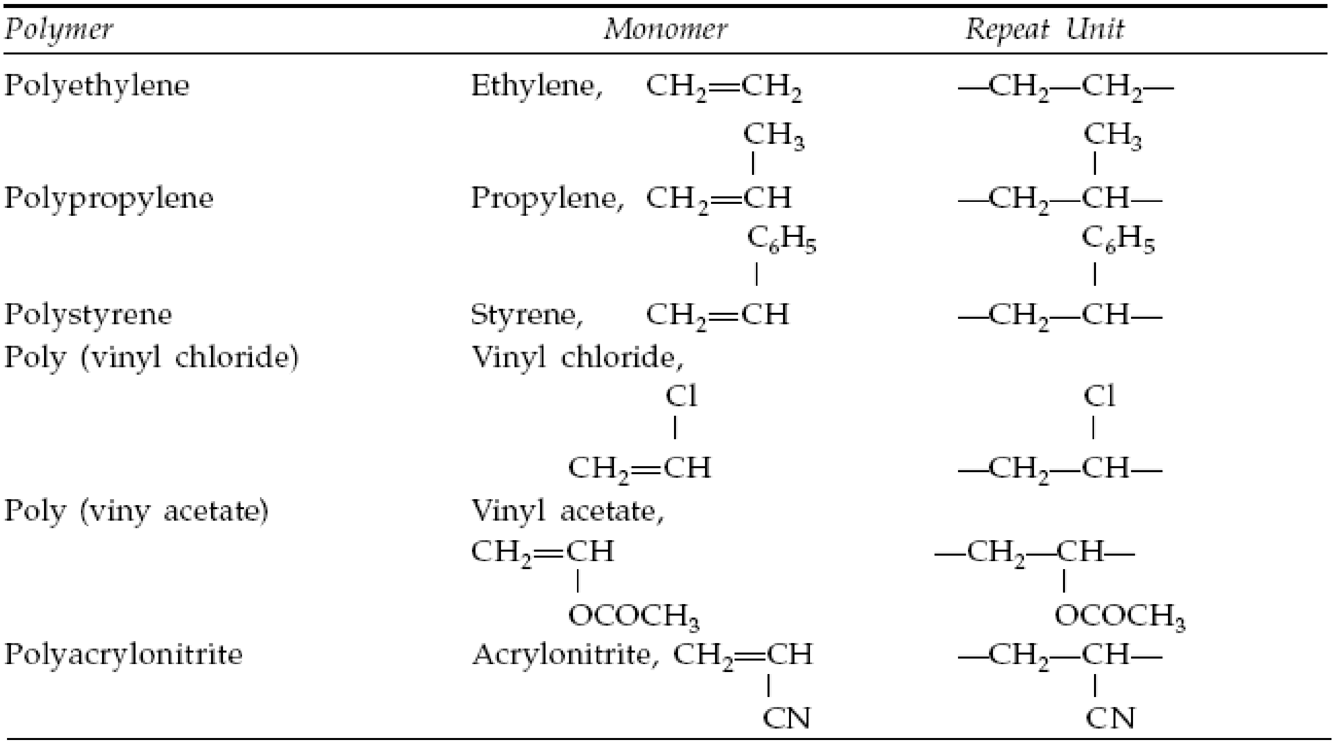
A stage was reached by the middle of the 20th century, when the possibility of attaining almost any conceivable material property of structural importance through polymerization, copolymerization or polycondensation and through modification of available polymers by chemical treatment, reinforcements, compounding or blending, thermal or mechanical treatment, irradiation, etc., appeared to be within our competence. We had reached the era of tailor-made polymers in a comprehensive sense. Material prospect brightened through what may be called "molecular engineering". Nowadays, through proper selection of monomers and their combinations, catalysts and other additives and adopting appropriate polymerization conditions and techniques, experts are able to construct polymer molecules of almost any desired size, shape and complexity and of any desired chemical structure suited to almost any contemplated end-use.

1.3. Structural Features of a Polymer

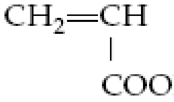
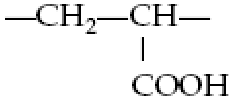
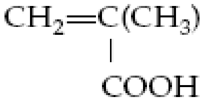
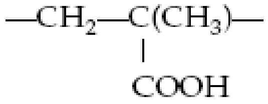
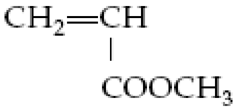
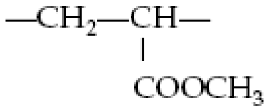
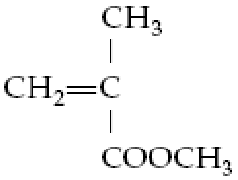
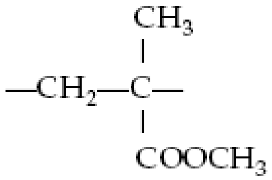
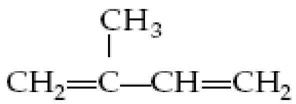
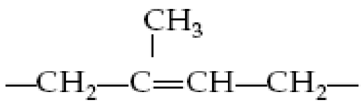
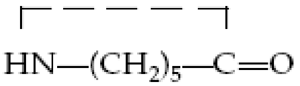
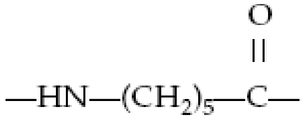
The word polymer literally means many(*poly*) units(*mer*). A simple chemical unit repeats itself a very large number of times in the structure of a polymer molecule; this unit may consist of a single atom, or more commonly, a small group of atoms linked chemically. An example of the first kind (repeat units consisting of a single atom) is the well-known plastic sulphur, -S-S-S-S-S-S-, in the molecules of which the repeating S atoms are joined together by covalent bonds. This polymeric sulphur is, however, unstable and it slowly changes back to the powdery form of sulphur on keeping at room temperature.

In bulk of the polymers, the repeating unit or simply the repeat unit is constituted of a small group of atoms combined in a specific fashion. The simple molecule from which its polymer is obtained or to which a polymer may be degraded is called the monomer. Table 1.1 lists some polymers and structures of the respective monomers and repeat units.

Table 1.1. Some polymers and respective monomers and repeat units



Polymer	*Monomer*	*Repeat Unit*
Polyethylene	Ethylene, $CH_2{=}CH_2$	$—CH_2—CH_2—$
Polypropylene	Propylene, $CH_2{=}\overset{\overset{CH_3}{\vert}}{CH}$	$—CH_2—\overset{\overset{CH_3}{\vert}}{CH}—$
Polystyrene	Styrene, $CH_2{=}\overset{\overset{C_6H_5}{\vert}}{CH}$	$—CH_2—\overset{\overset{C_6H_5}{\vert}}{CH}—$
Poly (vinyl chloride)	Vinyl chloride, $CH_2{=}\overset{\overset{Cl}{\vert}}{CH}$	$—CH_2—\overset{\overset{Cl}{\vert}}{CH}—$
Poly (viny acetate)	Vinyl acetate, $CH_2{=}\underset{\underset{OCOCH_3}{\vert}}{CH}$	$—CH_2—\underset{\underset{OCOCH_3}{\vert}}{CH}—$
Polyacrylonitrite	Acrylonitrite, $CH_2{=}\underset{\underset{CN}{\vert}}{CH}$	$—CH_2—\underset{\underset{CN}{\vert}}{CH}—$

Poly (acrylic acid)	Acrylic acid,  $CH_2{=}CH(COOH)$	 $-CH_2-CH(COOH)-$
Poly (methacrylic acid)	Methacrylic acid,  $CH_2{=}C(CH_3)(COOH)$	 $-CH_2-C(CH_3)(COOH)-$
Poly (methyl acrylate)	Methyl acrylate,  $CH_2{=}CH(COOCH_3)$	 $-CH_2-CH(COOCH_3)-$
Poly (methyl methacrylate)	Methyl methacrylate,  $CH_2{=}C(CH_3)(COOCH_3)$	 $-CH_2-C(CH_3)(COOCH_3)-$
Poly (tetrafluoroethylene)	Tetrafluoroethylene, $CF_2{=}CF_2$	$-CF_2-CF_2-$
Poly (oxymethylene)	Formaldehyde, $CH_2{=}O$	$-CH_2O-$
1,4 Polyisoprene	Isoprene,  $CH_2{=}C(CH_3)-CH{=}CH_2$	 $-CH_2-C(CH_3){=}CH-CH_2-$
Polycaprolactam (Nylon 6)	Caprolactam,  $HN-(CH_2)_5-C{=}O$	 $-HN-(CH_2)_5-C(=O)-$

The number of repeat units in a given polymer molecule is known as its chain length or degree of polymerization(DP). The molecular weight of the polymer is the product of the molecular weight of the repeat unit and DP.

When more than one kind of repeat units are present in a polymer, it is known as a copolymer. Polymers having molecular weight roughly in the range of 1000–20,000 are called low polymers and those having molecular weights higher than 20,000 as high polymers.

1.4. Length to Diameter Ratio

Length to diameter ratio of a polymer molecule is very high compared to that of a simple molecule. If a small molecule such as the ethylene molecule is represented by a dot (·), then the molecule of a polymer, say polyethylene of 1000 DP will be represented by a line (—) formed by addition or sticking together of 1000 dots in a linear fashion. This characteristic difference in length to diameter ratio between a small molecule and a polymer or a high polymer molecule makes all the difference in their physical properties.

Due to their long lengths, molecules in a given sample of a polymer material remain in a state of entanglement, both intermolecular and intramolecular. High melting or softening temperature, high melt or solution viscosity exhibited by polymer materials arise as a consequence of the big size of their molecules and the entanglements of the molecular chains.

1.5. Classification of Polymers

Important classifications of polymers are shown in Table 1.2. The bases of classification and major classes of polymers along with examples are given below:

Table 1.2. Classification of polymers

Basis of Classification	Polymer Types
Origin	Natural, semisynthetic, synthetic
Thermal response	Thermoplastic, thermosetting
Mode of formation	Addition, condensation
Line structure	Linear, branched, cross-linked
Application and physical properties	Rubbers, plastics, fibres
Tacticity	Isotactic, syndiotactic, atactic
Crystallinity	Non-crystalline (amorphous), semi-crystalline, crystalline

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The basis of classification and major classes of polymers along with examples are also given below.

1.5.1. Origin

a. ***Natural Polymers*** They are available in nature. Examples of such polymers are: natural rubber (1, 4-*cis*-polyisoprene), natural silk, cellulose, starch, proteins, etc.

b. ***Semisynthetic Polymers*** They are chemically modified natural polymers such as hydrogenated, halogenated or hydro-halogenated natural rubber, cellulosics, i.e., esters and ethers of cellulose such as cellulose nitrate, methyl cellulose, etc.

c. ***Synthetic Polymers*** They are man-made polymers prepared synthetically. Polyethylene, polystyrene, poly (vinyl chloride), polyesters, phenol-formaldehyde resins, etc., are example of synthetic polymers.

1.5.2. Thermal Response

a. ***Thermoplastic Polymers*** They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions, e.g., polyolefins, polystyrene, nylons, linear polyesters and polyethers, poly (vinyl chloride), etc. They normally remain soluble and fusible after many cycles of heating and cooling.

b. ***Thermosetting Polymers*** They can be obtained in soluble and fusible forms in early or intermediate stages of their synthesis, but they get set or cured and become insoluble and infusible when further heated or thermally treated; the curing or setting process involves chemical reactions leading to further growth and cross linking of the polymer chain molecules and producing giant molecules, e.g. phenolic resins, urea/melamine resins, epoxy resins, diene rubbers, unsaturated polyesters, etc.

1.5.3. Mode of Formation

a. ***Addition Polymers*** They are formed from olefinic, diolefinic, vinylic and related monomers. They all have —C—C— linkages along the main chains of the polymer molecules and usually no other atom appears in the main chain. These polymers are formed by simple additions of monomer molecules to each other in quick succession by a chain mechanism. This is known as addition polymerization or chain-growth polymerization. The examples of such polymers are: polyethylene, polypropylene, polystyrene, polybutadiene, poly (vinyl chloride), etc. (*See also* Chapters 3 and 8).

b. ***Condensation Polymers*** They are formed from intermolecular reactions between bifunctional or polyfunctional monomer molecules having reactive functional groups such as —OH, —COOH, —NH_2, —NCO, etc. The related functional groups react with each other in a stepwise manner producing condensed structural linkages, usually with the elimination of a simple, small byproduct molecule in each step of reaction. Besides —C—C— linkages, they contain such atoms as O, N, S, etc., at regular intervals in the main chain. The process of their formation is called condensation polymerization or step-growth polymerization. Polyamides, polyesters, polyethers, polyurethanes, phenolics, epoxy resins, etc., are examples of condensation polymers. (*See also* Chapters 2 and 8.)

1.5.4. Line Structure

a. ***Linear Polymers*** They can schematically be represented by lines of finite lengths (Fig. 1.1). They are formed from olefinic, vinyl or related polymerization under suitable conditions or by condensation polymerization of bifunctional monomers. Linear polymers such as high density polyethylene, poly(vinyl chloride), polystyrene, nylon 6, etc., are soluble and fusible.

b. ***Branched Polymers*** They can be schematically represented by lines of finite lengths with short or long branch structures of repeat units (Fig. 1.1). The branches appear as a consequence of uncontrolled side reactions during polymerization or by design of polymerization. Branched polymers are usually more readily soluble and fusible than linear polymers of comparable chain length or molecular weight.

c. ***Cross-linked or Network Polymers*** They can be represented by a network structure, planar-network as in graphite or space-network as in diamond (Fig. 1.1). Cross-linked polymers are insoluble and infusible as the molecules in them are giant molecules, often of unusually high or infinite molecular weight. Depending on the nature and frequency of cross-links, such polymers may show different orders of swelling in solvents. Examples are: phenol-formaldehyde resins, epoxy resins, vulcanized rubber, etc.

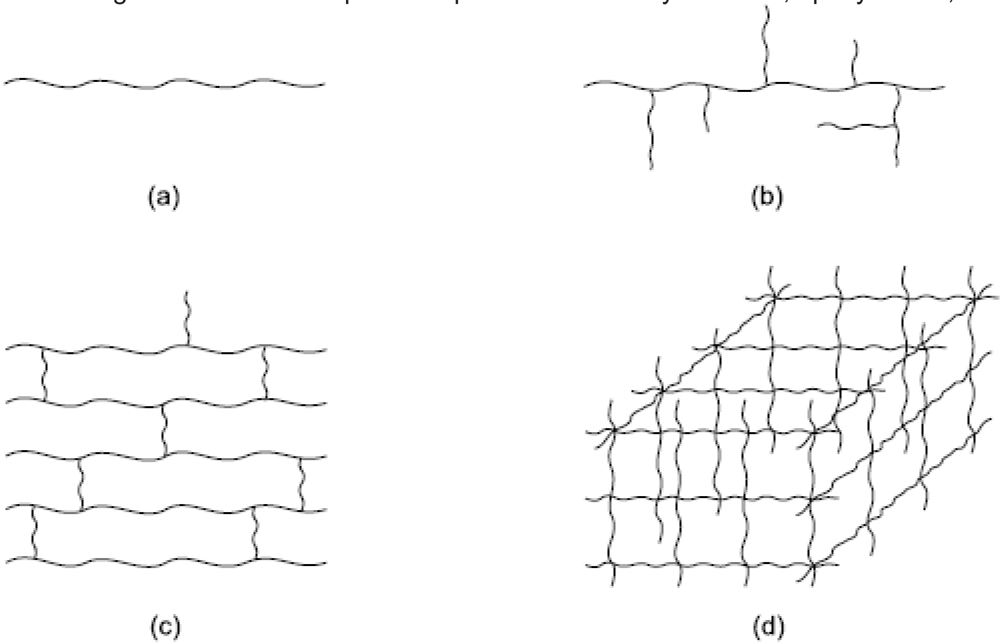


Figure 1.1. Schematic representation of (a) linear (b) branched (c) planar network, and (d) space network polymer structures

1.5.5. Application and Physical Properties

a. ***Rubbers*** These polymers are characterized by long-range elasticity. On consideration of mechanical strength, they are rather weak, dimensionally unstable and undergo high elongations even on application of low stresses. They exhibit tensile strengths in the range of 300–3000 psi and elongation at break ranging between 300–1000%. Examples are natural rubber and synthetic rubbers. They are also known as elastomers. Technically, rubbers become useful if cross-linked to the desired extent. The cross-linking of rubber is commonly known as vulcanization. The rubbery polymers are characterized by low molar cohesion (< 2 kcal/g mol per 5Å chain length).

b. ***Plastics*** These are usually much stronger than rubbers. Some of them are hard, horny, rigid, stiff and dimensionally stable, while others may be soft and flexible. Plastics exhibit tensile strength ranging between 4,000–15,000 psi and elongation at break ranging usually from 20 to 200% or even higher. The examples of plastics are: polyethylene, polypropylene, polystyrene, poly(vinyl chloride), nylon polyamides, urea-formaldehyde resins and phenol-formaldehyde resins, polycarbonates, etc. Plastics usually exhibit molar cohesion in the range of 2–5 kcal/g mol per 5Å chain length.

c. ***Fibres*** They are the strongest of the three different types of polymers mentioned here. Among the natural polymers of industrial importance, the foremost place is occupied by fibres, which may be of either plant or animal origin. The suitability of fibres, natural or synthetic, for use as textile materials is unique and it is associated not only with their high mechanical strength (tensile strength in the range of 20,000–150,000 psi) but also with other useful properties such as warmth or thermal insulation, softness and flexibility. Cotton cellulose, wool, silk, synthetic polyamides and polyester fibres, and acrylic fibres fall in this clan of polymers. They usually exhibit molar cohesion in the range of 4–10 kcal/g mol per 5 Å chain length.

1.5.6. Tacticity

A vinyl polymer, $—(CH_2—CHR)_n—$ is characterized by an asymmetric carbon atom in each of the repeat units of the chain molecule, and a type of stereochemical difference that may arise in the segments of the chain is *d*, *l* isomerism. In a polymer of this kind, such as polypropylene or polystyrene (Fig. 1.2), every alternate carbon atom indicated by an asterisk along the chain backbone is asymmetric:

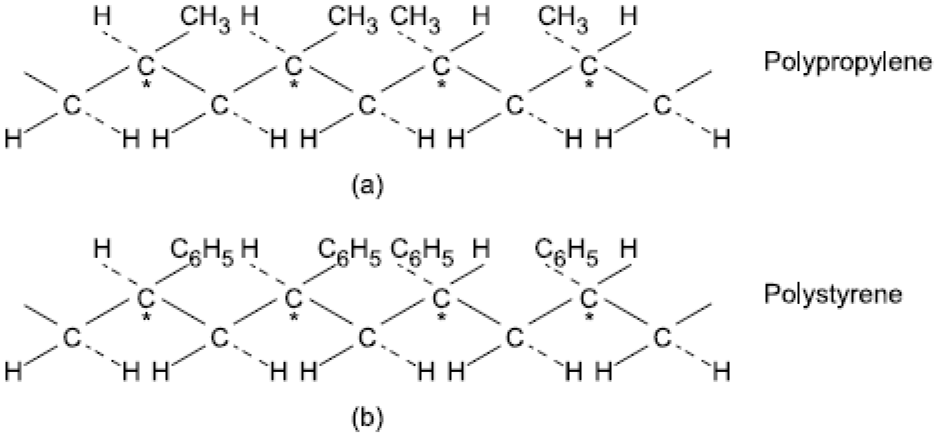


Figure 1.2. Structures showing stereochemically similar and different sequences of repeat units for (a) polypropylene and (b) polystyrene

Considering head to tail linkage of the repeat units, the first two asymmetric carbon atoms in each case (Fig. 1.2) have a different configuration in comparison with the last two, giving stereochemical sequences represented as *–d–d–l–l*. Depending on the tacticity or spatial disposition of the substituents attached to the asymmetric carbon atoms in the chain, we can have three major and distinctive sequences; (i) isotactic sequence represented as *–d–d–d–d–d–* or *–l–l–l–l–l*, giving similar or identical spatial disposition of the substituent in the repeat units, (ii) syndiotactic sequence represented as *–d–l–d–l–d–l–* where the steric placements of the substituent are such as to give strictly alternating *d* and *l* configurations, and (iii) completely random placements of the *d* and *l* configurations giving what is known as the atactic structure represented as *–d–l–d–d–l–l–l–l–d–l–d–d–*, which ultimately turns out to be a combination of isotactic and syndiotactic sequences of varying lengths. Because of high order of steric regularity in isotactic structures fostering close packing of molecular chains, isotactic polymers are usually highly crystalline, whereas the randomness in placements of *d* and *l* configurations hinders molecular packing and hence development of crystallinity in atactic polymers. Syndiotactic structure, being also regular through alternation of *d* and *l* configurations, shows good tendency to crystallize. Differences in molecular structure due to tacticity difference may be understood from the line structures (Fig. 1.3).

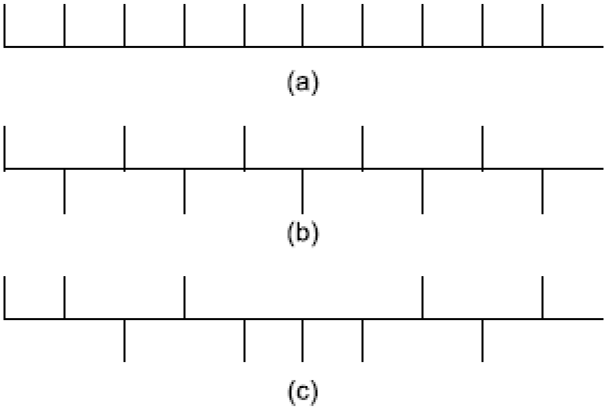


Figure 1.3. Line structures for (a) isotactic (b) syndiotactic, and (c) atactic sequences. Small branches or vertical lines indicate the spatial dispositions of the substituent groups (R) attached to the alternate carbon atoms along the length of the vinyl polymer chain, —(CH_2—CHR)$_n$, represented by the horizontal line

1.5.7. Crystallinity

When cooled from molten state, different polymers exhibit different tendencies to crystallize at different rates depending on many factors including prevailing physical conditions, chemical nature of the polymers, their molecular symmetry and structural regularity or irregularity. Bulky pendent groups or short-chain branches of different lengths hinder molecular packing and inhibit crystallization. The nature of the crystalline state of polymers is not simple and it should not be confused with the regular geometry of the crystal of low molecular weight compounds such as sodium chloride and benzoic acid. There are polymers which are, by and large, amorphous and have very poor tendency to get transformed into ordered or oriented structures on cooling to near or even below room temperature. Natural or synthetic rubbers, and glassy polymers such as polystyrene, acrylate and methacrylate polymers are polymers of this nature. In a crystalline polymer, a given polymer chain exists in or passes through several crystalline and amorphous zones. The crystalline zones are made up of intermolecular/intramolecular alignment or orderly (and hence closely packed) arrangement of molecules or chain segments, and a lack of it leads to formation of amorphous zones. Polymers showing a high extent of crystallinity (>60%) are commonly known as crystalline polymers and those showing a significant but relatively poor degree of crystallinity are termed as semicrystalline polymers. Stress-induced molecular orientation in a polymeric system is schematically represented in Fig. 1.4 (*See also* Secs. 7.21 to 7.29).

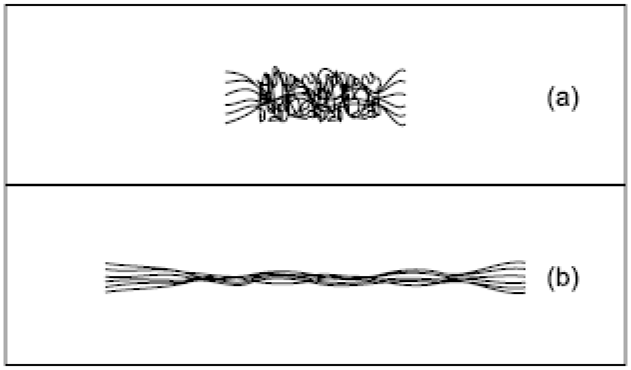


Figure 1.4. Schematic representation of (a) unoriented (melt normally cooled), and (b) oriented (cold drawn from melt) structures of polymer molecules, orientation having taken place in the direction of the applied stress

1.6. Structure–Property Relationship

The wide variety of natural, semisynthetic and synthetic polymers known today exhibit wide diversity of properties. Some are rigid, hard and strong and dimensionally stable, while others are soft, flexible or largely deformable under stress. Some are soluble and fusible while others are more resistant to heat and solvents and may be even insoluble and infusible. All such properties vary from a polymer of one type to a polymer of another type. They may vary even between samples of the same type of polymer depending on how they were prepared and treated thermomechanically before being tested. Depending on the property ranges they exhibit, the polymers are classified as rubbers, plastics and fibres. To find a relation between the structure of a polymer and its physical properties, the factors which largely influence the properties should be primarily considered. These factors are: molecular weight, polarity, crystallinity, molar cohesion, linearity and non-linearity of polymeric chains, thermomechanical history of the polymer and temperature of observation, etc. The simple consideration of chemical structure of the repeat units to predict properties, particularly the mechanical behaviour has certain limitations. This is because the chemical structure of individual molecules or segments thereof contributes partly and often indirectly to mechanical properties and a more consequential and direct role is very often played by the supramolecular structure, i.e. the physical arrangement of the chain molecules with respect to each other, more so for crystalline polymers.

1.6.1. Molecular Weight

The molecular weight and molecular weight distribution in polymer systems play an important role in determining their bulk properties. Higher molecular weight permits greater degree of chain entanglements resulting in higher melting or softening temperature and tensile strength. The general trend of variation of melting (softening) point and tensile strength of a polymer is shown in Fig. 1.5.

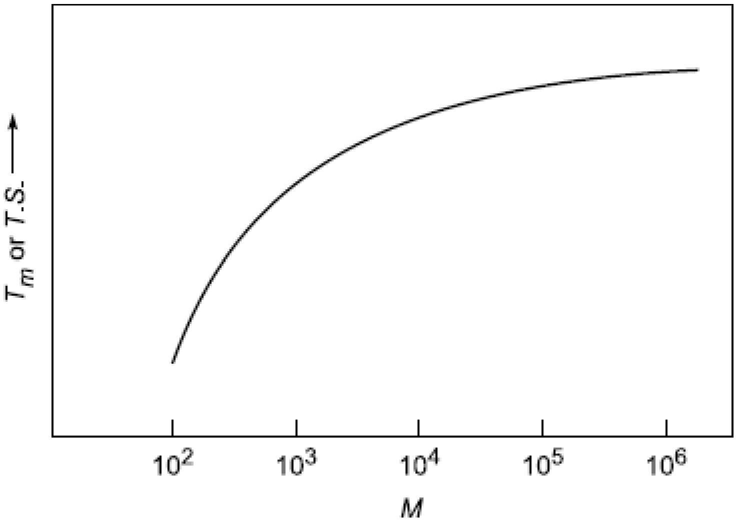


Figure 1.5. General trend of variation of melting (softening) temperature, (T_m) and tensile strength (T.S.) of a polymer with variation of molecular weight (M)

1.6.2. Linearity and Non-linearity of Polymer Chains

The properties of a polymer would largely depend on whether its chains are predominantly linear, branched to different extents or cross-linked. Linear polymers are mostly soluble and fusible. Small extents of branching make the otherwise equivalent polymer less resistant to solvents, chemicals and heat, owing to enhanced molecular mobility manifested through the branches or pendent groups. High degrees of branching and ultimate cross-linking make the polymer relatively stiff through greater degree of chain entanglements and ultimately forming giant molecules of a network structure, thus restraining large scale molecular mobility or chain slippage and improving dimensional stability. Polymers thereby become less soluble and less fusible, and ultimately, insoluble and infusible. The mechanical strength increases substantially due to crosslinking which is clearly exemplified by the curing or cross-linking of a host of thermosetting polymer systems such as the curing of phenolic and urea resins, vulcanization of rubbers, etc.

Through establishment of cross-links, basic structural changes in the polymers are introduced and consequently, basic changes or improvements in properties are often achieved. By proper design of the process and according to the set objectives, different levels of cross-linking, low or high, may be achieved (Fig. 1.6).

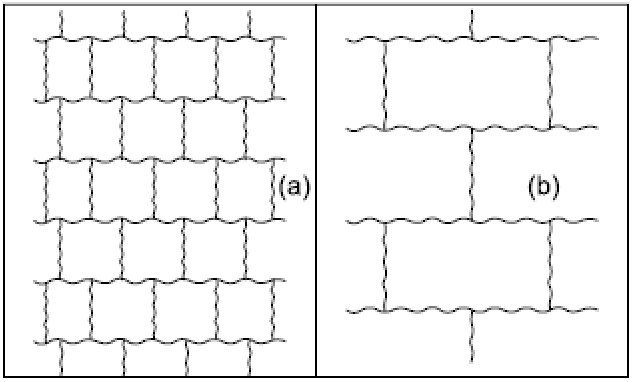
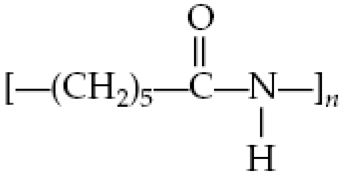


Figure 1.6. Schematic representation of cross-linked polymer structures: (a) high cross-link density, and (b) low cross-link density

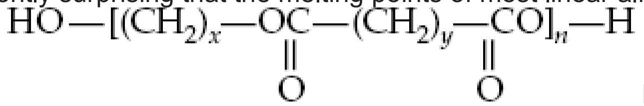
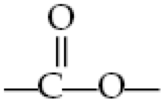
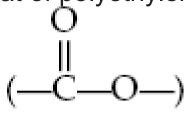
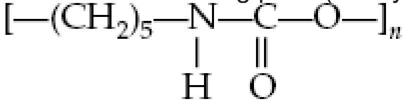
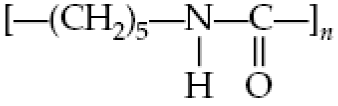
In most commercial cross-linkable polymer systems, the established cross-links are covalent bonds and the process limitation is that the shaping of the polymer to a useful article must be accomplished before completion of the cross-linking. The process is mostly irreversible, and regeneration of the heat softenable uncross-linked structure for reprocessing is seldom possible.

1.6.3. Molar Cohesion, Polarity and Crystallinity

These factors or parameters are interrelated. A chain molecule having a strong polar structure for each repeat unit exerts strong attractive force on molecules around it. In the absence of such polar structures, the molar cohesion would be weak. Let us consider the two polymers: polyethylene, $—(CH_2—CH_2)_n—$, and nylon 6 polyamide,  $[—(CH_2)_5—\overset{\overset{O}{\|}}{C}—\underset{\underset{H}{|}}{N}—]_n$. The methylene links in each polymer are practically non-polar, whereas the interunit amide linkage (—CONH—) in the polyamide is strongly polar. Assuming degree of polymerization such that the chains are of equal lengths, the forces of attraction between the polyamide chains will be very much stronger than those between the polyethylene chains. This is reflected in much higher rigidity, tensile strength, melting point and crystallizing tendencies of the polyamide. Moreover, extensive intermolecular hydrogen bond formation takes place in the polyamide, particularly on stretching it from the melt condition as it is cooled, resulting in the formation of the polyamide fibre.

Again, though polyethylene has a weak molar cohesion which is of the same order as for the various rubbers, natural and synthetic, it does not really exhibit rubbery properties: instead, it is one of the most useful plastics known. Its improved physical (mechanical) properties are basically due to its very simple chemical structure. The architectural symmetry of its molecules facilitates close packing of the chains into a lattice structure, inducing crystallinity and strength. Besides the architectural symmetry, recurrence symmetry is also important in determining the total forces of attraction between chains, particularly when oriented. This is very often illustrated by copolymerization of two monomers leading to loss of recurrence symmetry, and also by chain branching. Thus, polyethylene prepared by the high-pressure method (free radical mechanism) and the one by the low-pressure method (anionic co-ordination mechanism) greatly differ in their properties; the low-pressure polyethylene being higher melting, its density and rigidity being higher and this polymer having higher degree of crystallinity. The reason is that the low-pressure polyethylene is predominantly linear and hence it has high degree of molecular symmetry, while the high pressure polyethylene is fairly branched, thus poorer in molecular symmetry.

The influence of molecular symmetry on polymer properties is also exemplified by the chemical modification of cellulose. Cellulose, originally an infusible fibre of good strength, resistant to solvents and having a good degree of crystallinity due to extensive intermolecular hydrogen bonds through the hydroxyl groups, is easily transformed into useful plastic products with good solubility in selected solvents and more or less well defined softening or melting points on progressive substitution of OH groups by esterification and etherification. As a consequence of these reactions, the high architectural and recurrence symmetry of cellulose chain molecules are progressively lost and hydrogen bonds are destroyed considerably. The completely modified cellulose, giving a degree of substitution equal to three, would normally have better strength characteristics than the incompletely modified products, because by complete modification the overall molecular symmetry is regained.

It is apparently surprising that the melting points of most linear aliphatic polyesters  $HO—[(CH_2)_x—\underset{\|}{\overset{}{}}\!\!\underset{O}{OC}—(CH_2)_y—\underset{O}{CO}]_n—H$ having polar  $—\overset{O}{\overset{\|}{C}}—O—$ interunit linkages lie well below that of polyethylene[6] (Fig. 1.7). This may be partly explained considering that the contributions of the polar  $(—\overset{O}{\overset{\|}{C}}—O—)$ groups in enhancing molar cohesion are far outweighed by the flexibility effects imparted to the chains through the oxygen linkages in the chain backbone. The increase in chain flexibility and hence lowering of melting point by oxygen linkages in the main chain is also illustrated by a much lower melting point (nearly 150°C) for the polyurethane  $[—(CH_2)_5—\underset{H}{\underset{|}{N}}—\underset{O}{\underset{\|}{C}}—O—]_n$ than that for the analogous polyamide  $[—(CH_2)_5—\underset{H}{\underset{|}{N}}—\underset{O}{\underset{\|}{C}}—]_n$ having melting point of 215°C.

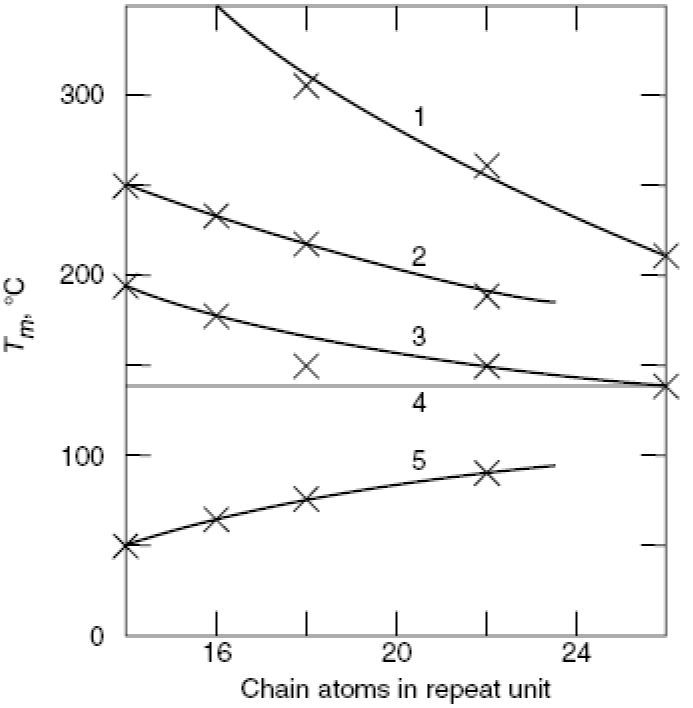
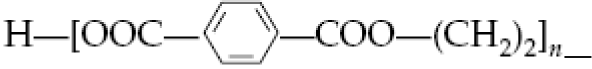
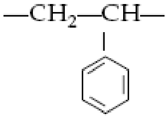
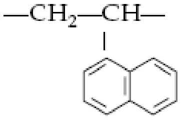
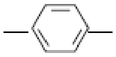
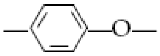
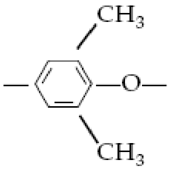


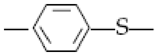
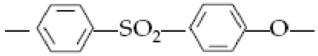
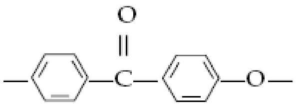
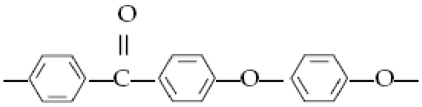
Figure 1.7. Trend of change of melting point (T_m) with variation of number of chain carbon atoms in repeat units in several linear (aliphatic) condensation polymers, viewed against the melting point of linear polyethylene (Curve-4): Curves 1, 2, 3 and 5 are for polyureas, polyamides, polyurethanes and polyesters respectively. The melting points approach that of polyethylene[6] as spacing between the polar interunit linkages is increased (Hill & Walker, 1948; Courtesy, Wiley-Interscience, New York)

Incorporation of rigid bulky groups such as an aromatic ring in the chain makes the polymer more stiff and hence higher melting.[7] Thus, while linear aliphatic polyesters are highly flexible and low melting polymers (Fig. 1.7), the aromatic linear polyester, poly(ethylene terephthalate),  —OH is a relatively rigid polymer of high melting point (>250°C) and it can be readily drawn into a fibre of high strength, crystallinity and resistance to solvents and weathering conditions. Its improved physical properties are not due to enhanced molar cohesion, since an aromatic ring has nearly the same molar cohesion as six linear methylene groups, but are mostly due to the bulk and rigidity of the aromatic ring in each repeat unit, resulting in great hindrance to rotation and thus, reducing chain flexibility and at the same time enhancing chain stiffness enormously. Symmetrical structure of the terephthalic acid units also permits a close fitting of the chain molecules into a crystal lattice. On the other hand aromatic bifunctional compounds having functional groups in the *ortho* and *meta* positions yield similar polymers with inferior physical and mechanical properties mainly due to their poor molecular symmetry, resulting in their inability to fit into a lattice structure as closely as for polymers from the corresponding aromatic bifunctional compounds with functionalities in the *para* positions.

The intermolecular forces are opposed by thermal agitation. The effect of chain length is mainly extensive, i.e. total force of intermolecular attraction increases owing to greater molecular surface while the force per unit length or area remains constant. By contrast, polarity is intensive; more polar the structure, greater the attractive force per unit length or area. It is important to note that the effects of these factors are relatively short range and hence, minor or subtle variations in chemical structure may notably affect the physical behaviour of polymers. Structure–property relationship highlighting differences effected by aliphatic and aromatic structural units and the effects of flexible (—O—, —S—) and polar (—SO_2—) interunit linkages can be further appreciated by examining Table 1.3.

Table 1.3. Thermal properties of some aliphatic and aromatic polymers (thermoplastics)

Polymer	*Repeat Unit*	T_g, °C	T_m, °C	*Remarks*
Polyethylene (linear), PE	$—CH_2—CH_2—$	–115, –60	137	General purpose, low modulus polymer with good degree of toughness; excellent electrical insulator
Polystyrene, PS		80 to 100	240	Rigid, brittle transparent polymer; excellent insulator
Poly(vinyl naphthalene), PVN		150	360	Highly, rigid, brittle polymer; excellent insulator
Poly(*para*-phenylene), PPP		—	530	Tough, thermostable, intractable polymer with semiconducting or even good conducting (when doped) properties with electrical conductivity in the range 10^{-18} to 10^{2} $(\Omega\ \text{cm})^{-1}$
Poly(tetramethylene oxide), PTMO	$—(CH_2)_4—O—$	–80	60	Weak, flexible polymer
Poly (phenylene ether), PPE		80	300	A good engineering thermoplastic, having high strength and toughness
Poly(phenylene oxide), PPO		209	—	Very low water absorption; more resistant (chemically, mechanically and thermally) than PPE

Poly (tetramethylene sulphide), PTMS	$—(CH_2)_4—S—$	—	70	Weak flexible polymer
Poly(phenylene sulphide), PPS		90	295	Strong, tough, thermally resistant polymer. Normally a good insulator, but when properly doped, say with 2–5% AsF_5, it assumes a semiconducting character
Poly(tetramethylene sulphone), PTMSO	$—(CH_2)_4—SO_2—$	—	270	Presence of strongly polar sulphone ($—SO_2—$) links makes the polymer mechanically strong and thermally more stable, as can be realized by comparing PTMSO with PTMS or PTMO
Poly(phenylene sulphone), PPSO		350	525	Mechanically very strong and thermally stable up to 500 °C; high-performance plastic
Poly(ether sulphone), PES		230	—	Thermostable, high performance transparent thermoplastic with improved processability in comparison with PPSO
Poly(ether ketone), PEK		155	365	High performance thermoplastic with excellent environmental stress cracking resistance; continuous use temperature nearly 275°C
Poly(ether ether ketone) PEEK		140	343	High performance, chemical resistant thermoplastic, showing a high continuous use temperature (250°C)

Rigid, bulky aromatic ring substituent makes a vinyl polymer more rigid and brittle. When aromatic rings constitute the chain backbone, the polymer becomes rigid, stiff, strong and tough. —S— and —O— inter unit linkages make the polymer weak, relatively soft and flexible, while highly polar $—SO_2—$ linkages along the chain backbone make the polymer more rigid, strong and thermostable.

The polymer properties are also highly dependent on the spatial disposition of the side groups or side chains. The stereoregular (isotactic) polymers are of high degree of crystallinity and they exhibit higher strength and melting point than those exhibited by the corresponding random (atactic) polymers. The lengthening of the substituent group of the higher isotactic poly(α-olefin) homologues decreases the melting point up to polyheptene; from this point the melting point curve follows an increasing trend (Fig. 1.8). The initial falling trend in melting point is due to repulsion of the bulky side groups in the crystalline region. The upward trend in melting point is probably a result of developing trends in crystallinity involving the relatively long flexible side groups, i.e. a case of side chain crystallinity. Further, dependence of physical properties on structural isomerism is vividly reflected in the well-known examples of 1,4-*cis*-polyisoprene (natural rubber) and 1,4-*trans*-polyisoprene (*gutta percha*) (*See also* Sec. 5.9); the former, being normally devoid of or poorer in crystallinity, is more flexible and behaves as a rubber, while the latter is a good plastic having good order of crystallinity in the normal condition.

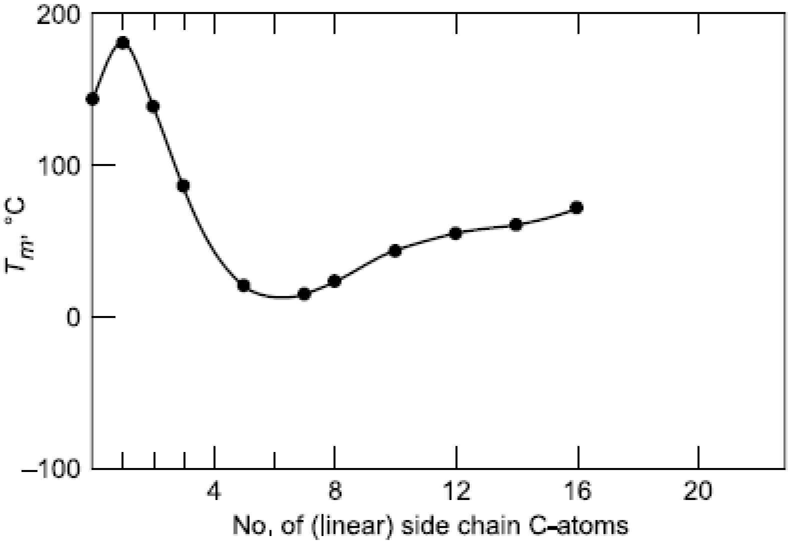


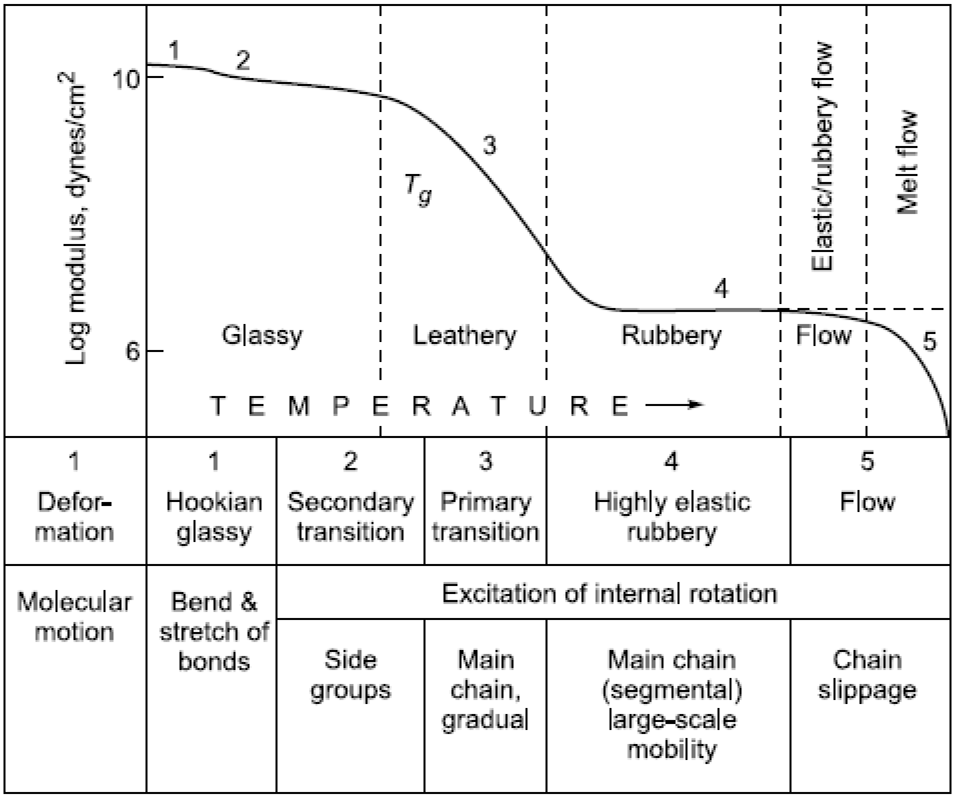
Figure 1.8. Effect of variation of branch (substituent) length on the melting point of isotactic poly(α–olefins), —(CH_2—CHR)$_n$

1.6.4. Effect of Temperature

Roughly speaking, all linear amorphous polymers can behave as Hookian elastic (glassy) materials, highly elastic (rubbery) substances or viscous melts according to the prevailing temperature and time-scale of experiments. Different property profiles for the same polymer at different temperatures are related to variation in the physical structures or arrangements of the chain molecules as a consequence of different types and degrees of deformation.

1.6.5. Survey of Deformation Behaviour in the Amorphous State

An idealized graph of log (shear) modulus vs. temperature is shown in Fig. 1.9. The modulus curve usually shows a number of transitions each of which is connected with the gradual development of a specific kind of molecular movement.



1 Deformation	1 Hookian glassy	2 Secondary transition	3 Primary transition	4 Highly elastic rubbery	5 Flow
Molecular motion	Bend & stretch of bonds	Excitation of internal rotation			
		Side groups	Main chain, gradual	Main chain (segmental) large-scale mobility	Chain slippage

Figure 1.9. Temperature dependence of log (shear) modulus in polymer system showing molecular mechanism of the deformations taking place at different points

At a temperature below the corresponding transition temperature, the molecular processes in question are frozen in. With rise in temperature, and in the vicinity of a transition point, an additional molecular movement begins to contribute to the deformation mechanism and hence lowers the resistance to deformation, i.e. the modulus.

At very low temperatures, the only deformation occurring is Hookian elastic deformation which is time-independent and mechanically reversible. It takes place almost instantaneously and the deformation recovers instantaneously and completely on removal of the force or stress applied. The deformation is also thermodynamically reversible, as no energy is dissipated during the stress–strain cycle. The Hookian deformation is attributed to the small changes in valence angles and valence distances (bend or stretch of bonds) that take place against the strong binding forces of the homopolar bonds (dissociation energy, 30–200 kcal/mol), (Table 1.4), and therefore, it is associated with a high modulus in the region of 10^{10}dynes/cm^2 or higher. At sufficiently high temperatures, flow which is totally irreversible, both mechanically and thermodynamically, takes place. The deformation energy is dissipated as heat in the viscous melt and little configurational free energy is left after the deformation and hence there is no recovery. A polymer melt may be viewed as a cluster of randomly coiled or intercoiled molecules with very limited or no restriction on rotation of molecular segments due to closely neighbouring molecules. The deformation mechanism involved at this stage is slippage of molecular chains relative to each other but at the same time large scale displacement of chain segments normal to their chain axes is restricted, thereby giving rise to high melt viscosity. Cross-linked polymers are not expected to exhibit the flow phenomenon.

Table 1.4. Characteristics of typical primary valence bonds

Nature/Type of Bond	Average Bond Distance, Å	Average Dissociation Energy, kcal/mol
C—H	1.10	98

Nature/Type of Bond	Average Bond Distance, Å	Average Dissociation Energy, kcal/mol
C—C	1.54	80
C=C	1.34	145
C—O	1.46	85
C=O	1.21	180
C—N	1.47	75
C≡N	1.15	215
C—Cl	1.77	80
C—F	1.32–1.40	100–125
O—H	0.96	110
N—H	1.01	92
O—O	1.32	34

1.6.6. Transitions and Rubbery Region

The intermediate regions present some interesting deformation behaviours. The different transitions, shown schematically in Fig. 1.9, are manifestations of viscoelastic deformations which are time-dependent in nature, reaching at the respective point an equilibrium value after a certain time and recovering after a time of the same magnitude. The deformation in these regions is often mechanically reversible, but owing to time-dependency, thermodynamically irreversible. A part of the deformation energy is stored as free energy which takes care of mechanical reversibility and the remaining part of the deformation energy is dissipated as heat (Sec. 7.18).

The transitions schematically shown as primary and secondary transitions may be close or widely separated depending on the nature and molecular weight of the polymer. The secondary transition(s) arise as a consequence of inducement of thermal excitations involving rotation of the side groups of the polymeric chains and it generally leads to relatively small decrease in modulus. Although, inception of rotation of small segments of the main chains is also attributed to such transitions but, by and large, the rotation about the bonds of the backbone chain is still strongly hindered and the molecular chains as a whole remain stiff.

The primary transition corresponds to what is commonly known as the glass transition temperature (T_g), and this transition arises as a consequence of excitation of rotation of segments of the main chains. Almost all polymers show a primary transition or a characteristic glass transition, but many of them may not exhibit a distinct secondary transition (*See also* Sec. 7.20). Through the glass transition or primary transition, the polymers suffer a sharp and large change in modulus.

1.6.7. Property Demand and Polymer End-Use

A schematic, though rough and approximate phase diagram for polymers is given in Fig. 1.10. It shows (i) how the melting temperature (T_m) and the glass transition temperature (T_g) vary and tend to level off with increase in molecular weight (*See also* Fig. 1.5), (ii) how viscosity of melts varies with extension of chain lengths and (iii) the different regions or zones over which properties typical of plastics, rubbers, viscous fluids, etc. may be found.

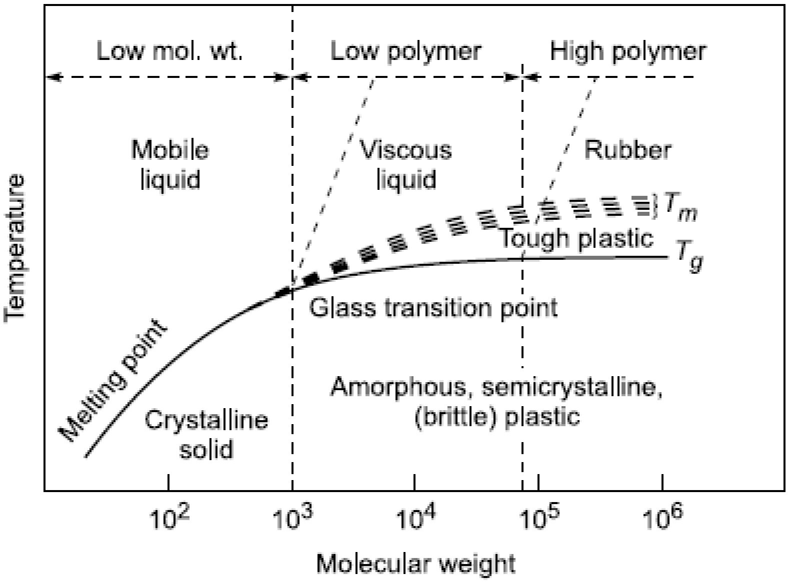


Figure 1.10. A schematic phase diagram showing variation of melting point (T_m), glass transition point (T_g) and consistency or viscosity of melt with variation of molecular weight

a. ***Elastomers or Rubbers*** It is apparent from the diagram that while useful plastic properties may be exhibited by polymers of wide molecular weight range (low polymer and high polymer), good useful rubbery properties are exhibited by polymers which are essentially high polymeric in nature. For revelation of rubberiness, the polymers must be far above their T_g and for practical advantage and common use, T_g for elastomers or rubbers should be in the range – 40 to – 80°C. This is very commonly attained in systems of low cohesive energy density (Table 1.5), and poor molecular symmetry resulting in amorphousness, at least in the unstrained state and permitting enough freedom of molecular motion so that deformation of high magnitude takes place rapidly. Although, these requirements and features for elastomers imply high local or segmental mobility, the gross or full-scale mobility as in the flow region must be low in practical elastomers. Restricted chain slippage must be assured in view of property demand in the form of regain of original shape and dimension on release of stress. This restriction is technically achieved through introduction of widely spaced primary valence cross-links in the chain molecular system such that on application of forces of extension, large deformations can take place without rupture of primary bonds.

Table 1.5. Cohesive energy densities of some linear polymers[8,9]

Polymer	Repeat Unit	Cohesive Energy Density, cal/cm³
Polyethylene	$—CH_2—CH_2—$	56–64
Polystyrene	$—CH_2—CH(C_6H_5)—$	75–88
Polyisobutylene	$—CH_2—C(CH_3)_2—$	56–64
Polyisoprene (natural rubber)	$—CH_2—C(CH_3){=}CH—CH_2—$	60–67
Poly(vinyl acetate)	$—CH_2—CH(OCOCH_3)—$	82–94

Polymer	Repeat Unit	Cohesive Energy Density, cal/cm^3
Poly(vinyl chloride)	$—CH_2—CHCl—$	85–95
Poly(methy1 methacrylate)	$—CH_2—C(CH_3)(COOCH_3)—$	78–85
Poly(ethylene terephthalate)	$—OCH_2CH_2OOCC_6H_4CO—$	90–115
Poly(hexamethylene adipamide, nylon–66	$—HN(CH_2)_6NHCO(CH_2)_4CO—$	180–220
Polyacrylonitrile	$—CH_2—CH(CN)—$	150–230

b. ***Fibres*** For a typical fibre, showing high tensile strength and modulus, the polymer must normally possess a combination of high molecular symmetry and high cohesive energy density manifested through polar structures in the repeat units fostering high order of permanent crystallinity (in the useful temperature zone) on cold drawing. The crystalline melting point, T_m (without decomposition) must normally be above 200°C and below 300°C to make it suitable for hot pressing or ironing and for its trouble-free spinning into a fibre. Resistance to common solvents is an advantage keeping dry cleaning in view. Again, the molecular weight should not be too high for synthetic fibre-forming polymers to ensure speedy and trouble-free spinning from melts or solutions and at the same time it should be high enough to ensure full development of tensile strength and related properties. Extensive intermolecular hydrogen bond formation is a key factor in synthetic fibre technology.

c. ***Plastics*** In general, the properties of plastics are more or less intermediate between those of fibres and elastomers, with good amount of overlap on one or the other side. Plastics are put to use in a wide range of applications and hence a wide variety of property combinations is associated with them. Consequently, a wide variety of structures may adequately describe them. Some polymers having high cohesive energy density such as the nylon polyamides, behave as plastics when used without orientation of the molecules by stretching. But on orientation of the molecules by stretching or cold drawing, major changes in the structure of their physical agglomerates take place leading to high order of crystallization and the respective polymers then behave as excellent fibres.

The difference between rubbers, plastics and fibres is not really basic or very intrinsic, it is rather a matter of degree. Small or minor variations in chemical structure or physical conditioning often bring about significant property variations and may transform a rubber to a resin or a plastic or vice-versa and a plastic to a fibre or vice versa. Thus, (i) moderate to extensive cyclization, hydro-halogenation or halogenation of natural rubber, transforms it into a resinous product; (ii) limited chlorosulphonation of polyethylene introducing Cl atoms and $—SO_2Cl$ groups in the chain molecule through simultaneous treatment with chlorine and sulphur dioxide gas under pressure breaks its molecular symmetry and transforms this general purpose plastic into a synthetic rubber despite enhancement of polarity; blending or mixing with a liquid plasticizer readily transforms the hard rigid plastic poly(vinyl chloride), PVC, into a leathery or rubbery product; (iii) limited N-alkylation of nylon polyamides makes them stretchable even when made into a fibre, and highly N-alkylated polyamides of comparable chain length become very soft or even liquids. Cellulose, an insoluble and infusible fibre, is readily transformed into good plastics on esterification or etherification. N-alkylation for the aliphatic polyamides and substitution of OH groups in cellulose reduce intermolecular hydrogen bond formation, resulting in weakening of the polymer systems.

1.6.8. Nature of Intermolecular Forces

Between molecules or chain segments not connected by primary (covalent) bonds, the so-called secondary bonds or Van der Waals forces give rise to attractive forces. The energy of the intermolecular attractive forces varies as the inverse sixth power of the intermolecular separation. It is nearly two orders of magnitude weaker than the covalent bond. The cohesive energy amounts to the total energy required to remove a molecule in a liquid to a position far from its neighbours. The cohesive energy per unit volume, widely referred to as the cohesive energy density for a few commonly used polymers is listed in Table 1.5 which clearly shows how variation in this parameter depends on molecular structure.

Among the different types of secondary valence forces known, one type arises from polarity of the molecules and it is manifested through *interaction of dipoles.* The magnitude of such interaction energy is dependent on the mutual alignment of the interacting dipoles. As molecular alignments are opposed by thermal agitation, the dipole forces are very much dependent on temperature.

Another kind of intermolecular interaction is that induced by polar molecules or segments through the dipoles on surrounding molecules or segments that do not have permanent dipoles.

The secondary bond forces consequent to *interactions between permanent dipoles and induced dipoles* are known as the *induction forces*.

The cohesive energy corresponding to the induction force is small and it does not depend on temperature.

There are also *dispersion forces* which are not dependent on polarity or permanent dipoles but which are consequences of different instantaneous configurations of electrons and nuclei of all kinds of molecules, resulting in *time-varying dipole moments* that average out to zero. The dispersion forces exist in all molecular systems, polar or non-polar and constitute a major part of the cohesive forces except in systems having strong dipoles. In non-polar materials the molar cohesion is due only to the dispersion forces which are also independent of temperature. The energy of all the above secondary valence forces usually ranges between 2–5 kcal/mol.

A fourth but an important and major kind of intermolecular attraction, particularly in polar molecules containing fluorine, nitrogen, oxygen and occasionally chlorine atoms is due to hydrogen bonding. The energy of *hydrogen bonds* usually ranges between 5–10 kcal/mol and its overall cumulative effect in polymer material systems is very pronounced and sometimes overwhelming, so much so that suitable polymers having frequent and extensive hydrogen bonds along the chains, such as cellulose, polyamides, polyacrylonitrile, etc., are inherently crystalline and resistant to heat and solvents (*see* the idealized structure of pairs of molecules in each case in Fig. 1.11). The exact nature of the hydrogen bond depends on the chemical nature and environment of the concerned polar groups and it is considered, in most systems, electrostatic or ionic in character. The average attractive force between sections of polymer molecules in an oriented domain or crystal lattice is higher than that between sections that are not in a lattice. Crystallites are usually 10–15% more dense than the supercooled melt at the same temperature.

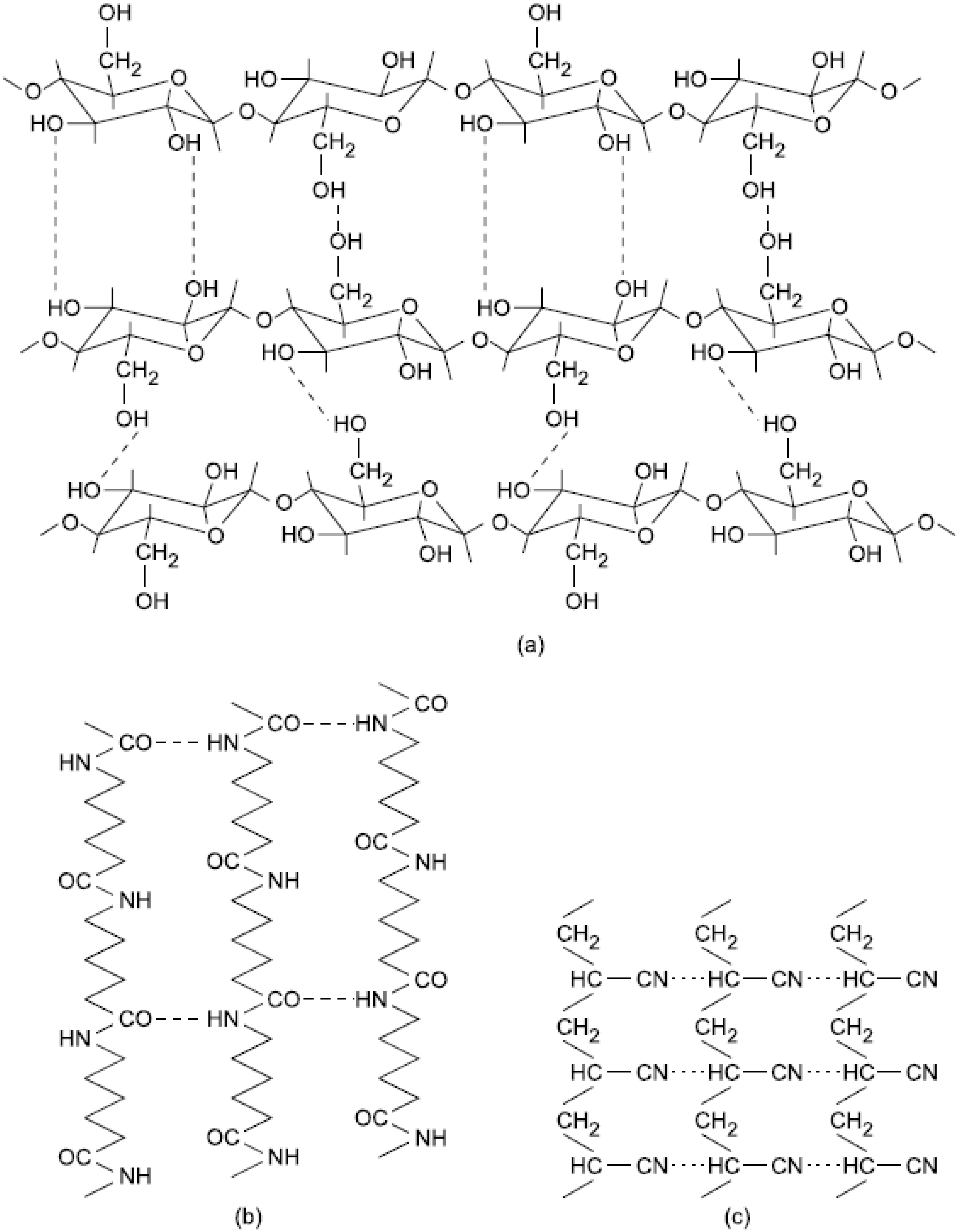


Figure 1.11. Idealized representation of segments of chain molecules of (a) cellulose fibre (b) (melt drawn) oriented nylon 6 polyamide fibre, and (c) oriented polyacrylonitrile fibre, showing formation of intermolecular hydrogen bonds in each case

1.7. References

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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

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

$$\bar{M}_n = \frac{\Sigma N_iM_i}{\Sigma N_i}$$
(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,

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

$$\bar{M}_w = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$$
(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 $[\eta]$ value (Fig. 6.1).

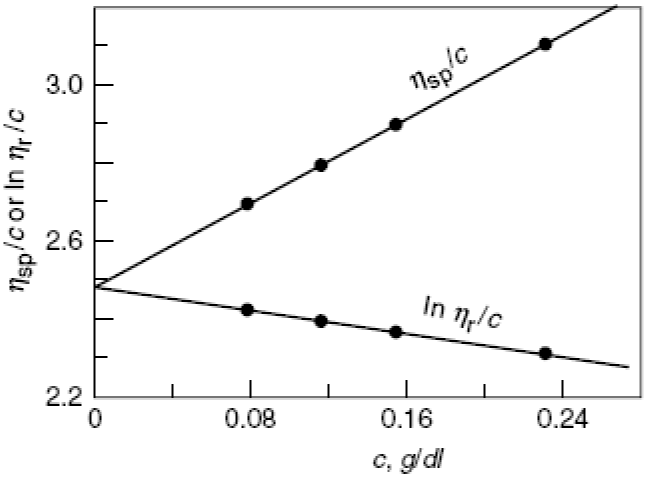

Figure 6.1. Typical plots showing η_{sp}/c vs c and ln η_r/c vs c using common ordinate and abscissa for the determination of intrinsic viscosity $[\eta]$ of a given polymer–solvent system at a given temperature

The relationship between $[\eta]$ 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 $[\eta]$ 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 $[\eta]$ 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.

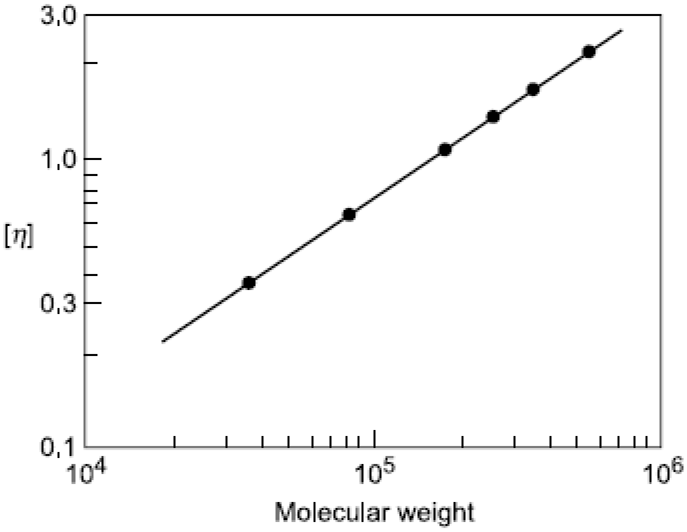

Figure 6.2. Intrinsic viscosity–molecular weight relationship at 30° for polyisobutylene in cyclohexane[18] *(Krigbaum and Flory, 1953; Courtesy, American Chemical Society, Washington)*

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 ($c \to 0$) 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.

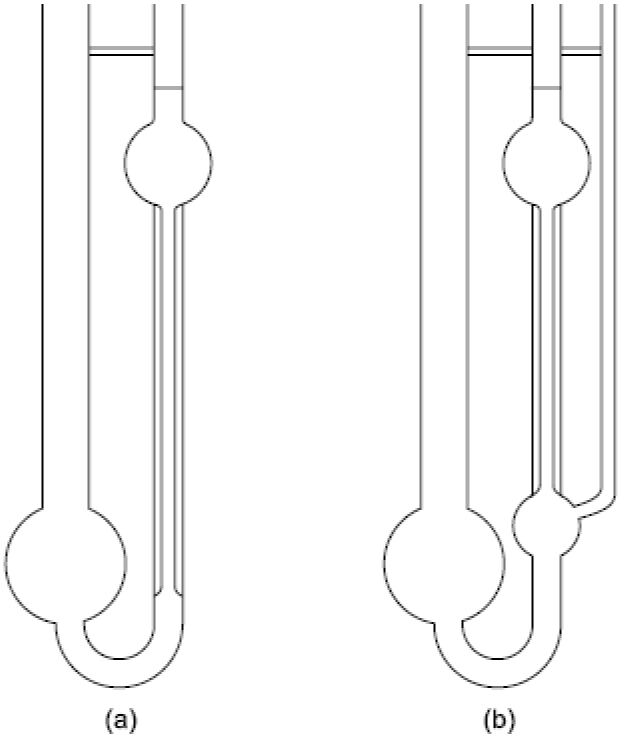

Figure 6.3. Capillary viscometers: (a) Ostwald type, (b) Ubbelohde type

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.

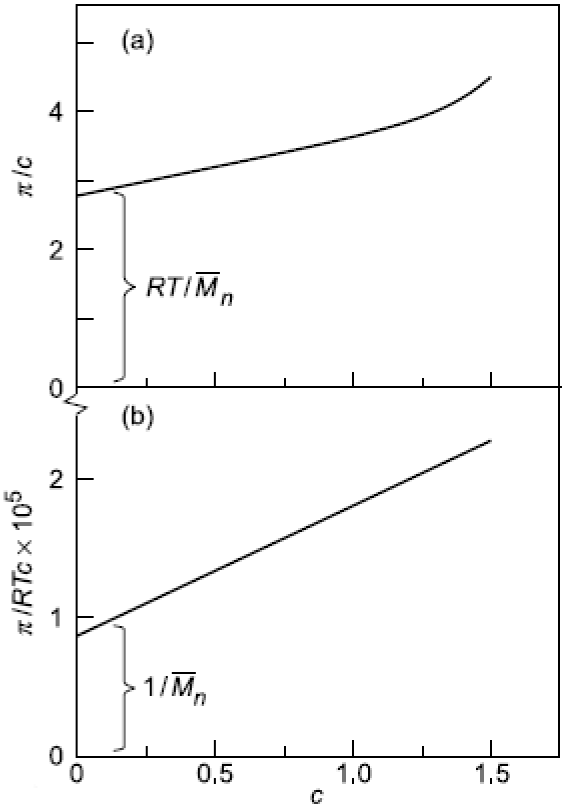

Figure 6.4. Typical plots showing (a) π/c vs and (b) π/RTc vsc for determination of M-macr_n.

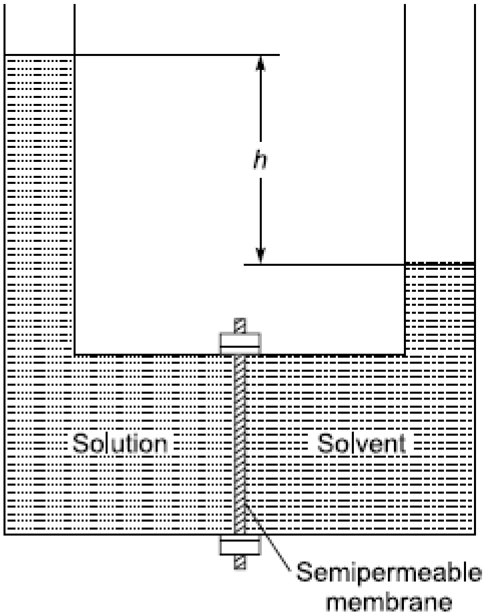

Figure 6.5. Operating principle of a membrane osmometer

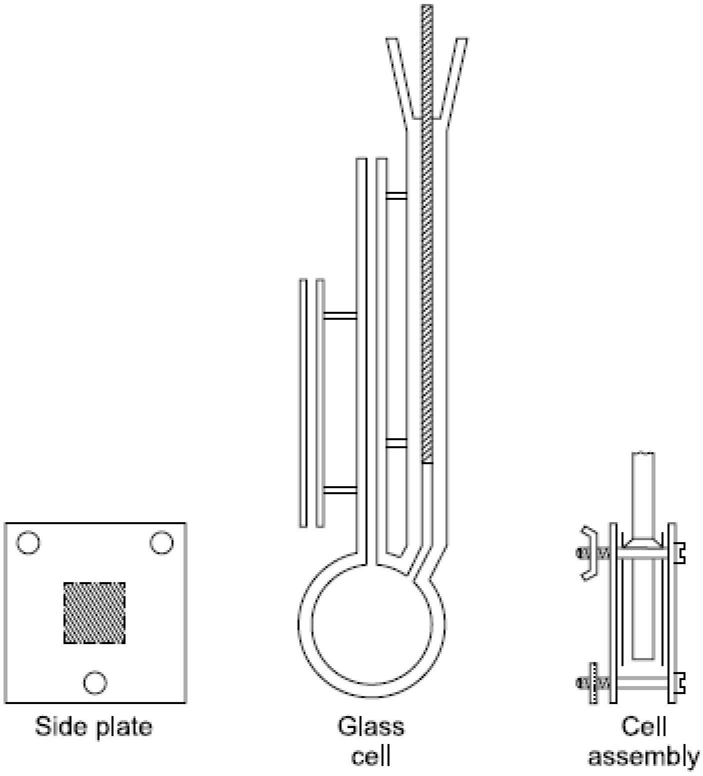

Figure 6.6. Sketch of a Zimm-Meyerson osmometer

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, $\overline{M}_w$.

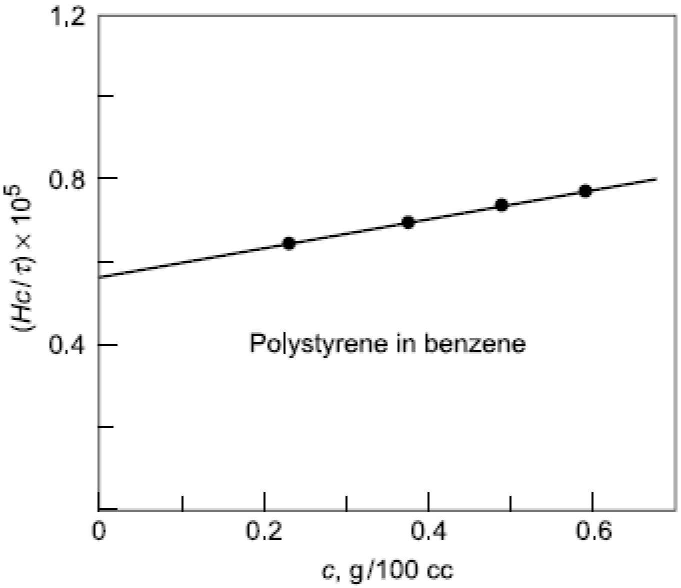

Figure 6.7. A typical plot of Hc/τ vs c for determination of M-macr$_w$

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 $N_i M^2_i$ and the total intensity of light scattered by all the molecules in the unit volume is proportional to $\Sigma N_i M^2_i$ 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

$$R_\theta = \frac{Kc}{1/M + A_2 c + \ldots}$$

(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.

$$\frac{Kc}{R_\theta} = \frac{1}{M} + A_2 c + \ldots$$

(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

$$(Kc/R_\theta) = (1/M \cdot P(\theta)) + A_2 c + \ldots$$

(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)

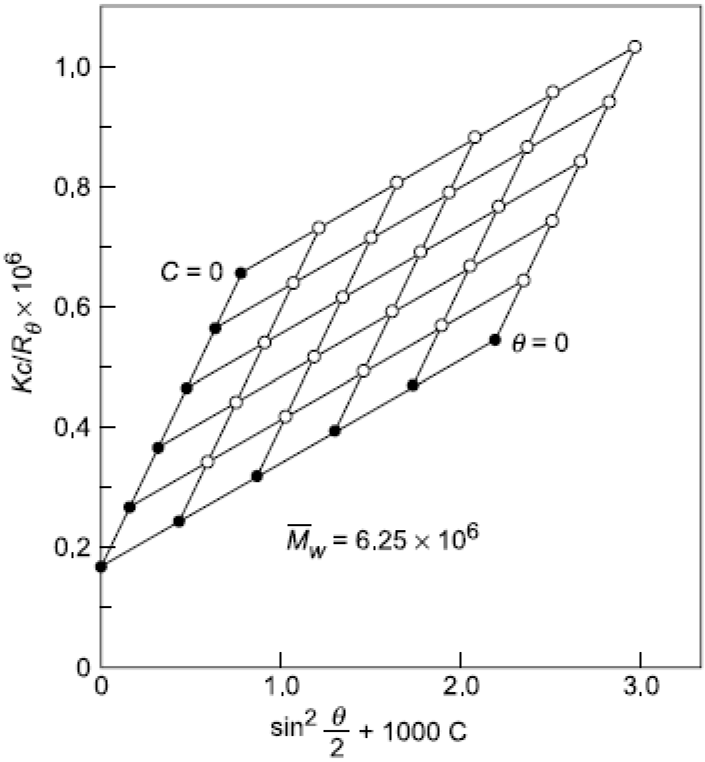

Figure 6.8. A typical Zimm plot, Kc/R_θ vs. $\sin^2(\theta/2) + kc$ from light scattering measurements for sodium amylose xanthate in 1 M NaOH solution at 30°C

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.

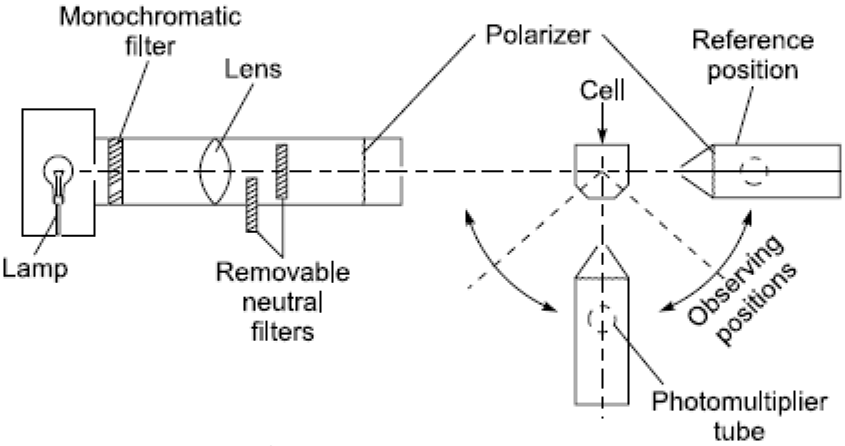

Figure 6.9. Principle of light scattering measurements

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 $(i_{45°}/i_{135°})$, 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]

6.11. 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 $N_iM_i^2$ 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.

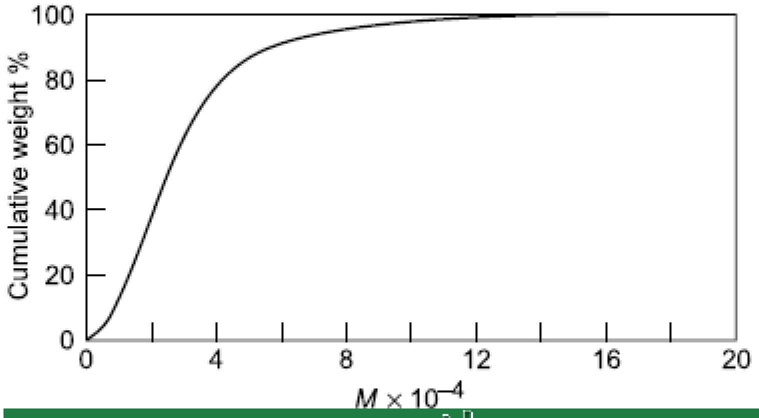

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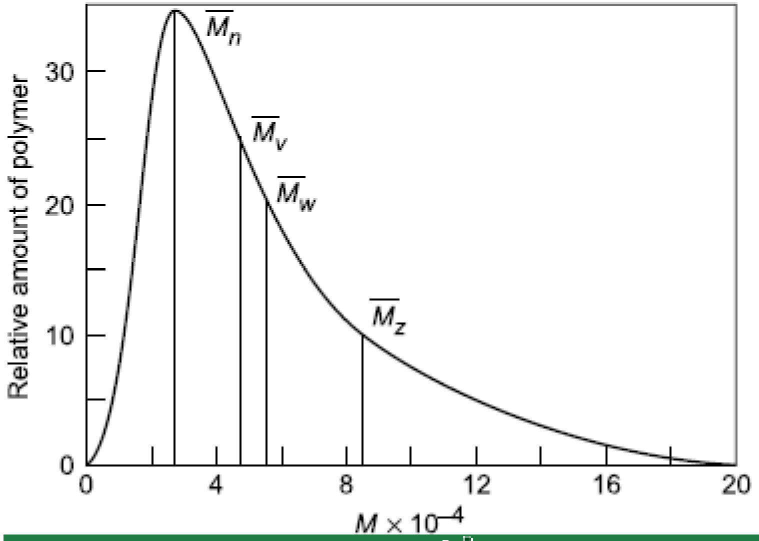
Figure 6.10. A typical integral molecular weight distribution curve: plot of cumulative weight % vs molecular weight



Click to load interactive graph

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.

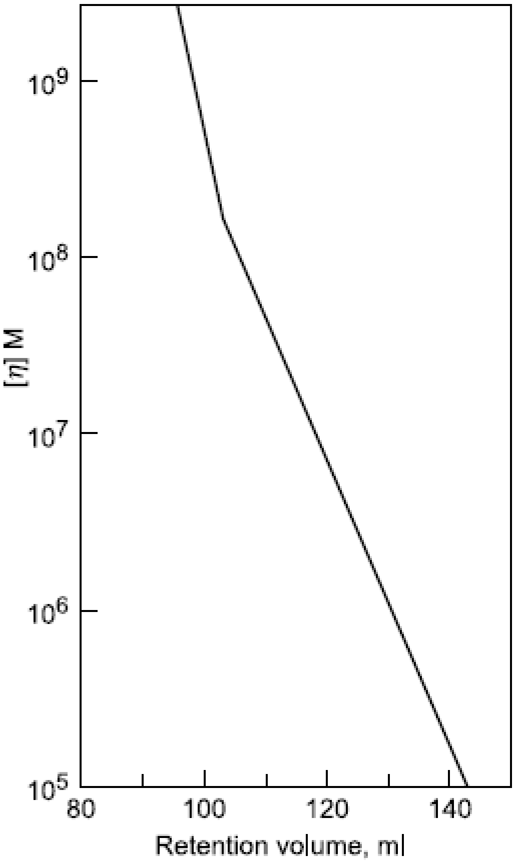


Figure 6.12. Calibration curve for gel permeation chromatography: plot of [η]M vs retention volume[50] *(Grubisic, Remp and Benoit, 1967;Courtesy, Wiley-Interscience, New York)*

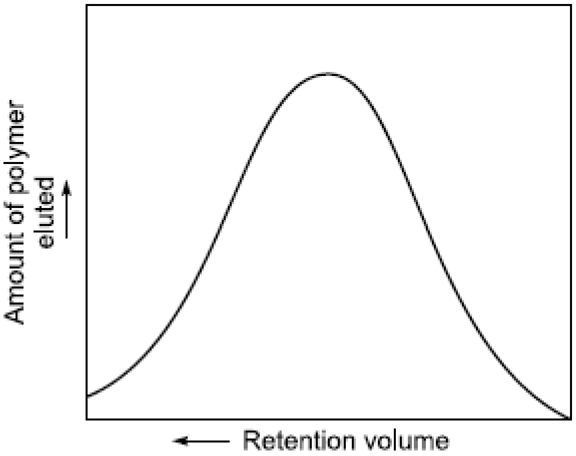


Figure 6.13. A typical GPC chromatogram

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.

Viscosity Average Molecular Weight

The viscosity of a polymer solution is considerably higher compared to the pure solvent. The increase in viscosity imparted by the macromolecules in solution is a direct function of the hydrodynamic volume and hence the molecular weight of the macromolecule. The ratio η/η_o is Known as relative viscosity, where
η = viscosity of polymer solution and
η_o= viscosity of pure solvent.
This and other terms related to viscosity measurements are given below:
Relative viscosity, $\eta_r = \eta/\eta_0 = t/t_0$
Specific viscosity, $\eta_{sp} = (\eta - \eta_0) / \eta_0 = (t - t_0) / t_0 = (\eta_r - 1)$
t and t_o are the times (in sec) for the flow of the equal volume of solution and solvent respectively.

Reduced viscosity $= \eta_{sp}/c = \eta_{red}$, dl/g, where
c = concentration of the solution in g/dl
Inherent viscosity, $\eta_{in} = \ln (\eta_r /c)$ in dl/g.
Intrinsic viscosity $[\eta] = (\eta_{sp}/c)c\text{-}o = \ln (\eta_r/c)c\text{-}o$, dl/g

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.

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

and

$$\ln \eta_r/c = [\eta] + k_2[\eta]^2 c \qquad \text{....................(6.20)}$$

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 $[\eta]$ value (Fig. 6.1).

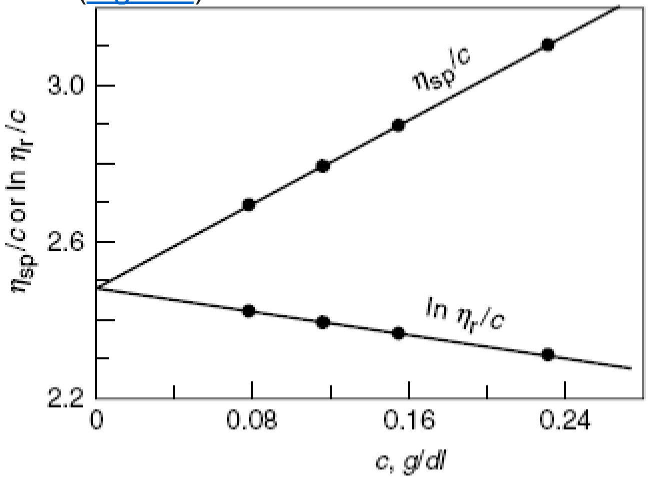


Figure 6.1. Typical plots showing η_{sp}/c vs c and ln η_r/c vs at a given temperature

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

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

where *K* and *a* are constants for a particular polymer–solvent system at a given temperature.